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Stannasiloxanes: from rings to polymers

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Dedicated to Professor Martin Dräger on the occasion of his 60th birthday

Contents

Abstract

A review is given with 140 references on the recent progress in the chemistry of *cyclo*-stannasiloxanes of different ring size, such as *cyclo*-$R_2Sn(OSiR'_2)_2O$, *cyclo*-$R_2Sn(OSiPh_2O)_2SnR_2$, *cyclo*-$R_2Sn(OSiPh_2O)_2SiPh_2$, *cyclo*-$R_2Sn(OSiPh_2)_2SiPh_2$ and *cyclo*-$R_2Sn(OSiPh_2)_2$ (R = alkyl, aryl, intramolecularly coordinating built-in ligand, transition metal fragment; R′ = Me, *i*-Pr, Ph); and their potential in ring-opening polymerization reactions is critically evaluated and compared with that of related *cyclo*-borasiloxanes, *cyclo*-germasiloxanes, and *cyclo*-siloxanes.

Keywords: Silicon; Tin; Siloxane; Polymerization

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1. Introduction

The study of inorganic polymers and ring systems is an attractive research field that allows work on both the solution of fundamental questions in chemistry and the development of materials with interesting properties on a molecular level. Typical questions associated with the nature of these compounds are: (i) preferences between different ring sizes; (ii) the magnitude of ring strain; (iii) the nature of the bonding, e.g. existence of π-electron delocalization around the ring; (iv) the preferred conformation of rings and polymers; and (v) the chain lengths of the polymers [1–3]. The interest in material science aspects is based on (i) the great variety of possible applications for inorganic polymers [4,5] and (ii) the suitability of inorganic rings as single source precursors for ceramics or related materials [6–15].

Three classes of inorganic polymers are considered to be well established in the literature, namely polysiloxanes, $(R_2SiO)_n$ (**I**) [16,17], polyphosphazenes, $(R_2PN)_n$ (**II**) [18,19], and polysilanes, $(R_2Si)_n$ (**III**) [20,21]. All three classes are of great industrial interest owing to their unique physical properties, which allows their use in a diverse range of applications (Chart 1) [5].

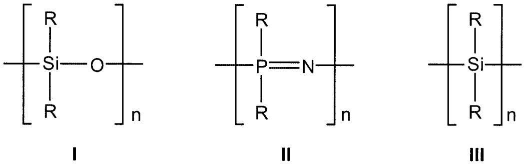


Chart 1.

A convenient method for the synthesis of the polymers of types **I**–**III** is the ring-opening polymerization, hereafter referred to as ROP, of strained rings [22], which exploits the release of ring strain as the thermodynamic driving force. Although this method usually provides the most desirable results in terms of chain lengths and molecular weight distributions, stringent control of the reaction conditions are required in order to avoid the formation of by-products, such as short oligomers and rings [5,17]. ROP reactions may proceed either via kinetic or thermodynamic control, which has dramatic consequences for the product distribution. Under kinetic control, the selective cleavage of the precursors and chain propagation occur almost exclusively, providing high-molecular weight polymers and barely any by-products. Under thermodynamic reaction control, equilibrium mixtures are obtained which generally consist of low-molecular weight polymers and considerable amounts of smaller oligomers and ring species [16]. The formation of equilibrium mixtures stems from depolymerization processes associated with unselective bond cleavages at higher temperatures. The breakdown to smaller molecules can also be interpreted as an increase in the entropy of the system, which has direct bearing on the $T\Delta S$ term of the Gibbs free enthalpy [23]. Consequently, it can be surmised that the polymer yield of any ROP process should increase with a decrease in temperature. However, exceeding the activation barrier towards ring-opening often requires substantial thermal induction, and thus, strained precursors with practically no ring-opening activation barrier would represent ideal candidates for the synthesis of well-defined polymers.

On the other hand, the high-yield synthesis of inorganic rings, which may be potential precursors for the ROP process, still remains challenging as product mixtures of different ring sizes are usually obtained, alongside with short oligomers and polymers [2,3]. The ring size distribution is mainly influenced by the nature of the exocyclic substituents and the concentration of the reactants, e.g. high dilution usually favors the formation of smaller rings.

The aforementioned circumstances demonstrate the close relationship of ring systems with their respective polymers and the number of parameters that has to be taken into account when considering the high yield synthesis of polymers via ROP.

The industrial scale production of low-molecular weight polydimethylsiloxane, $(Me_2SiO)_n$, utilizes the relatively cheap hydrolysis/condensation of dimethyldichlorosilane, Me_2SiCl_2, and is accompanied by substantial amounts of undesired oligomers and ring species [17]. As a result of the small and flexible methyl substituents, polydimethylsiloxane is very soluble in a great number of organic solvents. The ROP of highly strained methyl-substituted six-membered trisiloxane ring, *cyclo*-$(Me_2SiO)_3$ (D_3), is a good, but expensive alternative to the hydrolysis/condensation method and results in high-molecular weight polymers, provided the reaction proceeds under kinetic control [16,17]. On the other hand, the ROP of practically strainless methyl-substituted eight-membered tetrasiloxane ring, *cyclo*-$(Me_2SiO)_4$ (D_4), exclusively provides equilibrium mixtures consisting of low-molecular weight polymers and a large amount of by-products [16,17]. Moreover, a comparison of different equilibrium mixtures of diorganosiloxanes, $(R_2SiO)_n$ (R = alkyl, aryl), bearing various substituents, reveals a dramatic decrease of the polymer yield with increasing size and polar character of the organic groups.

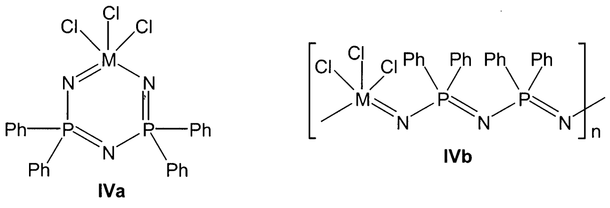
The hydrolysis of diphenyldichlorosilane, Ph_2SiCl_2, gives perphenylated six- and eight-membered siloxane rings *cyclo*-$(Ph_2SiO)_n$ ($n = 3$, 4), and open-chain α,ω-sil(ox)anediols $HO(Ph_2SiO)_nH$ ($n = 1–4$), depending on the reaction conditions applied [24–31]. It is important to note that polydiphenylsiloxane, hereafter referred to as PDPhS, is not formed in this reaction. The synthesis of PDPhS is extremely difficult and requires the kinetically controlled ROP of *cyclo*-$(Ph_2SiO)_3$ at temperatures between 150 and 190°C, in the presence of an initiator [32–38]. Higher reaction temperatures provide equilibrium mixtures, which are dominated by practically strainless eight-membered tetrasiloxane ring *cyclo*-$(Ph_2SiO)_4$ [32–34]. Perphenylated *cyclo*-siloxanes and α,ω-sil(ox)anediols as well as PDPhS in general show a lower solubility as compared to the permethylated analogues and a high degree of crystallinity and all isolated products were investigated by X-ray diffraction. The six-membered trisiloxane ring *cyclo*-$(Ph_2SiO)_3$ is almost planar and crystallizes in orthorhombic [36,39,40] and triclinic [36,41] modification. For *cyclo*-$(Ph_2SiO)_4$, monoclinic [42–44] and triclinic [42,45,46] polymorphs are known which reveal eight-membered rings that are only slightly puckered. In the solid state, diphenylsilanediol, $Ph_2Si(OH)_2$ [47,48], 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $HO(Ph_2SiO)_2H$ [49–51], and 1,1,3,3,5,5-hexaphenyl-1,3,5-trisiloxane-1,5-diol, $HO(Ph_2SiO)_3H$ [50,52], are involved in inter- and intramolecular hydrogen bonding, and consequently the structures do not resemble short chains of PDPhS. However, molecules of 1,1,3,3,5,5,7,7-octaphenyltetrasiloxane-1,7-diol, $HO(Ph_2SiO)_4H$, are not linked by hydrogen bonds and can be regarded as model compounds for the yet unknown conformation of PDPhS [53,54], which has been the subject of controversial discussion in recent years [55–59]. Despite the difficulties in its preparation, PDPhS has attracted considerable attention as it shows enhanced stability toward oxidation and thermolysis and a very high melting point of about 260°C. Above the melting point a mesophase is formed which persists at temperatures exceeding 500°C, and thus, PDPhS holds potential for liquid-crystal applications in a high-temperature range [32–35,60]. Furthermore, PDPhS films show a unique long lifetime visible light emission upon UV laser irradiation [61], which is very likely a result of π-electron delocalization across the $Si–C_{Phenyl}$ bonds [62].

ROP of *cyclo*-trisiloxanes, *cyclo*-$(R_2SiO)_3$, as initiated by nucleophiles such as organolithiums, proceeds via fast nucleophilic attack at silicon followed by the breaking of a Si–O bond and a slower chain propagation step involving silanolates [16]. This mechanism is supported by the results obtained from the stoichiometric reaction of organolithiums, $R'Li$ ($R' = Me$, *n*-Bu, *s*-Bu, *t*-Bu), with six-membered trisiloxane rings $(R_2SiO)_3$ ($R = Me$, Ph), which provides lithium triorganosilanolates, $R_2R'SiOLi$ in almost quantitative yield [63]. Recently, the X-ray structure of $[KO(Ph_2SiO)_2H]_2 \cdot C_6H_6$ was reported. This compound can be regarded as the initial product of a ring-opening reaction of $(Ph_2SiO)_3$ with KOH [64].

Considering the different results of ROP involving cyclotri- or cyclotetrasiloxanes, the ring strain appears to be the parameter that has the most influence on the product distribution [17]. Surprisingly, the results of calorimetric determinations of ring strain are controversial [17,65–67] and computational estimates are rare [68].

Unlike the ROP process of cyclosiloxanes, the hydrolysis/condensation method of diorganodichlorosilanes, R_2SiCl_2, is poorly understood, which basically stems from the heterogeneous nature of the reaction [17]. The lipophilic silanes are mostly separated from the aqueous layer, and therefore, the reaction may occur at the phase boundary. In the absence of base, the evolution of hydrogen chloride gas is an additional source of difficulty when considering studies of this type of reaction. Therefore, some recent works are devoted to the anhydrous 'hydrolysis' of diorganodichlorosilanes, R_2SiCl_2 ($R = Me$, Ph), with dimethylsulfoxide, DMSO, which serves as both an oxide source and solvent [69–71]. The reaction takes place in a homogeneous reaction mixture and can be monitored by NMR spectroscopy. However, this reaction also produces hydrogen chloride gas as a major by-product, alongside with other unpleasant sulfur-containing species [69–71]. The mechanism of this type of reaction is a matter of controversial discussion, and both ionic species and silanones have been suggested as key intermediates along the reaction pathway [69–71]. Notably, when applying this method, the yield of six-membered siloxane rings, *cyclo*-$(R_2SiO)_3$ ($R = Me$, Ph), is substantially higher than in the conventional hydrolysis/condensation method.

In addition to the well-established polymers of types (**I**)–(**III**), a diverse range of new polymer classes incorporating main group [4] as well as transition metals [72] in the polymer skeleton has been explored during the last few decades. One strategy for their synthesis involves the modification of known polymers by formal substitution of single atoms within the polymer skeleton. The substitution usually occurs on a molecular level in the design of the polymer precursors. For instance, the six-membered rings *cyclo*-$Cl_3M(NPPh_2)_2N$ (**IVa**; M = Mo, W), can be derived from the parent cyclophosphazene $(Ph_2PN)_3$, in which a diphenylphosphorous segment is formally replaced by a transition metal trichloride. Thermally induced ROP of these compounds provide polymers of the type $[MCl_3NPPh_2NPPh_2N]_n$ (**IVb**; M = Mo, W) (Chart 2) [73].



M = Mo, W

Chart 2.

Until now, the same concept has not been applied yet to synthesize poly(heterosiloxanes). This is somewhat surprising, because organosilanols [74] are readily available as building blocks for the synthesis of metallasiloxanes, and many members of the latter class of compounds have been prepared in recent years [75,76]. In particular, the aforementioned perphenylated α,ω-sil(ox)anediols, $HO(Ph_2SiO)_nH$ ($n = 1-4$) have been frequently utilized for the synthesis of a great variety of cyclometallasiloxanes [77].

