Hexakis(2,4,6-tri*iso*propylphenyl)*cyclo*tristannoxane – a Molecular Diorganotin Oxide with Kinetically Inert Sn–O Bonds[1)]

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Abstract. The single-crystal X-ray structure analysis of hexakis(2,4,6-tri*iso*propylphenyl)*cyclo*tristannoxane, *cyclo*-[(2,4,6-i-Pr_3-$C_6H_2)_2SnO]_3$ (**1**), is reported and reveals this compound to contain an almost planar six-membered ring. Redistribution reactions of **1** with *cyclo*-(t-$Bu_2SnO)_3$ and t-Bu_2SiCl_2, respectively, failed and indicate an unusual kinetic inertness of the Sn–O bonds in **1** as compared to related molecular diorganotin oxides containing less bulkier substituents. The redistribution reaction of *cyclo*-(t-$Bu_2SnO)_3$ with *cyclo*-(t-$Bu_2SnS)_2$ leads to an equilibrium involving the trimeric diorganotin oxysulphides *cyclo*-t-$Bu_2Sn(OSn$$t$-$Bu_2)_2S$ (**2a**) and *cyclo*-t-$Bu_2Sn(SSn$$t$-$Bu_2)_2O$ (**2b**).

Keywords: Tin; Oxide; Sulphide; X-ray structure; NMR

Hexakis(2,4,6-tri*iso*propylphenyl)*cyclo*tristannoxan – Ein molekulares Diorganozinnoxid mit kinetisch stabilen Sn–O Bindungen[1)]

Inhaltsübersicht. Es wird die Einkristallröntgenstrukturanalyse von Hexakis(2,4,6-tri*iso*propylphenyl)*cyclo*tristannoxan *cyclo*-[(2,4,6-i-Pr_3-$C_6H_2)_2SnO]_3$ (**1**) vorgestellt. Die Verbindung liegt als nahezu planarer sechsgliedriger Ring vor. Das Diorganozinnoxid **1** reagiert nicht mit *cyclo*-(t-$Bu_2SnO)_3$ bzw. t-Bu_2SiCl_2, was auf die ungewöhnliche kinetische Stabilität der Sn–O Bindungen in **1** im Vergleich zu ähnlichen molekularen Diorganozinnoxiden mit sterisch weniger anspruchsvollen Substituenten hinweist. Die Redistributionsreaktion von *cyclo*-(t-$Bu_2SnO)_3$ mit *cyclo*-(t-$Bu_2SnS)_2$ führt zu einem Gleichgewicht mit den trimeren Diorganozinnoxysulphiden *cyclo*-t-$Bu_2Sn(OSn$$t$-$Bu_2)_2S$ (**2a**) and *cyclo*-t-$Bu_2Sn(SSn$$t$-$Bu_2)_2O$ (**2b**).

Introduction

Diorganotin oxides $(R_2SnO)_n$ have been known for many years [1]. Depending on the steric demand of the organic substituents they are either polymeric (**I**, R = Me, Et, Bu, Vinyl, Ph) [1] or trimeric (**II**, R = CH_2SiMe_3, [2] t-Bu, [3, 4] Me_2EtC, [4] $(Me_3Si)_3C$/Me, [5] 2,6-Me_2–C_6H_3, [6] 2,6-Et_2–C_6H_3, [7] 2,4,6-$(CF_3)_3$–C_6H_2) [8]. While the six-membered ring structure of the latter compounds, (**II**), was established by X-ray diffraction studies, the polymeric nature of the former group, (**I**), was deduced from their virtual insolubility in common organic solvents, ^{119}Sn Mößbauer, [9, 10] and ^{119}Sn MAS NMR spectroscopy [11] revealing the presence of pentacoordinated tin atoms within these compounds (Chart 1).

Furthermore, one example of a dimeric diorganotin oxide containing extremely bulky substituents is known, namely *cyclo*-$\{[(Me_3Si)_2CH]_2SnO\}_2$, (**III**) (Chart 1) [12].

Bis(2,4,6-tri*iso*propylphenyl)tin oxide was prepared by hydrolysis of (2,4,6-i-Pr–$C_6H_2)_2SnBr_2$ under basic conditions [13–17] and it was reported to be a trimer, *cyclo*-[(2,4,6-i-Pr–$C_6H_2)_2SnO]_3$ [16]. Furthermore, it was claimed to appear from the oxidation of (2,4,6-i-Pr–$C_6H_2)_2Sn$ as a kinetically labile dimer, *cyclo*-[(2,4,6-i-Pr–$C_6H_2)_2SnO]_2$, which at room temperature rearranges into the thermodynamically more stable trimer within 24 h to a degree of more than 90% [15]. However, no experimental details on the preparation as well as the rearrangement step were given and spectroscopic data are available neither for the dimer nor the trimer [13–17].

