MeSi(CH₂SnRO)₃ (R = Ph, Me₃SiCH₂): Building Blocks for Triangular-Shaped Diorganotin Oxide Macrocycles

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Dedicated to Professor Manfred Scheer on occasion of his 65th birthday.

Abstract: The syntheses of the novel silicon-bridged tris(tertaorganotin) compounds MeSi(CH₂SnPh₂)₃ (2, R = Ph; 5, R = Me₃SiCH₂) and their halogen-substituted derivatives MeSi(CH₂SnPh₃-X)₃ (3, n = 1; 4, n = 2) and MeSi(CH₃SnI₂R)₃ (6, R = Me₃SiCH₂) are reported. The reaction of compound 4 with di-i-butyltin oxide (i-Bu₂SnO) gives the oktakaideka-nuclear (18-nuclear) molecular diorganotin oxide [MeSi(CH₂SnPhO)₃]₆ (7) while the reaction of 6 with sodium hydroxide, NaOH, provides the trikonta-nuclear (30-nuclear) molecular diorganotin oxide [MeSi(CH₃SnRO)₃]₁₀ (8, R = Me₃SiCH₂). Both 7 and 8 show belt-like ladder-type macrocyclic structures and are by far the biggest molecular diorganotin oxides reported to date. The compounds have been characterized by elemental analyses, electrospray mass spectrometry (ESI-MS), NMR spectroscopy, ¹H DOSY NMR spectroscopy (7), IR spectroscopy (7, 8), and single-crystal X-ray diffraction analysis (2, 7, 8).

Introduction

Metal chalcogenides with the empirical formula (MₙE)ₙ, (M = transition or main group metal; E = O, S, Se; n = infinite) are classical ionic compounds found as ores in nature. Their reactivity and structures in the solid state have been extensively studied since the beginning of chemical research and chemistry textbooks describe essential topics of these compounds.[1a-c] For a long time, metal chalcogenides mainly served as raw materials for the metallurgy. However, over the years, chemists learned also about some intriguing physical properties of these compounds, such as semiconductivity,[1d] nonlinear optoelectronic behaviour,[1e] and thermochromism,[1f] just to mention three out of many. Such properties are of utmost importance for high-tech applications. Academic curiosity and even more the need for a better understanding of structure-property relationships motivated chemists trying to cut out molecular entities from the three-dimensional polymeric metal chalcogenides. This was achieved by formally replacing metal-chalcogen bonds by a great variety of metal-ligand bonds, with the ligands being inorganic as well as organic moieties. As a result, the concept of polynuclear metal chalcogenido clusters was established and the achievements made over the years for both main-group and transition metal-containing such clusters were regularly reviewed.[2] This type of chemistry is also well established for the element tin. Randomly selected representatives are (R⁵Sn)ₙEₙ (R = organic substituent with or without additional functionality, E = O)[3] S[4][5] showing adamantane- or double decker-type structures, dodecanuclear tin oxo clusters (RSn)₂O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl),[5] Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂][6f] while the reaction of (RSn)₃O₄(OH)₂ (R = i-Pr, n-Bu, Me₃SiCH₂, ferrocenyl), Sn₃O₂(OH)₄(OEt)₁₂(HEt)₈[6a] [(BuSn)₃(µ-O)(µ-CH₂-OH)]·(L₁)·2EtOH[6b] [NaO₄(BuSn)₃(µ-O)(µ-OCH₂CH₂Sn(µ-OH))₃]·Se[6c] and [NaO₄BuSn(µ-OCH₂CH₂Sn(µ-OH))₃·(µ-OCH₂CH₂Sn(µ-OH))]·[6d] tetraorganodibisallyanes (R₃SnOsSnR₃) [R = organic substituent, X = electropositive substituent].[7] [(R⁵Sn)₃Sn(µ-OH)₂][6e] [(R⁵Sn)₃Sn(µ-OH)₂]...
Oxide dianion gives the corresponding diorganotin oxides \((R_2SnO)_n\). Depending on the identity of the organic substituents \(R\), these oxides can either be polymeric (type I, \(n = \infty\))\(^{114}\), trimeric (type II, \(n = 3\))\(^{115-23}\) or even dimeric (type III, \(n = 2\)) (Scheme 1)\(^{21-25}\). Sterically less demanding organic substituents such as \(n\)-alkyl or phenyl give polymers. These, because of intermolecular O–Sn interactions making the tin atoms five- or even six-coordinate, are almost insoluble in common organic solvents. Increasing the steric bulk of the organic substituents enables the formation of six- or even four-membered rings in which the tin atoms are four-coordinate. The same principle holds for the formation of the molecular diorganotin oxides of types IIa (in which two parallel six-membered \(SnO_3\) rings are linked to each other by three organic spacers)\(^{26}\), IV (adamantane-type structure)\(^{27}\), and V (the only crystallographically characterized diorganotin oxide containing an eight-membered \(SnO_4\) ring)\(^{27}\). More recently, intramolecular N–Sn or P=O–Sn coordination proved to be alternatives to steric bulk for the stabilization of type III diorganotin oxides\(^{24,25}\).