Our initial interest in this field was devoted to the synthetic applications of diorganotin oxides, such as *cyclo*-(t-$Bu_2SnO)_3$ [78], in organosilicon chemistry. In a preliminary study, we have shown that *cyclo*-(t-$Bu_2SnO)_3$ is a convenient proton-free oxide source in reactions with organochlorosilanes such as Ph_2SiCl_2 and t-$BuSiCl_3$, providing organosiloxanes and t-Bu_2SnCl_2 [79]. The reaction proceeds under virtually neutral conditions in a homogenous reaction mixture. The progress of the reaction can be conveniently studied by ^{119}Sn and ^{29}Si NMR spectroscopy, and a variety of cyclic and open-chain intermediates containing Si–O–Sn linkages was identified along the reaction pathway [80]. In contrast, the reaction of *cyclo*-(t-$Bu_2SnO)_3$ with the sterically overcrowded t-Bu_2SiCl_2 stopped at the stage of stannasiloxanes, and consequently, two compounds, namely *cyclo*-t-$Bu_2Si(OSn$t$-$Bu_2)_2O$ and *cyclo*-t-$Bu_2Si(OSn$t$-$Bu_2O)_2Sit-Bu_2, were isolated and fully characterized [80]. To our surprise, a literature search brought forward only a single monocyclic stannasiloxane, namely *cyclo*-t-$Bu_2Si(SnMe_2O)_2Si$t$-$Bu_2$, which was not structurally characterized [81]. On the other hand, a variety of stannasiloxane clusters was found [82–86], which may hold potential as model compounds [87,88] for organotin fragments grafted on silica surfaces. These organotin surface complexes fine-tune the activity of heterogeneous metal silica catalysts [89–91].

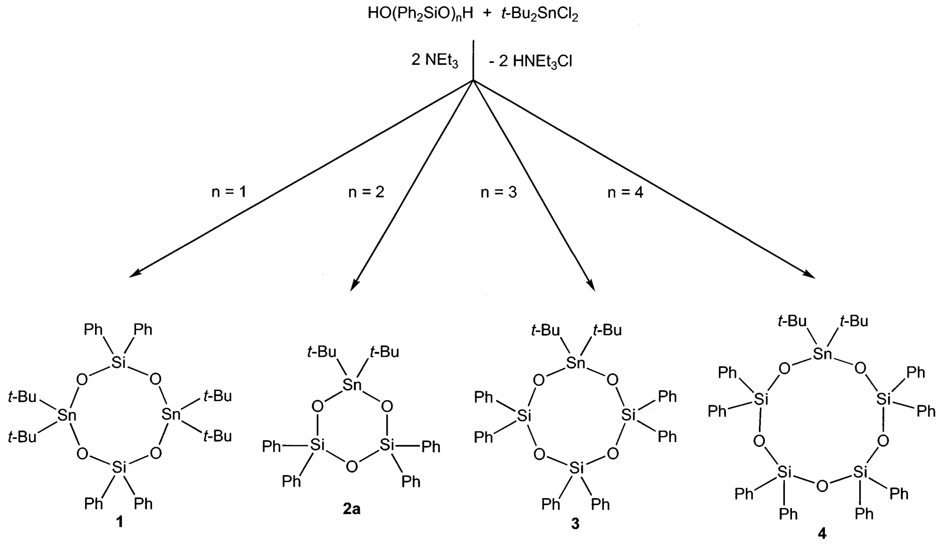
The exciting discoveries in this research field prompted us to study the chemistry of stannasiloxane rings and related compounds in greater detail; the results obtained so far are reported in the present review.

2. Results and discussion

The reaction between a series of perphenylated α,ω-sil(ox)anediols $HO(Ph_2SiO)_nH$ ($n = 1-4$) with di-*tert*-butyltin dichloride, t-Bu_2SnCl_2, in the presence of triethylamine provided in high yield, the stannasiloxanes *cyclo*-$Ph_2Si(OSnt$-$Bu_2O)_2SiPh_2$ (**1**), *cyclo*-t-$Bu_2Sn(OSiPh_2)_2O$ (**2a**), *cyclo*-$Ph_2Si(OSiPh_2O)_2Snt$-Bu_2 (**3**) and *cyclo*-t-$Bu_2Sn(OSiPh_2OSiPh_2)_2O$ (**4**), respectively, which contain either six-, eight-, or ten-membered rings in solution (Scheme 1) [54,79].

The eight-membered stannasiloxane rings **1** and **3** can be regarded as derivatives of the phenyl-substituted tetrasiloxane *cyclo*-$(Ph_2SiO)_4$, in which one or two diphenylsilyl segments are replaced by di-*tert*-butylstannyl segments, and consequently, they also resemble the structure of the parent *cyclo*-siloxane in the solid state [79]. Notably, the eight-membered stannasiloxane rings *cyclo*-t-$Bu_2Si(OSnt$-$Bu_2O)_2Sit$-Bu_2 (**5**) [79], *cyclo*-i-$Pr_2Si(OSnt$-$Bu_2O)_2Sii$-Pr_2 (**6**) [92], *cyclo*-t-$Bu(OH)Si(OSnt$-$Bu_2O)_2Si(OH)t$-Bu (**7**) [93], *cyclo*-t-$Bu(F)Si(OSnt$-$Bu_2O)_2Si(F)t$-Bu (**8**) [79], *cyclo*-t-$Bu_2Si(OSnMe_2O)_2Sit$-Bu_2 (**9**) [81] and *cyclo*-t-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Sit$-$Bu_2$ (**10**) [93] are analogues of compound **1** and most of these compounds were structurally characterized. The molecular structures of compounds **5** and **7** are shown in Figs. 1 and 2, respectively.

Despite bearing similar substituents, some of these compounds realize completely different ring conformations in the solid state [93]. Surprisingly, *cyclo*-t-$Bu_2Sn(OSiPh_2)_2O$ (**2a**) does not crystallize as a six-membered ring, but undergoes ROP instead to give the first well-defined polystannasiloxane (t-$Bu_2SnOSiPh_2OSiPh_2O)_n$ (**2b**) (Eq. 1) [94]. Previous attempts to prepare polystannasiloxanes by polycondensation provided only ill-defined products [95–100].



Scheme 1.

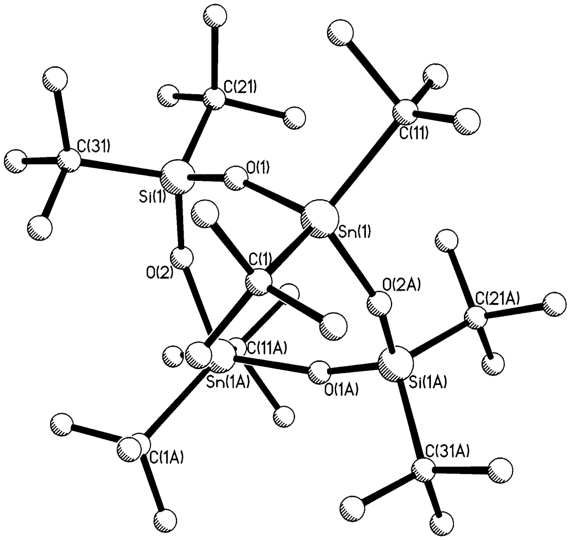


Fig. 1. Molecular structure of *cyclo*-*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2 (**5**). Selected bond angles: O(1)–Si(1)–O(2) = 112.2(2), O(1)–Sn(1)–O(2A) = 106.5(2), Si(1)–O(1)–Sn(1) = 159.4(3)°.

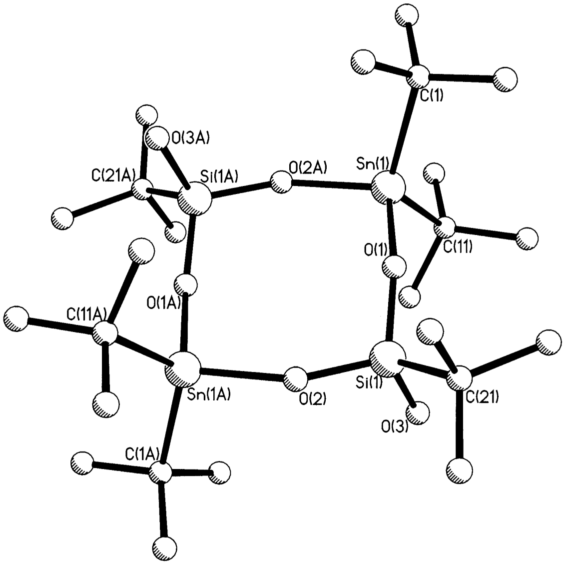
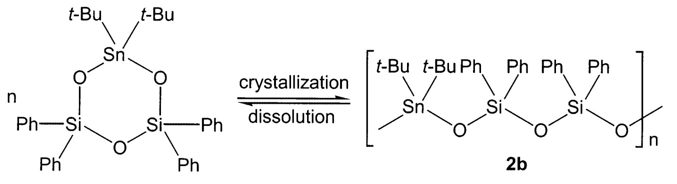


Fig. 2. Molecular structure of *cyclo*-*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu (**7**). Selected bond angles: O(1)–Si(1)–O(2) = 109.8(2), O(1)–Sn(1)–O(2A) = 105.7(2), Si(1)–O(1)–Sn(1) = 153.0(2), Si(1)–O(2)–Sn(1A) = 145.5(2)°.



2a (in solution) **2b** (in solid state) (1)

Apparently, the release of ring strain in *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**), similar to that in *cyclo*-$(Ph_2SiO)_3$, is the thermodynamic driving force for the ROP process. However, the formal replacement of a diphenylsilyl segment by a di-*tert*-butylstannyl segment drastically affects the activation barrier of the ROP process. In sharp contrast to the parent siloxane ring, *cyclo*-$(Ph_2SiO)_3$, the polymerization of *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**) occurs rapidly on the laboratory time scale at room temperature in the absence of any initiators [94]. The polymerization proceeds quantitatively and there is no evidence of any intermediate along the reaction pathway. Consequently, it can be surmised that the chain propagation takes place at the solid state/solution phase boundary. In further contrast to the parent compound, the ROP process of *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**) is completely reversible, as depolymerization occurs upon redissolving $(t\text{-}Bu_2SnOSiPh_2OSiPh_2O)_n$ (**2b**) in solvent. The facile and selective ROP makes it possible to grow single crystals of the polymer **2b**, and the latter was investigated by X-ray diffraction [94]. In the solid state $(t\text{-}Bu_2SnOSiPh_2OSiPh_2O)_n$ (**2b**) adopts a *zigzag* conformation (Fig. 3) similar to that suggested for PDPhS on the basis of X-ray powder diffraction and molecular modeling [57,58,101].

The preparation of large single crystals also holds consequences for the molecular weight in the solid state, which is literally only limited by the crystal dimensions. The low barrier for the interconversion between **2a** (in solution) and **2b** (in solid state) can be attributed to the kinetic lability of the Sn–O bond and the very fine balance between enthalpic and entropic factors, i.e. the energy gain associated with the release of ring strain upon polymerization is compensated for in solution by the entropy increase associated with the formation of a large number of six-membered

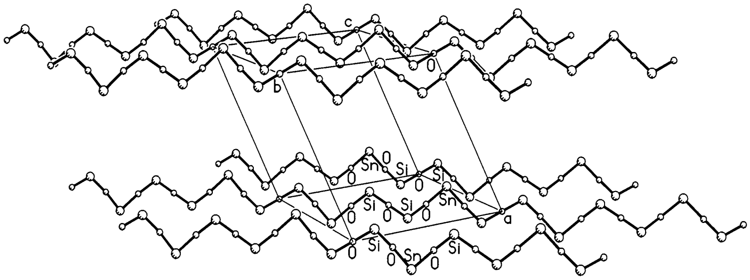


Fig. 3. Side view of the unit cell of $(t\text{-}Bu_2SnOSiPh_2OSiPh_2O)_n$ (**2b**) showing the *zigzag*-conformation of the polymer. The organic substituents at silicon and tin are omitted for clarity.