In addition to bis(2,4,6-tri*iso*propylphenyl)tin oxide, the closely related sulphide, *cyclo*-[(2,4,6-i-Pr–$C_6H_2)_2$-$SnS]_2$ [18, 19] and oxysulphide *cyclo*-O[(2,4,6-i-Pr–$C_6H_2)_2Sn]_2S$ [19] were reported, which both represent four-membered rings in the solid state.

Various redistribution reactions of diorganotin chalcogenides, $(R_2SnX)_n$, (R = alkyl, aryl; X = O, S, Se, Te; n = 2, 3) have demonstrated that the Sn–X bonds are kinetically labile and that reactions involving cleavage of these bonds are fast and proceed under mild conditions [20–23]. In a recent conference contribution it was pointed out that certain trimeric diaryltin sulphides, *cyclo*-$(R_2SnS)_3$ (R = Ph, *o*-Tol, *m*-Tol, *p*-Tol),

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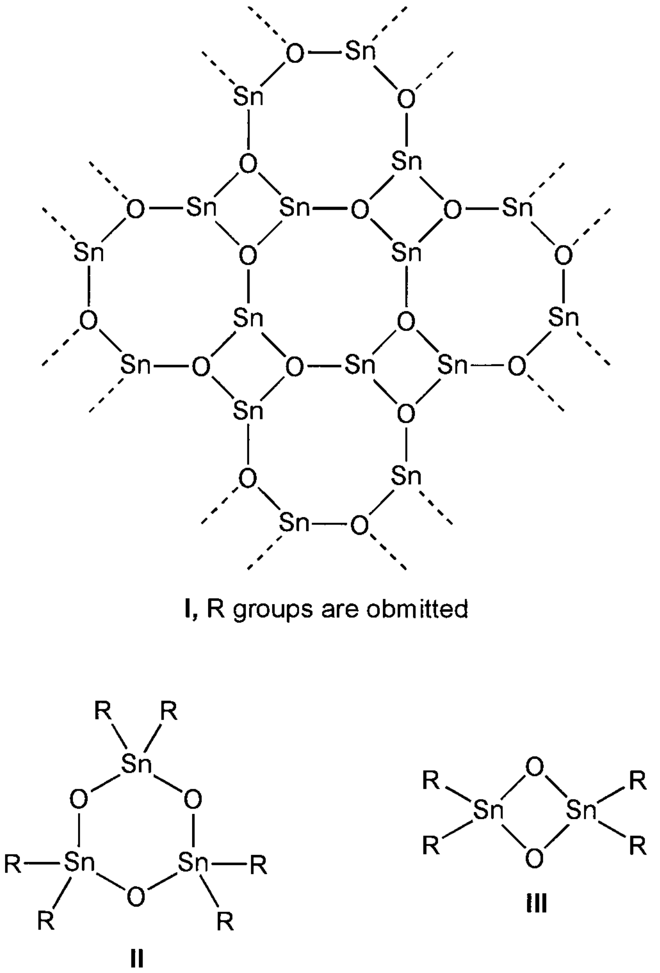
[1)] This work contains parts of the Ph.D. theses of J. B. and S. R., Dortmund University 1999.



I, R groups are obmitted

II

III

Chart 1

can be reversibly converted to their corresponding dimers, $(R_2SnS)_2$, by simply heating them in a high-boiling solvent [21, 22]. One possible explanation for this observation is the assumption of an equilibrium between these oligomers, with the position of this equilibrium being controlled by the entropy term of the Gibbs-Helmholtz equation.