Considering what is stated above, we pose the question whether diorganotin oxides can be synthesized the structures of which are in between the polymers of type I on the one hand and the eight-, six-, and four-membered rings of types II, III, and V on the other hand. Herein, we report that diorganotin diiodide precursors containing sterically less-crowded substituents (Ph, \(Me_3SiCH_2\)), but having a particular tripod architecture, give, by reaction with appropriate oxide, respectively hydroxide anion releasing reagents, cyclic polymeric molecular diorganotin oxides (Scheme 1, type VI) of unprecedented large sizes. In these, the tin atoms adopt the coordination number five.

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**Results and Discussion**

The reaction in tetrahydrofuran of methyl-tris(chloromethyl) silane, \(MeSi(CH_2Cl)_3\), (1)\(^{28}\) with three molar equiv triphenyl sodium stannide, \(NaSnPh_3\), gave \(tris\)(triphenylstannyl)methyl silane, \(MeSi(CH_2SnPh)_3\), (2) as colourless crystalline material in almost quantitative yield (Scheme 2). Compound 2 easily converted to the \(tris\)(mono) and \(tris\)(di) halogenated derivatives \(MeSi(CH_2SnPh)_3\) (3) and \(MeSi(CH_2SnI)_3\) (4) by its reaction with three, respectively six molar equiv of elemental iodine (Scheme 2). The treatment of 3 with three molar equiv trimethylisilylmethylmagnesium chloride, \(Me_3SiCH_2MgCl\), gave the corresponding tetraorganotin derivative \(MeSi[CH_2Sn(CH_2SiMe_3)Ph]\), (5) which, by reaction with six molar equiv elemental iodine, provided \(MeSi[CH_2Sn(CH_2SiMe_3)I]_3\), (6). Compound 2 is a colourless crystalline material while its derivatives 3–6...
represent slightly yellow oils. All compounds show good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, THF, and CH$_2$CN. The Supporting Information contains the analytical data including the molecular structure of 2 (Figure S12) as determined by single crystal X-ray diffraction analysis. The data are as expected and confirm unambiguously the identities of compounds 2–6.

Treatment in CH$_2$Cl$_2$ of the organotin iodide 4 with (-Bu$_3$SnO)$_3$ gave a reaction mixture a $^{119}$Sn NMR spectrum of which displayed four resonances at $\delta$ 61 (-Bu$_3$SnI), $\sim$203 (7), $\sim$225 (7), and $\sim$228 ppm (7), respectively (Supporting Information, Figure S59). The spectrum indicates complete oxygen transfer from (-Bu$_3$SnO)$_3$ to the organotin iodide 4 and formation of -Bu$_3$SnI and the oktokaideka-nuclear (18-nuclear) organotin oxide [MeSi(CH$_3$SnPhO)$_3$]$_3$, 7 (Scheme 2). The latter compound was isolated from the reaction mixture as colourless crystalline material.

It crystallized as a solvate from dichloromethane solution. Figure 1 shows its molecular structure. The Figure caption contains selected interatomic distances and angles. Compound 7 crystallizes in the monoclinic space group $P2_1$/n with four crystallographically equivalent molecules in the unit cell. Each of these contains six MeSi(CH$_3$SnPh)$_3$ moieties in which the tin atoms are connected by a total of 18 oxygen atoms giving a triangular shaped, belt-like macromolecule with diameters ranging between 20.06(1) (H44–H94) and 23.00(1) (H84–H134) and a thickness ranging between 10.47(1) (H55–H145) and 10.97(1) Å (H55–H1154) (Supporting Information Figure S51). Three MeSi moieties (containing Si1–Si3) are located above and three such moieties (containing Si4–Si6) are located below the belt formed by the 18 tin and 18 oxygen centres (Figure 1; Supporting Information, Figure S54).