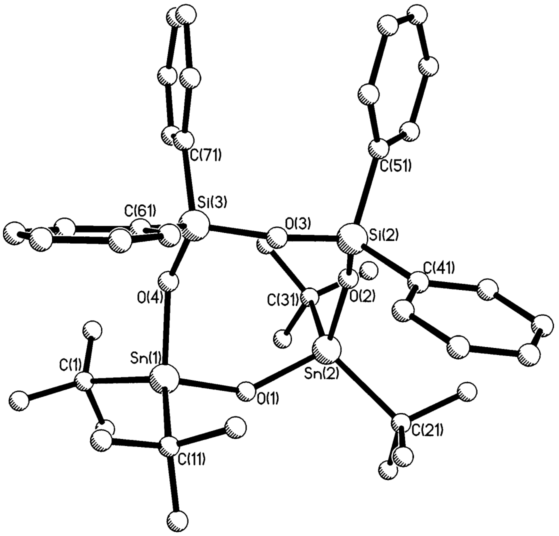
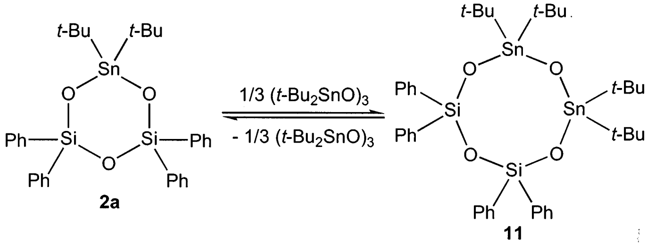


Fig. 4. Molecular structure of *cyclo*-O(SiPh$_2$OSn*t*-Bu$_2$)$_2$O (**11**). Selected bond angles: O(2)–Si(2)–O(3) = 113.2(2), O(3)–Si(3)–O(4) = 111.6(2), O(1)–Sn(1)–O(4) = 103.3(1), O(1)–Sn(2)–O(2) = 108.3(1), Sn(1)–O(1)–Sn(2) = 142.4(2), Sn(2)–O(2)–Si(2) = 156.4(2), Si(2)–O(3)–Si(3) = 140.3(2), Si(3)–O(4)–Sn(1) = 144.3(2)°.

rings [94]. The influence of the organic substituents on the spontaneous ROP behavior has been investigated in greater detail and is reported below. The reaction between *cyclo*-*t*-Bu$_2$Sn(OSiPh$_2$)$_2$O (**2a**) and *cyclo*-(*t*-Bu$_2$SnO)$_3$ resulted in ring enlargement to give the eight-membered stannasiloxane ring *cyclo*-O(SiPh$_2$OSn*t*-Bu$_2$)$_2$O (**11**) (Eq. 2) [79,94].



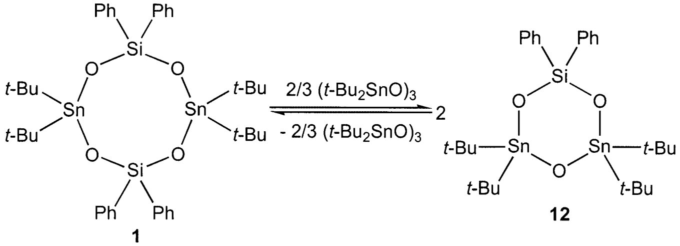
(2)

The reactivity of *cyclo*-*t*-Bu$_2$Sn(OSiPh$_2$)$_2$O (**2a**) toward *cyclo*-(*t*-Bu$_2$SnO)$_3$ can be interpreted in terms of the release of ring strain present in **2a**, and is associated with a decrease of entropy. Like the aforementioned eight-membered *cyclo*-stannasiloxanes, compound **11** exhibits very low strain, and consequently, it shows no tendency to undergo ROP. Its molecular structure is shown in Fig. 4.

In solution, an equilibrium takes place between **11**, **2a**, and *cyclo*-(*t*-Bu$_2$SnO)$_3$ [79,94]. Notably, the eight-membered *cyclo*-stannasiloxanes **3** and **11** represent constitutional isomers.

Preliminary attempts to prepare thin films on a silica surface by spin coating of the stannasiloxanes **1**, **2b**, **3**, and **11** were only successful in the case of the polymer **2b**. Remarkably, thin films of PDPhS are difficult to obtain, as conventional techniques such as spin coating cannot be applied due to the poor solubility of the polymer in organic solvents [32–34,60]. However, a sophisticated method was recently reported for the preparation of PDPhS films on silicon wafers by employing solid state ROP of *cyclo*-$(Ph_2SiO)_3$, initiated by sputtered metal particles, and subsequent removal of molecular residues by washing [102]. Thin films of PDPhS are of interest as they display a blue light emission upon UV laser irradiation [61].

In contrast to the reaction reported before, the eight-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2O)_2SiPh_2$ (**1**) reacts with *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$ under ring contraction to provide in solution the six-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**12**) (Eq. 3).

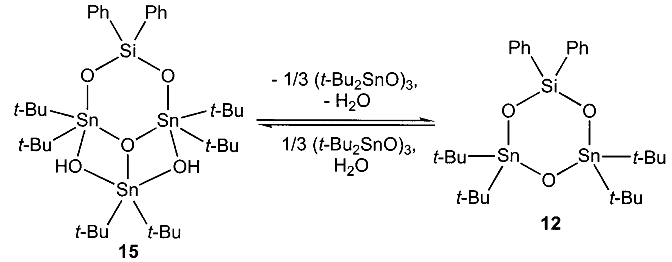


(3)

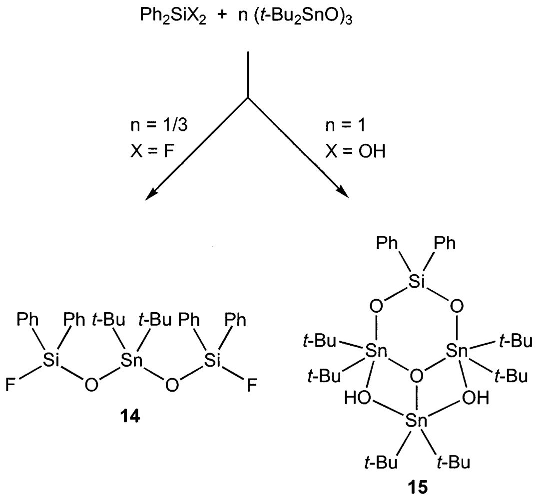
The six-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**12**) represents an analogue of compound **2a** containing an inverse silicon-to-tin ratio [79]. The thermodynamic driving force for the formation of compound **12** is the increase of entropy along the reaction. In turn, it can be surmised that the ring strain of the six-membered ring **12** is smaller than in the polymer precursor **2a**. However, there is still some ring strain present in *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**12**), as the reverse reaction occurred upon complete evaporation of a solution of **12** giving back a mixture of the starting compounds, *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2O)_2SiPh_2$ (**1**) and *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$, which was evidenced by ^{119}Sn MAS NMR spectroscopy [79]. The reason, why no polymerization of **12** occurs, may be traced to the greater number of kinetically labile Sn–O bonds which offers more options for the release of ring strain. Notably, the analogous six-membered stannasiloxane ring *cyclo*-$\textit{t}\text{-}Bu_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**13**) is stabilized by two bulky *tert*-butyl groups at silicon which prevents the reverse reaction to occur [79,103]. It is noteworthy that in the molecular structure of $\textit{t}\text{-}Bu_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**13**), the silicon and tin atoms are completely disordered [104].

As the reaction of di-*tert*-butyltin oxide, *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$, with diphenyldichlorosilane, Ph_2SiCl_2, proceeds under mild conditions with complete oxide transfer from tin to silicon [79], we posed the question how *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$ would react with diphenyldifluorosilane, Ph_2SiF_2, and diphenylsilandiol, $Ph_2Si(OH)_2$, respectively, as both consist of more stable Si–F, and Si–O bonds rather than the Si–Cl bonds in Ph_2SiCl_2. Regardless of the stoichiometric ratio applied, the reaction between *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$ and Ph_2SiF_2 gives the open-chain stannasiloxane, $\textit{t}\text{-}Bu_2Sn(OSiPh_2F)_2$ (**14**) and $\textit{t}\text{-}Bu_2SnF_2$. The stannasiloxane **14** can formally be regarded as a short unit of the polystannasiloxane (*t*-Bu_2SnO-$SiPh_2OSiPh_2O)_n$ (**2b**) (Scheme 2) [79]. The reaction of *cyclo*-(*t*-$Bu_2SnO)_3$ with $Ph_2Si(OH)_2$ provided the tricyclic stannasiloxane, [$Ph_2Si(OSn$*t*-$Bu_2)_2O$ · *t*-$Bu_2Sn(OH)_2$] (**15**), in which all the tin atoms adopt trigonal bipyramidal geometries (Scheme 2, Fig. 5) [103].

In contrast, the analogous reaction between *cyclo*-(*t*-$Bu_2SnO)_3$ and *t*-$Bu_2Si(OH)_2$ exclusively gave the six-membered stannasiloxane ring *cyclo*-*t*-$Bu_2Si(OSn$*t*-$Bu_2Sn)_2O$ (**13**) [103]. Notably, the reaction of Mes_3PbLi, *t*-Bu_2SnCl_2 and silicon grease in the presence of moisture serendipitously provided the tricyclic stannasiloxane, [$Me_2Si(OSn$*t*-$Bu_2Sn)_2O$ · *t*-$Bu_2Sn(OH)_2$] (**16**) [105], an analogue of compound **15**. The molecular structures of **15** and **16** resemble that of the tricyclic borastannoxane [$MesB(OSn$*t*-$Bu_2)_2O$ · *t*-$Bu_2Sn(OH)_2$] (**17**) [106]. The structural motif present in compounds **15**–**17** can be rationalized as a complex between a six-membered ring, *cyclo*-$M(OSn$*t*-$Bu_2)_2O$ ($M = Ph_2Si$ (**12**), Me_2Si, MesB) and di-*tert*-butyltin hydroxide, *t*-$Bu_2Sn(OH)_2$ [103]. Apparently, the stability of the structural motif is significantly influenced by the organometal fragment M. In chloroform solution, [$Ph_2Si(OSn$*t*-$Bu_2)_2O$ · *t*-$Bu_2Sn(OH)_2$] (**15**) is kinetically labile and exists in a temperature-dependent equilibrium with the six-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSn$*t*-$Bu_2)_2O$ (**12**), *cyclo*-(*t*-$Bu_2SnO)_3$ and water (Eq. 4) [103].



(4)



Scheme 2.

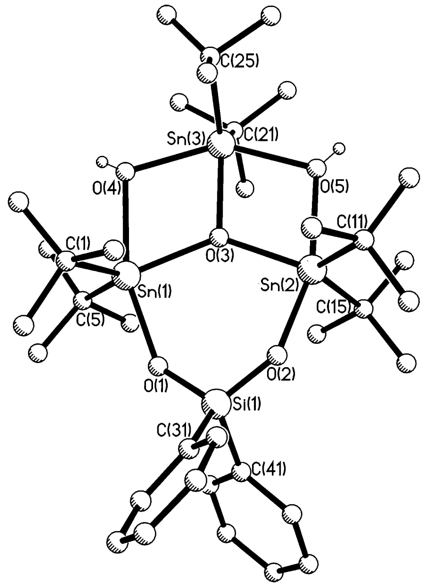


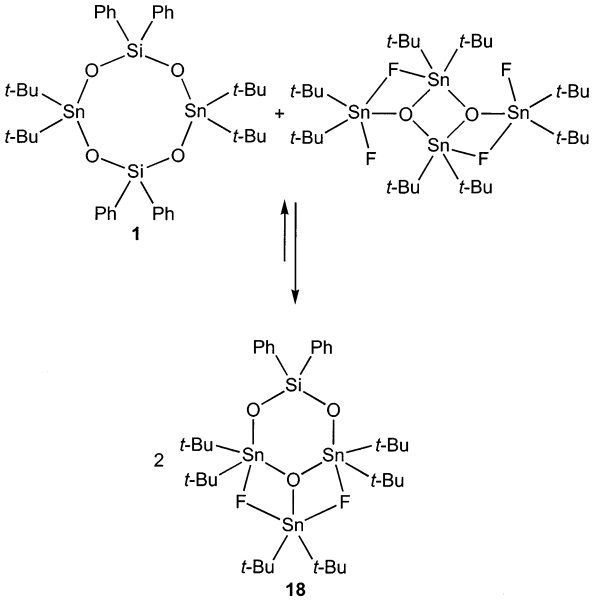
Fig. 5. Molecular structures of [$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2Sn(OH)_2$] (**15**). Selected bond lengths: Sn(1)–O(1) = 2.020(2), Sn(1)–O(4) = 2.261(3), Sn(1)–O(3) = 2.092(2), Sn(2)–O(2) = 2.018(3), Sn(2)–O(5) = 2.264(3), Sn(2)–O(3) = 2.093(2), Sn(3)–O(3) = 2.091(2), Sn(3)–O(4) = 2.106(3), Sn(3)–O(5) = 2.103(3) Å. Selected bond angles: O(1)–Sn(1)–O(4) = 160.8(1), O(2)–Sn(2)–O(5) = 161.9(1), O(4)–Sn(3)–O(5) = 146.5(1)°.