Herein, we revisit the synthesis of bis(2,4,6-tri*iso*-propylphenyl)tin oxide (**1**) and describe the single-crystal X-ray structure analysis of the trimer. Variable temperature ^{119}Sn NMR spectroscopic studies show no evidence for dimers or other related species. Instead, a remarkable kinetic inertness of the Sn–O bonds is observed in reactions with *cyclo*-(t-$Bu_2SnO)_3$ and t-Bu_2SiCl_2. Moreover, the redistribution reaction between *cyclo*-(t-$Bu_2SnO)_3$ and *cyclo*-(t-$Bu_2SnS)_2$, which gives rise to an equilibrium of the former with the oxysulphides, *cyclo*-t-$Bu_2Sn(OSn$$t$-$Bu_2)_2S$ and *cyclo*-t-$Bu_2Sn(SSn$$t$-$Bu_2)_2O$, suggests that the fully characterized oxysulphide *cyclo*-$O[(2,4,6$-i-Pr–$C_6H_2)_2Sn]_2S$ [19] is also kinetically stabilized rather than being the thermodynamically favored alternative to a mixture of the former with *cyclo*-$[(2,4,6$-i-Pr–$C_6H_2)_2SnS]_2$ and *cyclo*-$[(2,4,6$-i-Pr–$C_6H_2)_2SnO]_2$, or *cyclo*-$[(2,4,6$-i-Pr–$C_6H_2)_2SnO]_3$.

Diorganotin oxides, such as *cyclo*-(t-$Bu_2SnO)_3$, find synthetic applications as convenient proton free oxide sources as was recently demonstrated in reactions with spacer-bridged diorganotin dihalides [24], diphenyldichlorosilane [25], diphenyldichlorogermane, and phenylboron dichloride [26], respectively, and therefore a thorough knowledge of the reactivity of this class of compounds is highly desirable.

Results and Discussion

The hydrolysis of $(2,4,6$-i-Pr_3–$C_6H_2)_2SnBr_2$ with aqueous sodium hydroxide in toluene afforded *cyclo*-$[(2,4,6$-i-Pr_3–$C_6H_2)_2SnO]_3$ (**1**) in good yield (Eq. (1)).

$$3\ (2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)_2SnBr_2 \xrightarrow[-6\ NaBr,\ -3\ H_2O]{6\ NaOH} \underset{\mathbf{1}}{[(2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)_2SnO]_3} \quad (1)$$

The diorganotin oxide **1** is a colorless high-melting crystalline solid. The molecular structure is shown in Figure 1. Selected bond lengths and angles are listed in Table 1. Crystal data are given in Table 2.

The molecular structure consists of an almost planar central Sn_3O_3 ring with the largest deviation from the plane being 0.0115 Å. Notably, two tin atoms, Sn(2) and Sn(2 a), are crystallographically equivalent while the third one, Sn(1), is independent. However, the ^{119}Sn MAS NMR spectrum showed only one signal at

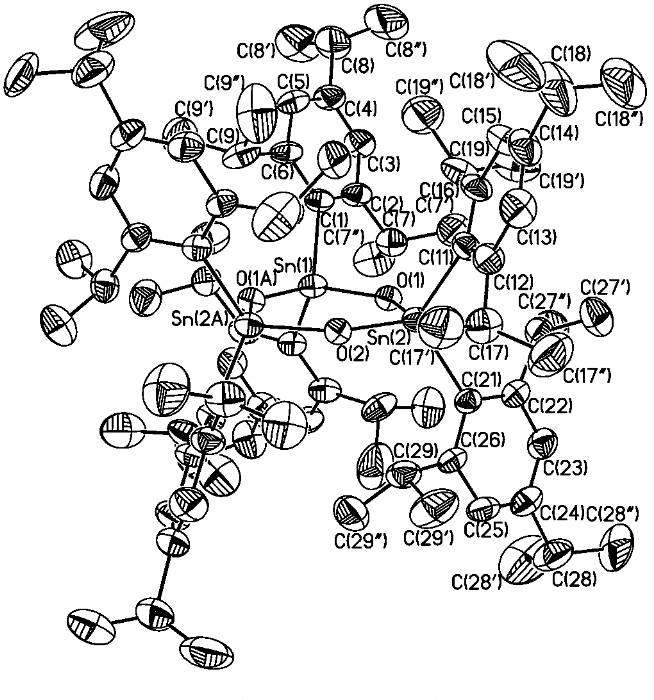


Fig. 1 General view (SHELXTL-PLUS) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom numbering.