Each of the 18 crystallographic independent tin atoms is pentacoordinated and shows a distorted trigonal bipyramidal environment. For each of the Sn(1), Sn(3), Sn(4), Sn(6), Sn(7), Sn(9), Sn(10), Sn(12), Sn(13), Sn(15), Sn(16), and Sn(18) atoms, the two carbon atoms (C$_1$ atom from the phenyl substituent and the methylene carbon atom) and one oxygen atom occupy the equatorial positions. The corresponding C$_{ax}$-Sn-C$_{eq}$ angles vary between 111.6(4) (C31-Sn3-C212) and 138.1(7)$^\circ$ (C1-Sn15-C151). Two oxygen atoms take the axial positions with the O$_{ax}$-Sn-O$_{eq}$ distances ranging between 147.8(3) (O3-Sn4-O4) and 150.8(3)$^\circ$ (O17-Sn18-O18). The corresponding Sn-O$_{ax}$ distances vary between 2.074(8) (Sn13-O13) and 2.158(7) Å (Sn4-O4). The Sn-O$_{eq}$ distances involving oxygen atoms in equatorial positions are slightly shorter and vary between 2.009(9) (Sn7-O16) and 2.055(8) Å (Sn9-O18). Notably, for the Sn(2), Sn(5), Sn(8), Sn(11), Sn(14), and Sn(17) atoms the corresponding methylene carbon atom and one out of the adjacent three oxygen atoms take the axial positions whereas the C$_1$ and the two remaining oxygen atoms occupy the equatorial positions. This is in contrast to a situation as expected from the polarity rule[29] according to which the electronegative substituents occupy the axial positions in a trigonal bipyramidal structure. The C$_{eq}$-Sn-O$_{ax}$ angles vary between 150.0(4) (C262-Sn17-O7) and 153.4(4)$^\circ$ (C232-Sn8-O17).

The crystal structure of 7 (Figure 2) is characterized by C–H···π interactions at a H(144)-centroid (C171–C176) distance of 2.89(1) Å.

The identity of compound 7 is retained in solution. The compound is kinetically inert on the $^1H$ NMR time scales. Thus, a $^{119}$Sn NMR spectrum of a solution of single crystalline 7 in CDCl$_3$ shows three equally intense resonances at $\delta$~204 ppm ($J$($^{119}$Sn-$^{11}$Sn) 180, 315 Hz; $J$($^{119}$Sn-$^{29}$Si) 59 Hz), $\delta$~225 ppm ($J$($^{119}$Sn-$^{117}$Sn) 315 Hz), and $\delta$~228 ppm ($J$($^{119}$Sn-$^{117}$Sn) 180 Hz). The chemical shifts are in agreement with pentacoordinated tin atoms showing a SnC$_3$O$_3$ substituent pattern.[30] $^1H$ DOSY NMR spectrum (CDCl$_3$ solution, room temperature, Figure 3) provided a diffusion coefficient of 3.9(1)$\times10^{-10}$ m$^2$s$^{-1}$. This, by using the Einstein-Stokes equation, gave a calculated hydrodynamic diameter of 20.8 Å and a sphere volume of 4813 Å$^3$. These values fit
from the reaction between 6 and NaOH (Scheme 2), perfectly matches with the empirical formula \([\text{MeSi(CH\text{3SnPhO})}_{10}]\). one cannot be sure whether it exclusively consists of the trikonta-nuclear species 8 \((n = 10)\). Given the insufficient amount of material, no powder X-ray diffraction analysis of the bulk material was performed.

Figure 4 shows its simplified molecular structure and the Figure caption contains selected interatomic distances and angles. The compound crystallizes in the triclinic space group \(P\overline{1}\) with two molecules in the unit cell.