It is worth mentioning that the initial dissociation product di-*tert*-butyltin dihydroxide, $\textit{t}\text{-}Bu_2Sn(OH)_2$, was not detected in solution. Apparently, it undergoes immediate self-condensation to give *cyclo*-($\textit{t}\text{-}Bu_2SnO)_3$ and water [103]. However, $\textit{t}\text{-}Bu_2Sn(OH)_2$ was isolated in the solid state and characterized by ^{119}Sn MAS NMR spectroscopy [103].

Compound [$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2SnF_2$] (**18**) is a structural analogue of [$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2Sn(OH)_2$] (**15**) in which the hydroxy groups are formally replaced by fluorine atoms [104]. It is accessible in almost quantitative yield by the reaction of the eight-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2O)_2SiPh_2$ (**1**) with the fluorine-containing tetraorganodistannoxane [$\textit{t}\text{-}Bu_2(F)SnOSn(F)\textit{t}\text{-}Bu_2]_2$ [107] (Eq. 5). The molecular structure of compound **18** is shown in Fig. 6.

The tricyclic stannasiloxane [$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2SnF_2$] (**18**), can formally be regarded as a complex between *cyclo*-$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O$ (**12**) and di-*tert*-butyltin difluoride, $\textit{t}\text{-}Bu_2SnF_2$. However, in chloroform solution compound **18** does not dissociate into the stannasiloxane ring **12** and $\textit{t}\text{-}Bu_2SnF_2$. Instead, it is in equilibrium with its starting compounds **1** and [$\textit{t}\text{-}Bu_2(F)SnOSn(F)\textit{t}\text{-}Bu_2]_2$ [104].

For the synthesis of siloxane rings and polymers, the nature of the organic substituents is one crucial parameter that determines the ring size and the product



(5)

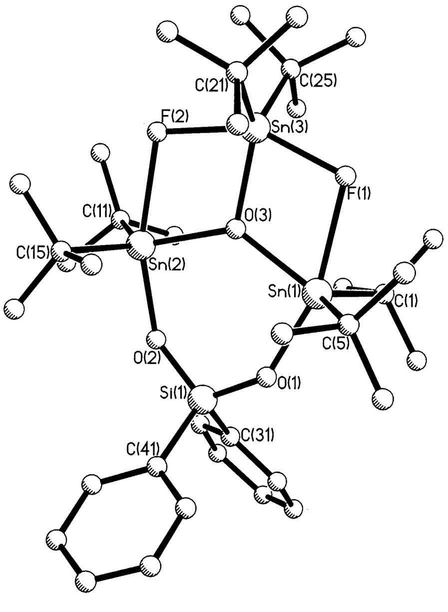
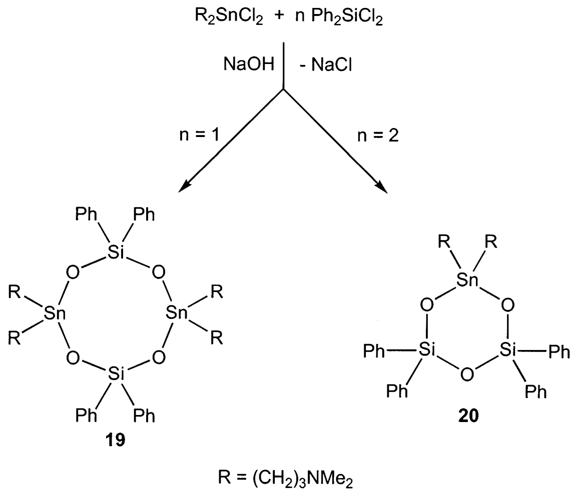


Fig. 6. Molecular structure of [$Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2SnF_2$] (**18**). Selected bond lengths: Sn(1)–F(1) = 2.339(3), Sn(1)–O(1) = 1.981(4), Sn(1)–O(3) = 2.098(4), Sn(2)–F(2) = 2.353(3), Sn(2)–O(2) = 1.999(4), Sn(2)–O(3) = 2.109(4), Sn(3)–F(1) = 2.074(3), Sn(3)–F(2) = 2.073(3) Å. Selected bond angles: F(1)–Sn(1)–O(1) = 162.5(1), F(2)–Sn(2)–O(2) = 162.7(1), F(1)–Sn(3)–F(2) = 150.8(1)°.



Scheme 3.

distribution, and the same should hold for stannasiloxane rings and polymers. This assumption prompted us to a thorough study on the role of the organic substituents at both silicon and tin on the polymerization behavior of six-membered stannasiloxane rings *cyclo*-$R_2Sn(OSiR'_2)_2O$ [108]. Depending on the stoichiometric ratio applied, the cohydrolysis under basic conditions of diphenyldichlorosilane, Ph_2SiCl_2, and intramolecularly hexacoordinated bis(3-dimethylaminopropyl)tin dichloride, $[Me_2N(CH_2)_3]SnCl_2$, gives either the eight-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSnR_2O)_2SiPh_2$ (**19**) or the six-membered stannasiloxane ring *cyclo*-$R_2Sn(OSiPh_2)_2O$ (**20**) ($R = (CH_2)_3NMe_2$), respectively (Scheme 3) [109].

Compound **19** is an analogue of *cyclo*-$Ph_2Si(OSn$*t*-$Bu_2O)_2SiPh_2$ (**1**) and *cyclo*-$(Ph_2SiO)_4$ and contains an eight-membered ring in the solid state (Fig. 7) [109].

Although the six-membered stannasiloxane ring **20** (Fig. 8) is an analogue of the polymer precursor **2a**, it does not undergo spontaneous ROP upon crystallization. We trace this behavior to the intramolecularly coordinating 3-dimethylaminopropyl ligands which induce an octahedral geometry at the tin center, associated with a decrease of the O–Sn–O bond angle and reduction of the ring strain [109]. The same observation holds for *cyclo*-$[CH_2(Me)N(CH_2)_3N]_2Sn(OSiPh_2)_2O$ (**21**), which also contains a six-membered ring both in solution and in the solid state [109]. Another member of this class of compounds, *cyclo*-$[Me_2N(CH_2)_2CMe_2]Sn(OSiMe_2)_2O$ (**22**) was isolated from a reaction of $[Me_2N(CH_2)_2CMe_2]SnCl_2$, silicon grease and sodium hydroxide [110]. Surprisingly, in this case Si–O–Si linkages are cleaved in favor of Si–O–Sn linkages. Notably, the attempt to formally replace the phenyl groups in the eight-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSnR_2O)_2SiPh_2$ (**19**) ($R = (CH_2)_3NMe_2$) with *t*-butyl groups failed. Instead, the cohydrolysis under basic conditions of di-*tert*-butyldichlorosilane, *t*-Bu_2SiCl_2, and bis(3-dimethylaminopropyl)tin dichloride, $[Me_2N(CH_2)_3]SnCl_2$, gives the open-chain stannasiloxane

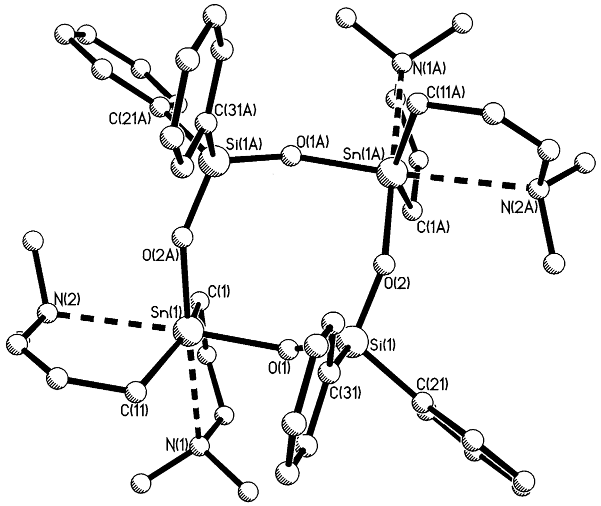


Fig. 7. Molecular structure of *cyclo*-$Ph_2Si(OSnR_2O)_2SiPh_2$ (**19**, R = $(CH_2)_3NMe_2$). Selected bond lengths: Sn(1)–N(1) = 2.721(4), Sn(1)–N(2) = 2.811(4) Å. Selected bond angles: O(1)–Si(1)–O(2) = 111.1(1), O(1)–Sn(1)–O(2a) = 97.4(1), Si(1)–O(1)–Sn(1) = 144.3(2)°.

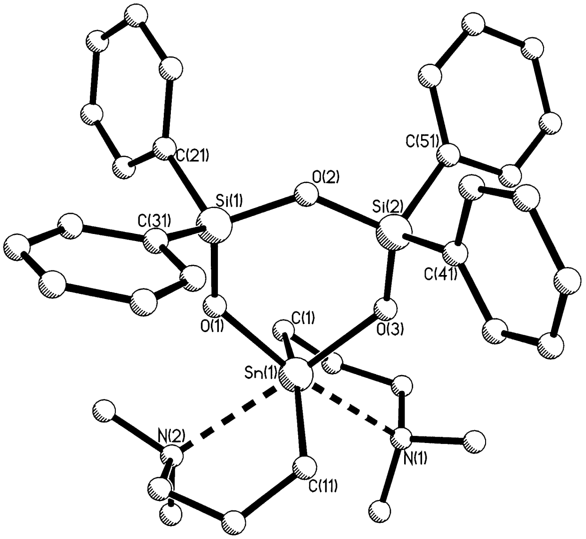


Fig. 8. Molecular structure of *cyclo*-$R_2Sn(OSiPh_2)_2O$ (**20**, R = $(CH_2)_3NMe_2$). Selected bond lengths: Sn(1)–N(1) = 2.621(4), Sn(1)–N(2) = 2.638(5) Å. Selected bond angles: O(1)–Si(1)–O(2) = 111.9(2), O(2)–Si(2)–O(3) = 113.2(2), O(1)–Sn(1)–O(3) = 92.4(1), Si(1)–O(1)–Sn(1) = 135.9(2), Si(2)–O(3)–Sn(1) = 134.2(2)°.

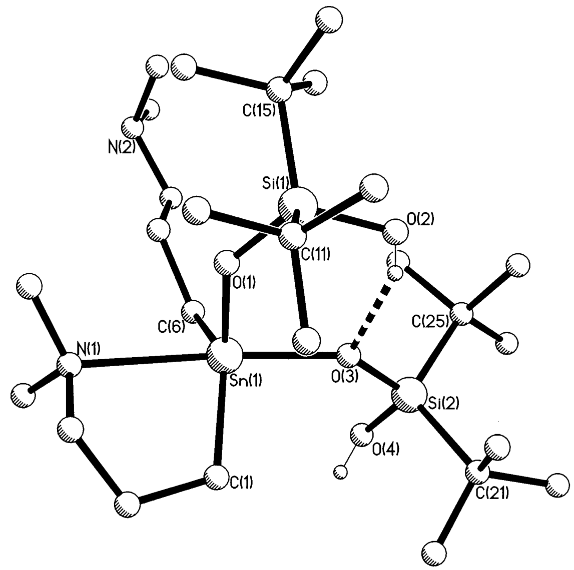
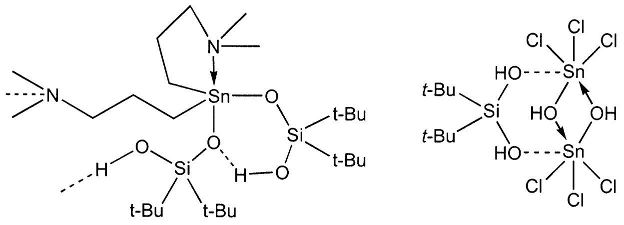


Fig. 9. Molecular structure of $[Me_2N(CH_2)_3]_2Sn[OSi(OH)\textit{t}\text{-}Bu]_2$ (**23**). Selected bond length: Sn(1)–N(1) = 2.567(2) Å. Selected bond angles: Si(1)–O(1)–Sn(1) = 138.76(8), Si(2)–O(3)–Sn(1) = 136.92(8), O(1)–Sn(1)–O(3) = 92.92(5)°.