Table 1 Selected Bond Lengths/Å and Angles/° for **1**[a)]

Sn(1)–O(1)	1.956(2)	Sn(1)–O(1 a)	1.956(2)
Sn(2)–O(1)	1.970(2)	Sn(2)–O(2)	1.969(1)
Sn(2 a)–O(2)	1.969(1)	Sn(1)–C(1)	2.150(4)
Sn(1)–C(1 a)	2.150(4)	Sn(2)–C(11)	2.162(4)
Sn(2)–C(21)	2.160(4)		
O(1)–Sn(1)–O(1 a)	105.1(1)	O(1)–Sn(1)–C(1)	104.1(1)
O(1 a)–Sn(1)–C(1)	117.3(2)	O(1)–Sn(1)–C(1 a)	117.3(2)
O(1 a)–Sn(1)–C(1 a)	104.1(1)	C(1)–Sn(1)–C(1 a)	109.5(2)
O(1)–Sn(2)–O(2)	103.6(1)	O(1)–Sn(2)–C(11)	115.2(2)
O(2)–Sn(2)–C(11)	105.0(1)	O(1)–Sn(2)–C(21)	101.4(1)
O(2)–Sn(2)–C(21)	115.9(1)	C(11)–Sn(2)–C(21)	115.5(2)
Sn(1)–O(1)–Sn(2)	135.5(1)	Sn(2)–O(2)–Sn(2 a)	136.6(2)

[a)] Symmetry transformation used to generate equivalent atoms: a = –x + 1, y, –z + 0.5

Table 2 Crystallographic Data for **1**

Compound number	1
Empirical formula	$C_{90}H_{138}O_3Sn_3$
Formular weight	1624.07
Crystal system	orthorhombic
Space group	Pbcn
Cell constants/Å and °	
a	24.577(1)
b	14.748(1)
c	24.246(1)
Volume/Å^3	8788.2(8)
Z	4
Density(calculated) (Mg/m^3)	1.227
Density(measured) (Mg/m^3)	1.254(1)
Absorption coeffizient/mm^{-1}	0.890
Crystal size/mm^3	0.25×0.15×0.15
Theta range for data collection	3.46 to 25.03
Reflections collected	114791
Independent reflections	7742 [R_{int} = 0.076]
Data/restraints/parameters	7742/0/454
Goodness–of–fit on F^2	0.756
R indices [I > 2sigma(I)]	R1 = 0.0346 wR2 = 0.0458
R indices (all data)	R1 = 0.1344 wR2 = 0.0552
Largest diff. peak and hole (e/Å^3)	0.250/–0.257

–128.6 ppm ($\nu_{1/2} \sim 350$ Hz) rather than the expected two signals in a ratio of 2 : 1. The mean Sn–O and Sn–C bond distances amount to 1.963(2) and 2.156(4) Å, respectively, and are comparable with those of other trimeric diorganotin oxides [4–8]. As a result of the bulky 2,4,6-tri*iso*propyl ligands, the tin atoms exhibit distorted tetrahedral geometries. The mean O–Sn–O angle in **1** amounts to 104.4(1)°, which is close to the corresponding angles in *cyclo*-t-Bu$_2$SnO)$_3$ (106.9(2)°), [4] *cyclo*-[(EtMe$_2$C)$_2$SnO]$_3$ (106.1(6)°), [4] *cyclo*-[(2,4-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ (101.4°), [6] *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ (103.2(2)°), [2] and *cyclo*-{[(Me$_3$Si)$_3$C]MeSnO}$_3$ (104.7(3)°) [5] whereas the corresponding O–Sn–O angle in the dimer *cyclo*-{[(Me$_3$Si)$_2$CH]$_2$SnO}$_2$ (82.5(6)°) [12] differs drastically. The mean C–Sn–C angle in **1** amounts to 112.5(2)° which is close to the corresponding angle in *cyclo*-[(2,4-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ (114.8°) [6] but somewhat smaller than those values reported for *cyclo*-(t-Bu$_2$SnO)$_3$ (119.5(4)°), [4] *cyclo*-[(EtMe$_2$C)$_2$SnO]$_3$ (118.(2)°), [4] *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ (118.3(2)°), [2] *cyclo*-{[(Me$_3$Si)$_3$C]MeSnO}$_3$ (116.1(6)°), [5] and *cyclo*-{[(Me$_3$Si)$_2$CH]$_2$SnO}$_2$ (119.9(9)°) [12]. The mean Sn–O–Sn angle in **1** amounts to 136.1(2)° which is close to the Sn–O–Sn angles reported for *cyclo*-(t-Bu$_2$SnO)$_3$ (133.1(3)°) [4], *cyclo*-[(EtMe$_2$C)$_2$SnO]$_3$ (134(1)°), [4] and *cyclo*-{[(Me$_3$Si)$_3$C]MeSnO}$_3$ (133.2(5)°), [5] but bigger than the angles found for *cyclo*-[(2,6-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ (120.8°) [6] and *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ (122.4(2)°) [2].