Compound 8 is a trikonta-nuclear (30-nuclear) molecular diorganotin oxide \([\text{MeSi(CH\text{3SnRO})}_{10}](R = \text{Me}, \text{SiCH\text{3}})\) in which ten \(\text{MeSi(CH\text{3SnRO})}_{10}\) moieties are connected giving a belt-like ladder-type heart-shaped macrocycle (Figure 4). In this, the three methyl groups attached to \(\text{Si}(14), \text{Si}(30),\) and \(\text{Si}(44),\) respectively, are above and the three methyl groups attached to \(\text{Si}(17), \text{Si}(32),\) and \(\text{Si}(43),\) respectively, are below the ring plane. The two methyl groups attached to \(\text{Si}(22)\) and \(\text{Si}(26),\) respectively, point into the ring cavity and the two methyl groups attached to \(\text{Si}(10)\) and \(\text{Si}(38),\) respectively, point outside the ring (Supporting Information, Figure S77, left). The methylene carbon atoms \(\text{C}(111), \text{C}(121), \text{C}(371), \text{C}(391), \text{C}(401),\) and \(\text{C}(491),\) which are attached to \(\text{Sn}(1), \text{Sn}(30), \text{Sn}(11), \text{Sn}(10), \text{Sn}(9),\) and \(\text{Sn}(2),\) respectively and which belong to the trimethylsilylmethyl substituents point also inside the ring while the remaining substituents point outside (Supporting Information, Figure S76, right).

The overall structure is rather complex. A closer inspection reveals it formally being composed of different subunits, i.e., the corner units \(\text{a}\) (with \(\text{Sn}3- \text{Sn}8\)), \(\text{b}\) (with \(\text{Sn}24- \text{Sn}29\)), and \(\text{c}\) (with \(\text{Sn}12- \text{Sn}17\)), the double spacer \(\text{d}\) (with \(\text{Sn}18- \text{Sn}23\)), and the single spacers \(\text{e}\) (with \(\text{Sn}1, \text{Sn}2, \text{Sn}30\)) and \(\text{f}\) (with \(\text{Sn}9- \text{Sn}11\)) (Figure 5).

Like in the oktokiaideka-nuclear diorganotin oxide 7, all tin centres in 8 are five-coordinated and, except \(\text{Sn}(1)\), show distorted trigonal bipyramidal environments. For the \(\text{Sn}(2)- \text{Sn}(4), \text{Sn}(7)-\text{Sn}(13), \text{Sn}(16)-\text{Sn}(25), \text{Sn}(29),\) and \(\text{Sn}(30)\) atoms, for each case two carbon atoms (the \(\text{MeSiCH}_3\) and the \(\text{MeSiCH}_2\) methylene carbon atoms) and one oxygen atom occupy the equatorial positions. The other two oxygen atoms take the axial positions. The corresponding \(\text{C}_{\text{eq}}-\text{Sn}-\text{C}_{\text{eq}}\) angles
carbon atom and one out of the adjacent three oxygen atoms take the axial positions whereas the Me₃SiCH₂ methylene carbon and the two remaining oxygen atoms occupy the equatorial positions. The C₃0-Sn-Oₘₙ angles vary between 146.2(11) (O6-Sn6-C432, in b) and 159.0(10)° (O14-Sn14-C322, in e). Figure 5 shows the packing of 8 in the crystal. The SnₙOₘₙ belt is located in the (2 - 0 2) plane.

A ¹¹¹Sn NMR spectrum of a CDCl₃ solution of the crystalline bulk material the single crystal was taken from, (Supporting Information, Figure S83) revealed three, within the experimental error almost equally intense, resonances at δ = 148 (J(¹¹¹Sn-¹³⁷Sn) = 230 Hz), δ = 159 (J(¹¹¹Sn-¹³⁷Sn) = 257 Hz), and δ = 164 ppm (J(¹¹¹Sn-¹³⁷Sn) = 219 Hz). In addition, there are broad, partially structured resonances between δ = 156 and δ = 146 ppm. A ²⁹Si NMR spectrum (Supporting Information, Figure S81) of the same sample showed a major intense broad unsymmetrically shaped signal at δ 0.9 ppm and a sharp resonance at δ = 21.9 ppm. A ¹H NMR spectrum (Supporting Information, Figure S79) revealed signals for the SiCH₃, SiCH₂Sn, SnCH₂SiMe₃, and Si(CH₃)₃ protons with correct integral ratio of 3:6:5:27. Attempts at obtaining ¹H DOSY NMR spectrum failed as the sample became gel-like over time. From the NMR data at hand, we conclude that the identity of 8 is not retained in solution. Apparently, the solution contains a mixture of different species. With caution and in analogy to 7, we assign the three sharp ¹¹¹Sn resonances (vide supra) to the oktokiaideka-nuclear diorganotin oxide [Me₃Si(CH₂Sn(CH₂SiCH₂)₂)₆]. Either the present right ligand from the beginning in the isolated bulk crystalline material or it forms upon dissolution of this material.