$[Me_2N(CH_2)_3]_2Sn[OSi(OH)\textit{t}\text{-}Bu]_2$ (**23**) which reveals both intra- and intermolecular hydrogen bonding in the solid state (Chart 3, Fig. 9) [111]. Remarkably, only one of the two potential so-called built-in ligands is involved in coordination with the tin atom.



23 **38**

Chart 3.

The eight-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSnR_2O)_2SiPh_2$ (**19**) (R = $(CH_2)_3NMe_2$) is an attractive precursor for the synthesis of further six-membered stannasiloxane rings. Its reaction under mild conditions with *cyclo*-$(\textit{t}\text{-}Bu_2SnO)_3$ provides the stannasiloxane ring *cyclo*-$(Ph_2SiOSnR_2OSn\textit{t}\text{-}Bu_2O)$ (**24**), which is a structural analogue of compound **12** [112]. Unlike the latter, the six-membered ring structure of **24** (Fig. 10) is also retained in the solid state, which again demonstrates the stabilizing effect of the intramolecularly coordinating 3-dimethylaminopropyl ligands.

In this context, the comparison of the Sn···N bond distances in the eight-membered ring **19** (Sn–N: 2.721(4); 2.811(4) Å) on the one hand, and the six-membered rings **20** (Sn–N: 2.621(4); 2.638(5) Å), and **24** (Sn–N: 2.683(3); 2.764(3) Å) on the other hand, reveal a significant shortening in the latter compounds. The geometry of tin atoms bearing these built-in ligands has to be considered as a [4 + 2]-coordination rather than true octahedral [109,112]. In turn, the flexibility of the tin geometry allows the adjustment of the O–Sn–O angles to meet the requirements of ring constrains, and thus to accommodate ring strain.

The same concept also applies to the synthesis of the ternary oxides, *cyclo*-($Ph_2SiOSnR_2OGe$*t*-Bu_2O) (**25**) and *cyclo*-($Ph_2SiOSnR_2OBPhO$) (**26**), which are accessible by the reaction of the eight-membered ring *cyclo*-$Ph_2Si(OSnR_2O)_2SiPh_2$ (**19**) ($R = (CH_2)_3NMe_2$) with di-*tert*-butylgermanium dihydroxide and phenylboronic acid, respectively (Scheme 4) [112].

The six-membered rings *cyclo*-($Ph_2SiOSnR_2OGe$*t*-Bu_2O) (**25**) and ($Ph_2SiOSnR_2$-$OBPhO$) (**26**) ($R = (CH_2)_3NMe_2$), are the first examples of organoelement oxides containing three different metals in the same ring [112]. These compounds are of potential interest as single-source precursors for the preparation of new ceramic materials [6–15].

The reactions of 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $HO(Ph_2SiO)_2H$ with other diorganotin dichlorides, R_2SnCl_2 (R = Me, Et, *i*-Pr, *n*-Bu, Ph, $CpFeC_5H_4$, $Cp(CO)_2Fe$, $Cp(CO)_3W$) were investigated in analogy to the preparation of the polymer precursor *t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**) (Scheme 5) [108]. In contrast to the

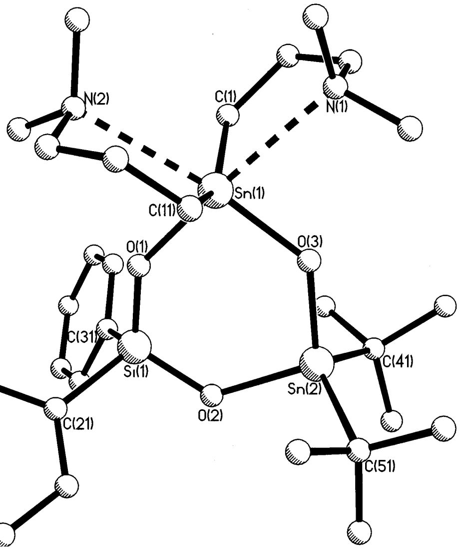
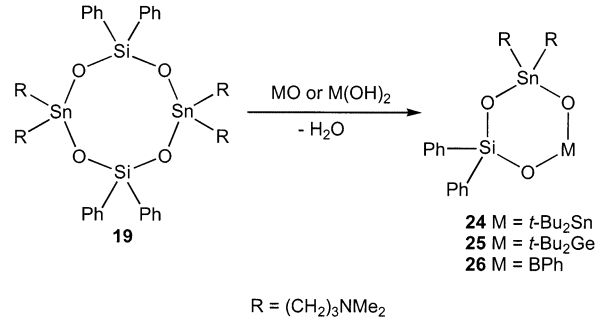
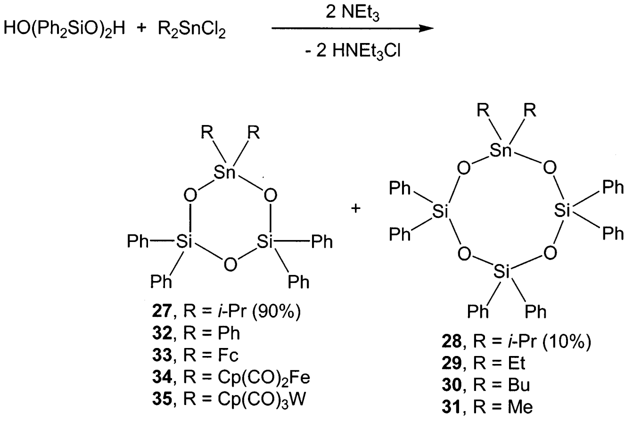


Fig. 10. Molecular structure of *cyclo*-($Ph_2SiOSnR_2OSn$*t*-Bu_2O) (**24**). Selected bond lengths: Sn(1)–N(1) = 2.683(3), Sn(1)–N(2) = 2.764(3) Å. Selected bond angles: O(1)–Si(1)–O(2) = 114.2(1), O(1)–Sn(1)–O(3) = 95.45(9), O(2)–Sn(2)–O(3) = 106.69(9), Si(1)–O(1)–Sn(1) = 142.0(1), Si(1)–O(2)–Sn(2) = 129.0(1), Sn(1)–O(3)–Sn(2) = 131.9(1)°.



Scheme 4.



Scheme 5.

synthesis of the latter compound, the reactions involving the aliphatic diorganotin dichlorides are more complex and give mixtures of products.

The unexpected formation of the eight-membered stannasiloxane rings **28**–**31** containing trisiloxane units suggests the selective Si–O bond cleavage and rearrangement of a disiloxane unit into a trisiloxane unit. The molecular structure of compound **31** as a representative of these eight-membered rings is shown in Fig. 11.

Bearing in mind the mild reaction conditions applied, these observations can be considered to be the first cases of Si–O bond activation mediated by soft organometallics, e.g. organotin compounds. This statement gets experimental support by the molecular structure of the related compound *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ revealing an intramolecular Sn–O coordination [113]. In the absence of organotin species, mixtures of silanols and amines usually remain unchanged [108].

It is worth noting that the reaction of lithium or sodium 1,1,3,3-tetraphenyldisiloxane-1,3-diolate, $O(SiPh_2OM)_2$ (M = Li, Na) with tin tetrachloride, $SnCl_4$, provides the tetracyclostannasiloxane **36** and the spirocyclostannasiloxane **37** rather than a monocyclic compound (Scheme 6) [114].

For the latter compound a disiloxane unit was also cleaved in favor of a trisiloxane unit. However, the rearrangement occurred in the presence of a strong base and is therefore not comparable with the Si–O bond activation under mild conditions mentioned before; alkali metal silanolates are well-known initiators in the ROP process [17]. Worth mentioning is also the reaction of di-*tert*-butylsilandiol, t-$Bu_2Si(OH)_2$, with tin tetrachloride, $SnCl_4$, which resulted in partial condensation to form the complex t-$Bu_2Si(OH)_2 \cdot (Cl_3SnOH)_2$ (**38**) and 1,1,3,3-tetra-*tert*-butylsiloxane-1,3-diol, $HO(Si$$t$-$Bu_2O)_2OH$ (Chart 3) [115].

The reaction between 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $HO(Ph_2SiO)_2H$ and transition metal-substituted tin dichlorides, $RR'SnCl_2$, gives the six-membered stannasiloxane rings *cyclo*-$RR'Sn(OSiPh_2)_2O$ (**34**, $R = R' = Cp(CO)_2Fe$; **35**, $R = t$-Bu, $R' = Cp(CO)_3W$), both of which retain their ring structures in the solid state (Scheme 5) [109]. The molecular structure of compound **34** is shown in Fig. 12.

Like for compounds **20** and **21**, the O–Sn–O angles found for these compounds are significantly smaller than the expected tetrahedral angle, which in turn reduce the ring strain.

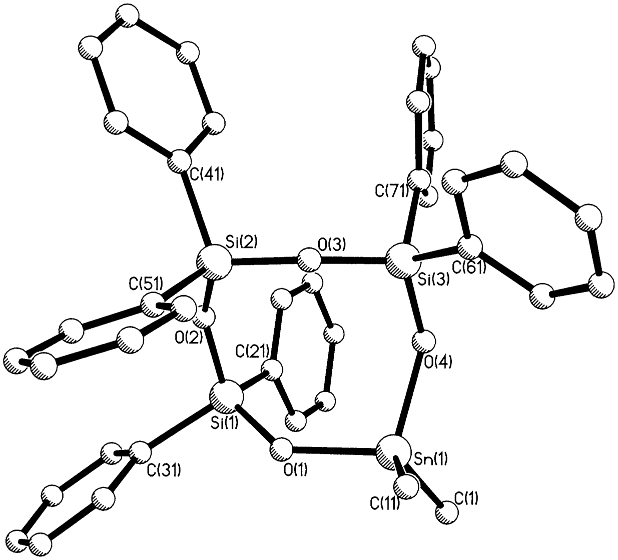
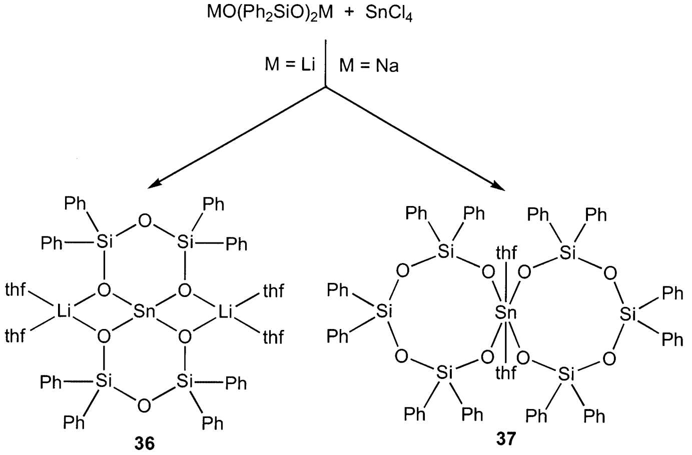


Fig. 11. Molecular structure of *cyclo*-$Me_2Sn(OSiPh_2O)_2SiPh_2$ (**31**). Selected bond angles: O(1)–Si(1)–O(2) = 110.51(8), O(2)–Si(2)–O(3) = 110.05(9), O(3)–Si(3)–O(4) = 111.21(9), O(1)–Sn(1)–O(4) = 103.03(7), Si(1)–O(2)–Si(2) = 144.2(1), Si(2)–O(3)–Si(3) = 151.4(1), Si(3)–O(4)–Sn(1) = 133.6(1), Si(1)–O(1)–Sn(1) = 137.4(1)°.



Scheme 6.

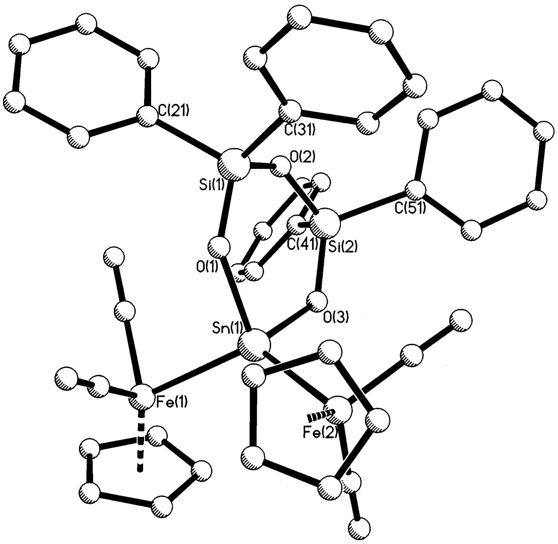


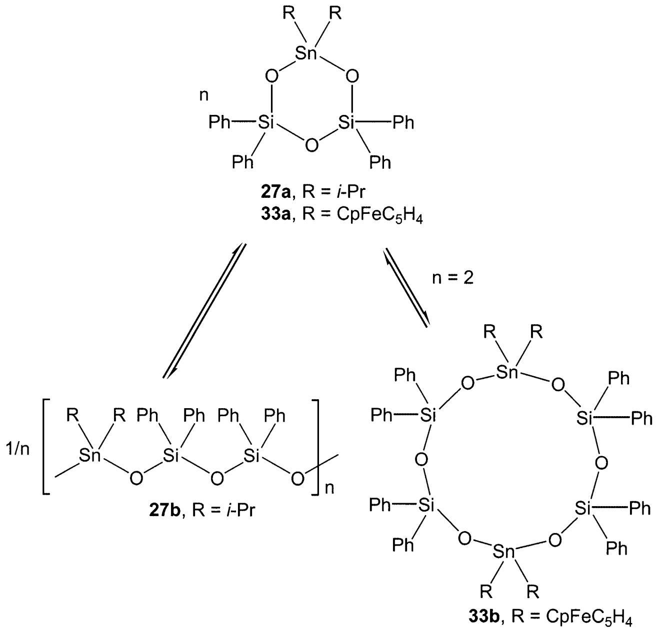
Fig. 12. Molecular structure of *cyclo*-$[Cp(CO)_2Fe]_2Sn(OSiPh_2)_2O$ (**34**). Selected bond angles: O(1)–Si(1)–O(2) = 111.1(1), O(2)–Si(2)–O(3) = 111.6(1), O(1)–Sn(1)–O(3) = 95.8(1), Si(1)–O(2)–Si(2) = 135.4(2), Si(1)–O(1)–Sn(1) = 132.6(2), Si(2)–O(3)–Sn(1) = 131.9(2)°.

The six-membered stannasiloxane rings *cyclo*-$R_2Sn(OSiPh_2)_2O$ (**27a**, R = *i*-Pr; **33a**, R = $CpFeC_5H_4$) containing tetrahedral tin atoms, indeed rearrange upon crystallization; compound **27b** also represents a polymer with a conformation similar to that found in (t-$Bu_2SnOSiPh_2OSiPh_2O)_n$ (**2b**). However, the ferrocene-substituted derivative **33a** gives the twelve-membered ring *cyclo*-$[(CpFeC_5H_4)_2Sn(OSiPh_2OSiPh_2O)_2Sn(C_5H_4FeCp)_2]$ (**33b**) but no polymer (Scheme 7, Fig. 13) [108,111].

In both cases, the release of ring strain is the thermodynamic driving force for the rearrangement process, and the reverse reaction takes place upon redissolving. However, the reason why a polymer is formed in one case, but a twelve-membered ring is formed in another still remains uncertain.

Our efforts have also been extended to the change of substituents at the silicon atoms. The reaction between 1,1,3,3-tetraisopropydisiloxane-1,3-diol, HO(*i*-$Pr_2SiO)_2H$, and di-*tert*-butyltin dichloride, *t*-Bu_2SnCl_2, was performed in analogy to the synthesis of the polymer precursor **2b**, and afforded the stannasiloxane ring *cyclo*-*t*-$Bu_2Sn(OSi$*i*-$Pr)_2O$ (**39**), which is a six-membered ring both in solution and in the solid state [108]. Compound **39** was also investigated by X-ray diffraction, which confirms the six-membered ring structure, but a satisfactory refinement could not be achieved due to disorder problems similar to that for *cyclo*-*t*-$Bu_2Si(OSn$*t*-$Bu_2)_2O$ (**13**) [104]. Apparently, the bulky isopropyl groups prevent the polymerization of **39**. Further variation of the substituents at silicon is still in progress and will be the subject of a forthcoming paper [108].

The aforementioned experimental results suggest that the formal substitution of silicon atoms in siloxane rings and polymers by other metals, such as tin, may change the reactivity of the parent compounds to a very large extent. However, the question how different metals influence on the reactivity of *cyclo*-metallasiloxanes and the corresponding polymers still remains unanswered. This is demonstrated by the following comparison of selected six-membered metallasiloxane and metallastannoxane rings. Recently, the synthesis and characterization of the six-membered borasiloxane ring *cyclo*-$PhB(OSiPh_2)_2O$ (**40**) (Chart 4), a structural analogue of the



Scheme 7.

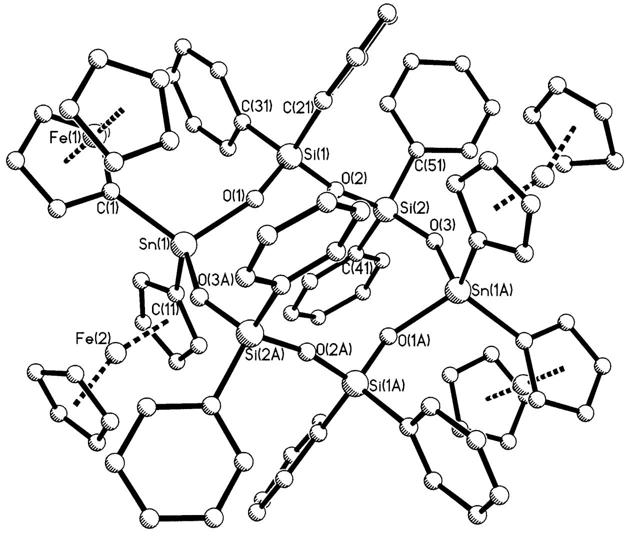


Fig. 13. Molecular structure of *cyclo*-[$(CpFeC_5H_4)_2Sn(OSiPh_2OSiPh_2O)_2Sn(C_5H_4FeCp)_2$] (**33b**). Selected bond angles: O(1)–Si(1)–O(2) = 110.8(1), O(2)–Si(2)–O(3) = 112.4(1), O(1)–Sn(1)–O(3A) = 101.63(9), Si(1)–O(2)–Si(2) = 167.7(2), Si(1)–O(1)–Sn(1) = 144.3(1), Si(2)–O(3)–Sn(1A) = 147.4(1)°.

polymer precursor *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**), was independently reported by two groups [116–118]. Although, it was designed for the purpose of ROP studies, all attempts to polymerize *cyclo*-$PhB(OSiPh_2)_2O$ (**40**) failed and gave only mixtures of molecular species [116,119]. This is somewhat surprising as the formal replace-

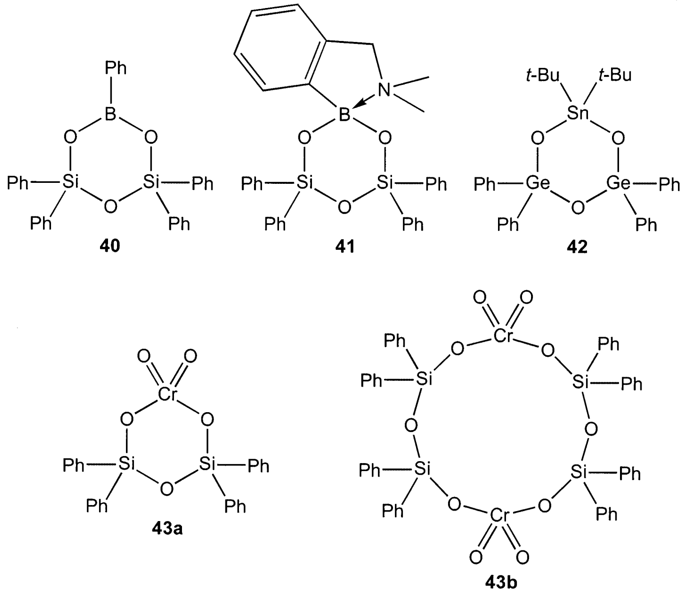


Chart 4.

ment of a diphenylsilyl segment in *cyclo*-$(Ph_2SiO)_3$ by a substantially smaller phenylboron segment was expected to increase the ring strain. The analogous six-membered borasiloxane ring *cyclo*-$RB(OSiPh_2)_2O$ (**41**) (R = *o*-$C_6H_4CH_2NMe_2$) (Chart 4, Fig. 14) contains a built-in ligand which induces a tetrahedral geometry at the boron center and makes the latter more silicon-like [111].

However, all attempts so far to polymerize **41** also failed (Chart 4). The six-membered germastannoxane ring *cyclo*-*t*-$Bu_2Sn(OGePh_2)_2O$ (**42**) (Chart 4) can be rationalized by formally replacing the silicon atoms in the polymer precursor *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ (**2a**) by germanium atoms [109]. Although the chemistry of silicon and germanium is comparable in many aspects and germanium atoms are only slightly larger than silicon atoms, no polymerization of **42** could be achieved. On the other hand, in a recent paper the molecular structure of the twelve-membered chromasiloxane ring *cyclo*-$O_2Cr(OSiPh_2OSiPh_2O)_2CrO_2$ (**43b**) was reported [120]. Although no molecular weight measurement was performed, a comparison of its ^{29}Si NMR chemical shift of -31.9 ppm with those of related six-membered stannasiloxane rings (δ ^{29}Si -35.9 to -41.0 ppm) [79,109] and of *cyclo*-$(Ph_2SiO)_3$ (δ ^{29}Si -33.3 ppm) [121] led us to propose compound **43b** to undergo monomerization upon dissolution to give the six-membered chromasiloxane ring *cyclo*-$O_2Cr(OSiPh_2)_2O$ (**43a**). This behavior is comparable to that found for the ferrocene-containing stannasiloxane rings **33a** and **33b** (Scheme 7). However, it seems that conclusions drawn from ^{29}Si NMR chemical shifts concerning the ring size of metallasiloxanes in solution have to be taken with caution as the 12-membered ring *cyclo*-$(t\text{-}BuN)_2Cr(OSiPh_2OSiPh_2O)_2Cr(Nt\text{-}Bu)_2$, the ring size of which

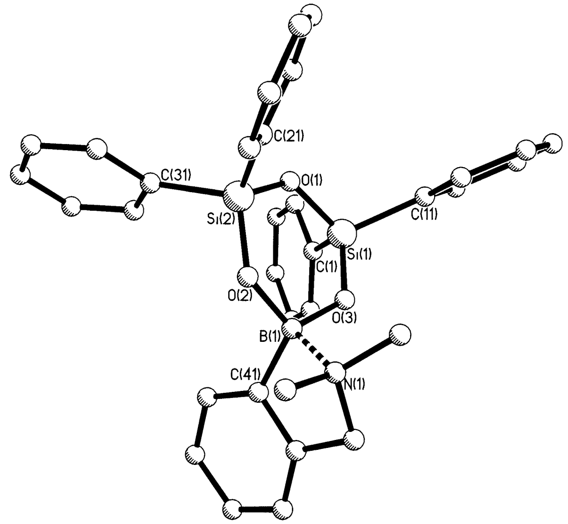


Fig. 14. Molecular structure of *o*-$Me_2NCH_2C_6H_4B(OSiPh_2)_2O$ (**41**). Selected bond length: N(1)–B(1) = 1.688(3) Å. Selected bond angles: O(1)–Si(1)–O(3) = 107.54(7), O(1)–Si(2)–O(2) = 108.50(6), O(2)–B(1)–O(3) = 113.1(2), Si(1)–O(1)–Si(2) = 125.56(8), Si(1)–O(3)–B(1) = 128.6(1), Si(2)–O(2)–B(1) = 130.4(1)°.