An ESI MS (Supporting Information, Figures S85–S94) of a solution of the microcrystalline bulk material in CH₂CN/CH₃Cl revealed mass clusters centred at m/z 750.9293, m/z 1646.8168, m/z 2254.7523, m/z 3077.6608, and m/z 4506.3980. These are assigned to [Me₃Si(CH₂Sn(CH₂SiCH₂)₂)₆ + H⁺], [Me₃Si(CH₂Sn(OH)₂CH₂SiCH₂)₂]₆ + 2H₂O + H⁺], [Me₃Si(CH₂Sn(CH₂SiCH₂)₂)₆ + 2H⁺]⁺, [Me₃Si(CH₂Sn(CH₂SiCH₂)₂)₆ + H⁺]⁺, and [Me₃Si(CH₂Sn(CH₂SiCH₂)₂)₆ + H⁺]⁺, respectively.
Although no detailed mechanistic studies have been performed, the formation of 7 and 8 can formally be seen as a stepwise process as shown in Scheme 3. Molecular diorganotin oxides A with adamantane-type structure undergo ring-opening dimerization via the intermediate B giving the hexanuclear product C. In case of R = Ph, three C-moieties assemble giving the oktokaideka-nuclear diorganotin oxide 7.

In case of R = MeSiCH₂, however, C-moieties combine with A- and B-moieties giving, as one product out of probably several, the trikonta-nuclear molecular diorganotin oxide 8. This view gets support from the ESI mass spectrometric studies revealing mass clusters that are in line with the presence of A- and C-moieties (vide supra).

**Scheme 3.** Association of two adamantane-type diorganotin oxide moieties A undergoing subsequent ring-opening dimerization giving C. The existence in solution of these moieties gets support from electrospray ionization mass spectrometry.

**Conclusion**

In conclusion we have shown that simple tripod-type diorganotin halides such as MeSi(CH₂SnRL₂)₃ (R = Ph, Me₂SiCH₂) serve as precursors for the synthesis of novel belt-shaped molecular diorganotin oxides [MeSi(CH₂SnRO)₃]ₙ of unprecedented oktokaideka (n = 18) and trikonta (n = 30) nuclearity. The results obtained fit well into the ongoing interest in large-sized metaloxido clusters in general[31] and tinoxido clusters of high nuclearity in partic-

ular.[5g,6b,12,31,32] The concept shown herein holds great potential for future work and we encourage interested readers to step into the field. Just to mention a few options out of many, the variation of the substituents R and/or replacing the CH₃ group with other substituents, the variation of the spacing between the silicon and tin centres as well as replacement of the MeSi bridgehead moiety with MeGe or with isoelectronic P. P = E (E = O, S, Se) or PM (M = transition metal moiety such as W(CO)₆ and others) might give a plethora of novel diorganotin oxides showing polynuclear structures. Moreover, replacing the organic substituent R in Roessler’s (RSn)O₆ (R = (Me₅Si)CH) [31] by a R’ of slightly reduced steric bulk could give well defined oligomers [(R’Sn)O₆]ₙ similar to 7 and 8.

**Acknowledgements**

We are grateful to Ms. Laura Schneider (research team Prof. Guido Clever, TU Dortmund) and Dr. Andreas Brockmeyer for measuring ESI mass spectra. We thank anonymous reviewers for valuable hints. We also acknowledge Prof. Christoph A. Schalley for helpful discussion concerning ESI mass spectra. Open access funding enabled and organized by Projekt DEAL.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** DOSY NMR spectroscopy · electrospray-ionization mass spectrometry · macrocycles · organotin oxides · X-ray crystallography

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