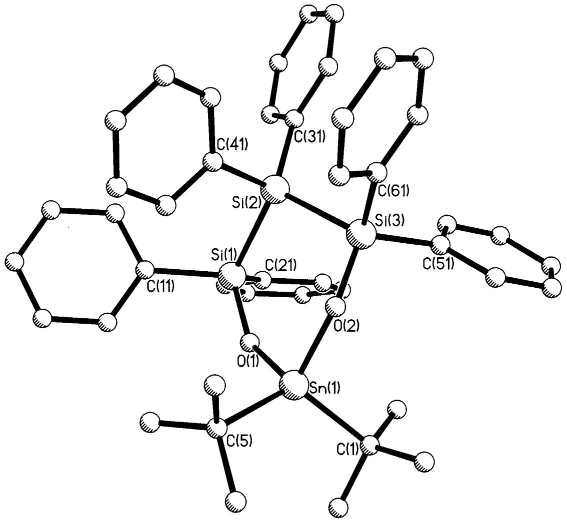


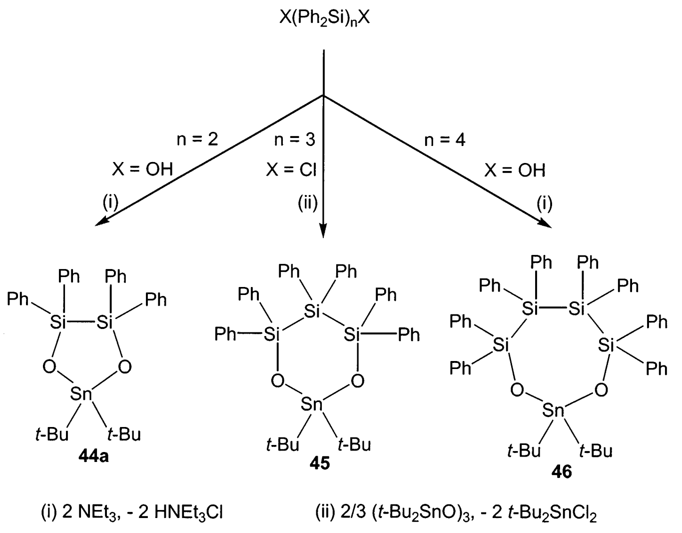
Fig. 15. Molecular structure of *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2(SiPh_2)$ (**45**). Selected bond angles: O(1)–Si(1)–Si(2) = 108.64(7), O(2)–Si(3)–Si(2) = 107.50(7), O(1)–Sn(1)–O(2) = 101.28(7), Si(1)–O(1)–Sn(1) = 144.5(1), Si(3)–O(2)–Sn(1) = 135.0(1), Si(1)–Si(2)–Si(3) = 105.87(4)°.

was established by molecular weight determination exhibits a δ ^{29}Si of -38.2 ppm [122,123].

The collection of the compounds **40**–**43b** shown in Chart 4 may suggest that the influence of various metals on the ring strain cannot simply be accounted for in terms of size of the metal atoms, and, is therefore less straightforward to predict. Further work in this field, including the results of DFT calculations, is in progress [124].

All compounds reported so far are exclusively assembled by M–O–M′-segments (M, M′ = Si, Sn, Ge, B, Cr). Some of our recent work is devoted to the synthesis of new classes of inorganic heterocycles containing M–E–M-segments (M = E = Ph_2Si; M = Ph_2Sn, E = CH_2). In general, these segments usually reveal substantially smaller M–E–M angles, and therefore, different ring size preferences are to be expected. The reaction between various α,ω-difunctional perphenylated oligosilanes with di-*tert*-butyltin dichloride, *t*-Bu_2SnCl_2, and di-*tert*-butyltin oxide, *cyclo*-(*t*-$Bu_2SnO)_3$, respectively, afford a series of stannasiloxane rings such as *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2$ (**44a**), *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2(SiPh_2)$ (**45**) (Fig. 15), and *cyclo*-*t*-$Bu_2Sn(OSiPh_2SiPh_2)_2$ (**46**) (Scheme 8) [111,125].

The ring strain in compounds **45** and **46** seems to be rather low as these derivatives contain, respectively, six- and seven-membered rings both in solution and in the solid state. On the other hand, the more strained five-membered stannasiloxane ring *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2$ (**44a**) reversibly dimerizes upon crystallization providing the ten-membered stannasiloxane ring *cyclo*-*t*-$Bu_2Sn(OSiPh_2$-$SiPh_2O)_2Sn$*t*-Bu_2 (**44b**) (Eq. 6, Fig. 16) [125].



Scheme 8.

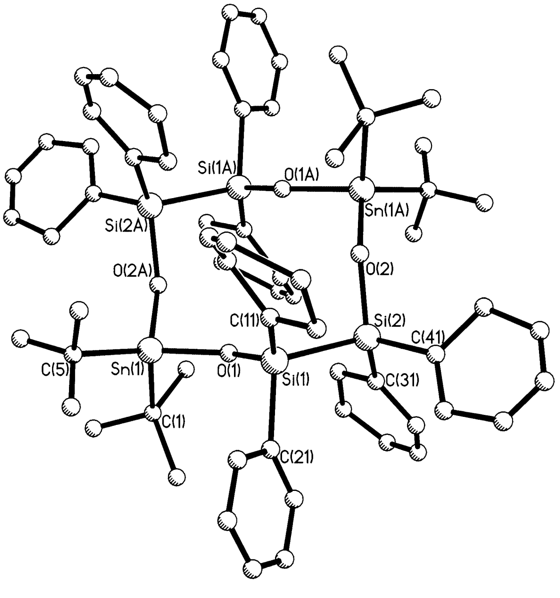
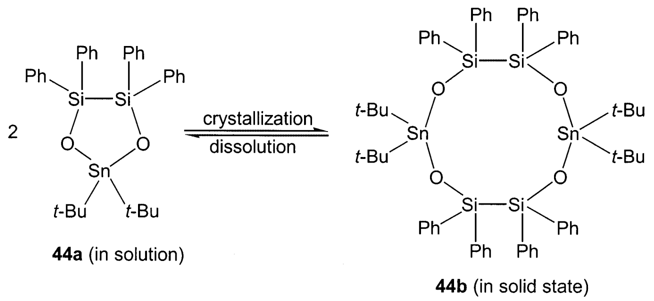
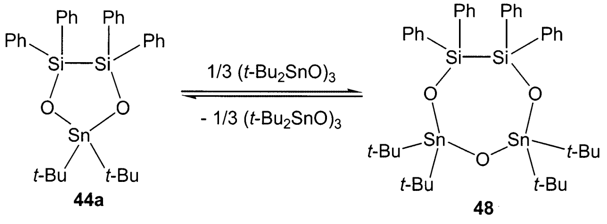


Fig. 16. Molecular structure of *cyclo*-*t*-$Bu_2Sn(OSiPh_2SiPh_2O)_2Sn$*t*-$Bu_2$ (**44b**). Selected bond angles: O(1)–Si(1)–Si(2) = 96.5(3), O(2)–Si(2)–Si(1) = 92.9(2), O(1)–Sn(1)–O(2A) = 100.2(4), Si(1)–O(1)–Sn(1) = 142.3(5), Sn(1)–O(2A)–Si(2A) = 128.5(3), Si(1)–Si(2)–O(2) = 92.9(2)°.



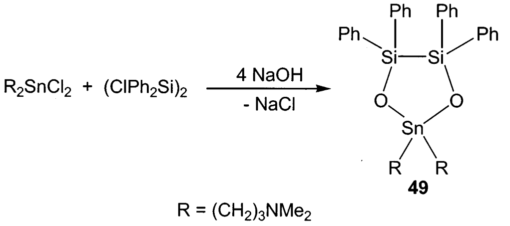
(6)

The same behavior was observed for *cyclo*-*t*-$Bu_2Sn[OSi(F)$*t*-$Bu]_2$ (**47a**) and *cyclo*-*t*-$Bu_2Sn[OSi(F)$*t*-$BuSi(F)t-BuO]_2$ (**47b**) [107]. The release of ring strain in *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2$ (**44a**) is also the thermodynamic driving force of its reaction with *cyclo*-(*t*-$Bu_2SnO)_3$ producing the seven-membered stannasiloxane ring *cyclo*-$(Ph_2SiOSn$*t*-$Bu_2)_2O$ (**48**) (Eq. 7) [125]. The six- and seven-membered stannasiloxane rings **45** and **46** containing three and four silicon atoms, respectively, are less strained and do not react with *cyclo*-(*t*-$Bu_2SnO)_3$.



(7)

The cohydrolysis under basic conditions of 1,1,2,2-tetraphenyl-1,2-dichlorodisilane, $(ClPh_2Si)_2$, and intramolecularly hexacoordinated bis(3-dimethylaminopropyl)tin dichloride, $[Me_2N(CH_2)_3]_2SnCl_2$, gives the five-membered stannasiloxane ring *cyclo*-$R_2Sn(OSiPh_2)_2$ (**49**) ($R = (CH_2)_3NMe_2)$) (Eq. 8) which is an analogue of compound **44a** [125].



(8)

Here again, the intramolecularly coordinating 3-dimethylaminopropyl ligands prevent the dimerization and consequently the *cyclo*-stannasiloxane **49** is a five-membered ring in solution as well as in the solid state (Fig. 17).

The condensation of equimolar amounts of perphenylated α,ω-sil(ox)anediols, $HO(Ph_2SiO)_nH$ ($n = 1$–4), with bis(diphenylhydroxystannyl)methane, (Ph_2SnOH)-CH_2, provides the stannasiloxane rings *cyclo*-$Ph_2Si(OSnPh_2)_2CH_2$ (**50**), *cyclo*-

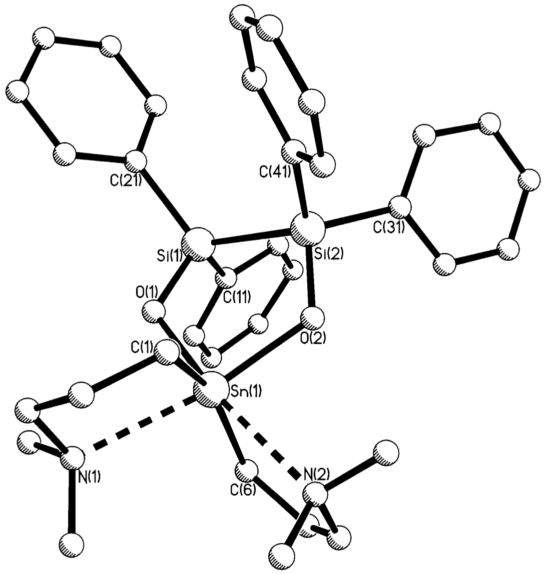
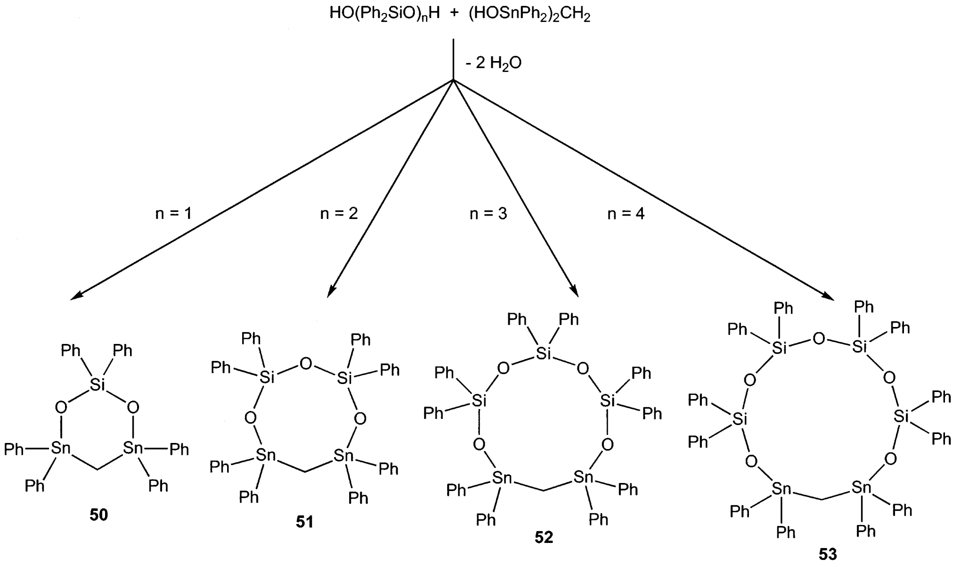


Fig. 17. Molecular structure of *cyclo*-$[Me_2N(CH_2)_3]_2Sn(OSiPh_2)_2$ (**49**). Selected bond lengths: Sn(1)–N(1) = 2.556(4), Sn(1)–N(2) = 2.700(4) Å. Selected bond angles: O(1)–Si(1)–Si(2) = 98.6(1), O(2)–Si(2)–Si(1) = 98.4(1), O(1)–Sn(1)–O(2) = 90.9(1), Si(1)–O(1)–Sn(1) = 122.0(2), Si(2)–O(2)–Sn(1) = 121.7(1)°.



Scheme 9.

$O(SiPh_2OSnPh_2)_2CH_2$ (**51**), *cyclo*-$Ph_2Si(OSiPh_2OSnPh_2)_2CH_2$ (**52**), and *cyclo*-$O(SiPh_2OSiPh_2OSnPh_2)_2CH_2$ (**53**), which are all stable in solution (Scheme 9) [126].

The eight-, ten-, and twelve-membered rings **51**–**53** were isolated in high yields. No oligo- or polymerization takes place upon crystallization of these compounds [126]. In contrast, all attempts to isolate the six-membered stannasiloxane ring **50** failed, as it irreversibly rearranges into the eight-membered stannasiloxane ring **51** and $(Ph_2SnOH)CH_2$, which is again attributed to the ring strain in **50**. Notably, the *t*-butyl-substituted compound *cyclo*-*t*-$Bu_2Si(OSnPh_2)_2CH_2$ (**54**) and its germanium analogue *cyclo*-*t*-$Bu_2Ge(OSnPh_2)_2CH_2$ (**55**) are six-membered rings both in solution and in the solid state [126]. During the course of this study, we also found, that small amounts of bis(diphenylhydroxystannyl)methane, $(Ph_2SnOH)CH_2$, effectively catalyze the condensation of diphenylsilandiol, $Ph_2Si(OH)_2$, to give mainly the eight-membered tetrasiloxane ring *cyclo*-$(Ph_2SiO)_4$ and traces of the six-membered trisiloxane ring *cyclo*-$(Ph_2SiO)_3$ [126]. The *cyclo*-stannasiloxanes **50**–**53** were found to be intermediates in this catalysis. In this context it is worth mentioning that the industrial relevant curing process also applies organotin catalysts for the condensation of oligomeric silanols into siloxanes [127–130]. Although somewhat less is known about the mechanism of this process, the aforementioned results may imply the involvement of stannasiloxane intermediates.

In addition to the stannasiloxane rings reported above, open-chain species such as $Ph_3SiOSnPh_3$ (**56**) [131], $Ph_3SnO(SiPh_2O)_2SnPh_3$ (**57**) [132], and *c*-Hex_3SnO-$(SiPh_2O)_4Sn$*c*-Hex_3 (**58**) have been investigated by single crystal X-ray diffraction [54]. These compounds are models for polystannasiloxanes, and reveal virtually strainless Si–O–Si and Si–O–Sn bond angles that more or less lie on the minima on their respective bending potentials.

2.1. Structural features of stannasiloxanes and related compounds

Many of the stannasiloxanes reported in this work have been the subjects of X-ray structural analyses. The comparison of the structural data of *cyclo*-stannasiloxanes with different ring size demonstrates that the Si–O and Sn–O bond lengths as well as the O–Si–O and O–Sn–O bond angles are comparable within these compounds, provided that compounds with similarly or equally substituted tin and silicon atoms are compared. The mean Si–O and Sn–O bond lengths amount to 1.62 and 1.96 Å, respectively, and the O–Si–O and O–Sn–O bond angles adopt values close to tetrahedral. However, in case of intramolecularly coordinating ligands attached to tin, the O–Sn–O bond angles are a notable exception of this rule of thumb. In these cases the tin atoms have to be considered to be $[4+2]$-coordinated, wherein the strength of the two additional *N*-donors can substantially vary.

In contrast, the Si–O–Si and Si–O–Sn angles are quite flexible and cover the range from 125.6 to 180°. It is interesting to note that these angles are in complete disagreement with the VSEPR-model [133], which suggests values around the ideal tetrahedral angle. The widening of the Si–O–Si angle has been addressed in a number of theoretical studies [134–138], and was previously attributed to lone pair delocalization into the d-orbitals at silicon, or later, to lone pair delocalization into

Table 1
Selected bond angles of stannasiloxanes and related compounds **1**–**58**[a]

Compound	Si–O–Sn	Si–O–Si	Si–O–M	Sn–O–M
1 [79]	138.9(2), 149.1(3)			
2b [94]	156.2(2), 158.6(2)	180.0		
3 [79]	148.0(1), 142.7(1)	145.7(1), 150.6(2)		
5 [79]	159.4(3), 157.6(3)			
6 [92]	159.7(2)			
7 [93]	145.5(2), 153.0(2)			
8 [79]	149.5(5)			
10 [93]	153.9(5), 156.6(5)			
	157.1(5), 157.7(5)			
11 [79]	144.3(2), 156.4(2)	140.3(2)		142.4(2) (M = Sn)
15 [103]	138.4(1), 138.5(1)			136.7(1) (M = Sn)[a]
16 [105]	142.2, 142.5			136.5 (M = Sn)
17 [106]				134(3) (M = B)
18 [104]	139.6(3), 140.6(2)			133.4(2) (M = Sn)[a]
19 [109]	145.9(2), 144.3(2)			
20 [109]	135.9(2), 134.2(2)	132.2(2)		
21 [109]	129.3(1), 129.9(1)	136.5(1)		
22 [110]	133.9(1), 133.5(5)	136.0(2)		
23 [111]	138.8(1), 136.9(1)			
24 [112]	129.0, 142.0			139.9 (M = Sn)
25 [112]	137.6		131.3 (M = Ge)	134.1 (M = Ge)
26 [112]	128.0		130.5 (M = B)	128.0 (M = B)
	125.9		130.4 (M = B)	131.1 (M = B)
27b [108]	151.3(2)	155.0(2)		
28 [108]	140.5(1), 148.9(1)	140.2(1), 145.1(1)		
31 [108]	133.6(1), 137.4(1)	144.2(1), 151.4(1)		
33b [111]	144.3(1), 147.4(1)	167.7(2)		
36 [114]	131.1(2), 130.0(2)	141.8(3)		
37 [114]	154.4(1), 153.3(1)	149.1(1), 164.1(1)		
40 [117,118]		127.1(1)	128.9(1) (M = B)	
41 [111]		125.6(1)	128.6(1), 130.4(1)	
42 [109]				125.5(1), 126.6(1) (M = Ge)[b]
43a [120]		169.2(1)	142.2(1) (M = Cr)	
44b [125]	128.5(3), 142.3(5)			
45 [125]	135.0(1), 144.5(1)			
47b [107]	145.0(2), 147.1(2)			
49 [125]	121.7(1), 122.0(2)			
51 [126]	171.5(2), 140.7(2)[c]	138.3(2)[c]		
	163.1(2), 138.8(2)	140.4(2)		
54 [126]	134.6(4), 136.4(4)			
56 [131]	144.2(6)			
57 [132]	140.0(8), 142.7(9)	165.4(10)		
58 [54]	145.6(2)	166.1(2), 180.0		

[a] Only the endocyclic angle of the six-membered ring is given.
[b] Ge–O–Ge angle: 127.1(1)°.
[c] Two molecules in the unit cell.

Si–H σ*-orbitals [136]. Although, these models appear attractive, both of them have been challenged in recent years. An alternative explanation points to the highly ionic character of the Si–O bonds, and traces the large Si–O–Si angles to steric and electrostatic repulsions between the silyl groups [138]. Indeed, core excitation spectroscopy on simple silanes such as R_3SiOX (R = Me, Ph; X = H, Me, $SiMe_3$), supports this explanation by indicating that the substituents X have no influence on the unoccupied electronic structure at silicon [62]. The calculated minimum Si–O–Si bond angle in siloxane model compounds is nearly unaffected by the nature of the substituents, especially when considering the flat bending potential and the small energy increase associated with an angle change around the minimum [139]. Selected M–O–M′ bond angles (M, M′ = Si, Ge, Sn, B, Cr) of compounds **1**–**58** are listed in Table 1. Comparing M–O–M′ bond angles (M, M′ = Si, Ge, Sn, B) with respect to the ring size, six-membered rings generally possess smaller M–O–M′ angles than the eight-membered rings. This observation can be attributed to the geometrical constraints, which define the internal angular sum of six- and eight-membered rings to be less than, for puckered rings, or equal to, for planar rings, 720 and 1080°, respectively. Given the relatively rigid O–M–O bond angles (M = Si, Ge, Sn, B) this further implies, that the M–O–M′ bond angles may be the major carriers of ring strain. The widening of these angles associated with the ROP process contributes directly to the energy gain. This idea is examined in greater detail in a forthcoming paper [124].

The qualitative comparison of the ring conformations from the heterocycles presented herein reveals that eight-membered rings are generally more puckered than their six-membered homologues. In particular, eight-membered stannasiloxane rings exhibit a great variety of different conformations, although many of them contain very similar substituents [79,93]. The conformations of most eight-membered stannasiloxane rings mentioned in this work have been classified by applying a method initially introduced for *cyclo*-germasiloxanes [140]. The origin of the different conformations in eight-membered rings is attributed to a combination of crystal packing effects and the avoidance of ring strain [93,124]. Apparently, six-membered rings are hardly affected by these factors, as the puckering is less pronounced in these compounds.

The conformation of PDPhS has been the subject of some controversy in recent years. Relying on the computer-assisted analysis of X-ray powder diffractograms, both helical and planar-*zigzag* conformations have been proposed for PDPhS, with the latter being more favored in recent years [57,58,101]. The conformations found for the polystannasiloxanes $(R_2SnOSiPh_2OSiPh_2O)_n$ (R = *t*-Bu (**2b**), *i*-Pr (**27b**)) and the model compounds $Ph_3SnO(SiPh_2O)_2SnPh_3$ (**57**) and *c*-$Hex_3SnO(SiPh_2O)_4Sn$*c*-Hex_3 (**58**) support this proposal [54,94,108,132].

3. Conclusions

The *cyclo*-stannasiloxanes reported in this work can be rationalized by the successive replacement of diorganosilyl by diorganostannyl segments. Compared to the parent *cyclo*-siloxanes, the substitution drastically affects the reactivity of *cyclo*-stannasiloxanes, which is attributed to the greater kinetic lability of the Sn–O bonds as compared to the Si–O bonds. As an important consequence, reactions involving Sn–O bonds usually proceed rapidly at room temperature on the laboratory time scale, i.e. with a very low activation barrier. For instance, the facile and selective ROP of *cyclo*-$R_2Sn(OSiPh_2)_2O$ (R = *t*-Bu (**2a**), *i*-Pr (**27a**)) occurs at room temperature in the absence of any initiator. In sharp contrast, ROP of *cyclo*-$(Ph_2SiO)_3$ is kinetically controlled and takes place only at temperatures between 150 and 190°C in the presence of an initiator, and is accompanied by substantial amounts of cyclic and oligomeric by-products. On the other hand, depolymerization upon redissolving the polymer in solution takes place for $(R_2SnOSiPh_2OSiPh_2O)_n$ (**2b**, R = *t*-Bu; **27b**, R = *i*-Pr), but not for PDPhS. As the kinetics generally plays only a minor role in the chemistry of *cyclo*-stannasiloxanes, this offers the opportunity to study the interplay of enthalpic and entropic parameters, which drive the reaction outcomes.

The material science aspects of the stannasiloxanes reported in this work are far from being fully explored. Certainly, one of the most striking features is the possibility of the six-membered rings *cyclo*-$R_2Sn(OSiPh_2)_2O$ (R = *t*-Bu (**2a**), *i*-Pr (**27a**) to undergo facile and highly selective ROP making possible the growth of large polymer crystals and the preparation of thin polymer films. The suitability of selected *cyclo*-stannasiloxanes to serve as single-source precursors for new inorganic materials is currently being actively investigated in our laboratory.

Acknowledgements

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