The diaryltin oxide *cyclo*-[(2,4,6-i-Pr$_3$–C$_6$H$_2$)$_2$SnO]$_3$ (**1**) is highly soluble in common organic solvents. According to a molecular weight determination in chloroform, the six-membered ring structure is retained in solution. The ^{119}Sn NMR spectrum (CDCl$_3$) of **1** shows one signal at –128.6 ppm being almost identical to the ^{119}Sn MAS NMR chemical shift mentioned above and very close to the ^{119}Sn NMR chemical shift reported for *cyclo*-[(2,6-Et$_2$–C$_6$H$_3$)$_2$-SnO]$_3$ (–125.0 ppm) [7]. Interestingly, the $^2J(^{119}\mathrm{Sn}–\mathrm{O}–^{117}\mathrm{Sn})$ coupling of 501 Hz is significantly bigger as compared to the corresponding coupling in the closely related diaryltin oxide *cyclo*-[(2,6-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ (320 Hz), [27] as well as in *cyclo*-(t-Bu$_2$SnO)$_3$ (369 Hz), [4] *cyclo*-[(Me$_2$EtC)$_2$SnO]$_3$ (394 Hz), [4] and *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ (335 Hz) [2]. This difference, especially in comparison with *cyclo*-[(2,6-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ having an almost identical substituent pattern at tin, is likely to originate from the well established dependence of the $^2J(^{119}\mathrm{Sn}–\mathrm{O}–^{117}\mathrm{Sn})$ coupling from the Sn–O–Sn bond angle [27, 28] and suggests this angle in compound **1** and in *cyclo*-[(2,6-Me$_2$–C$_6$H$_3$)$_2$SnO]$_3$ to be even more different in solution than in the solid state.

A ^{119}Sn NMR spectrum ([D$_8$]toluene) of **1** at 80 °C shows no significant change to the one described before, i. e., there is no indication for the formation of a dimer. A further interesting feature of compound **1** in solution is the observation in its ^{13}C NMR spectrum (CDCl$_3$) of six resonances for the aryl carbon atoms and nine resonances for the *iso*propyl carbon atoms, indicating rotation about the Sn–C$_i$ bond to be slow on the NMR time scale.

Redistribution Reactions

The diorganotin oxides *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ and *cyclo*-(t-Bu$_2$SnO)$_3$ are known to undergo a redistribution reaction under mild conditions and to form an equilibrium with the mixed oxides *cyclo*-t-Bu$_2$Sn-[OSn(Me$_3$SiCH$_2$)$_2$]$_2$O and *cyclo*-(Me$_3$SiCH$_2$)$_2$Sn(OSnt-Bu$_2$)$_2$O [20]. The same holds for diorganotin sulphides *cyclo*-(R$_2$SnS)$_3$ and *cyclo*-(R$'_2$SnS)$_3$ (R, R$'$ = Me, Bu, Ph, o-Tol) which realize equilibria of the mixed suphides *cyclo*-R$_2$Sn(SSnR$'_2$)$_2$S and *cyclo*-R$'_2$Sn(SSnR$_2$)$_2$S [21, 22]. Furthermore, dimethyltin chalcogenides *cy-*

clo-$(\text{Me}_2\text{SnX})_3$ and *cyclo*-$(\text{Me}_2\text{SnY})_3$ (X, Y = S, Se, Te) react with each other to give the mixed chalcogenides *cyclo*-$\text{Me}_2\text{Sn}(\text{XSnMe}_2)_2\text{Y}$ and *cyclo*-$\text{Me}_2\text{Sn}(\text{YSnMe}_2)_2\text{X}$ *in situ* [23]. These redistribution reactions proceed under very mild conditions which can be attributed to the high kinetic lability of the Sn–X bonds (X = O, S, Se, Te). Surprisingly, equimolar amounts of **1** and *cyclo*-$(t\text{-Bu}_2\text{SnO})_3$ do not react, even upon heating at reflux in [D_8]toluene for 6 d (Eq. (2)). The ^{119}Sn NMR spectrum ([D_8]toluene) of the reaction mixture exclusively showed two signals at –84.5 ($^2J(^{119}\text{Sn–O–}^{117}\text{Sn})$ 369 Hz, *cyclo*-$(t\text{-Bu}_2\text{SnO})_3$) and –128.4 ($^2J(^{119}\text{Sn–O–}^{117}\text{Sn})$ 501 Hz, *cyclo*-$[(2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{SnO}]_3$ (**1**)), demonstrating the coexistence of the reactants in solution.

$$[(2,4,6\text{-}i\text{-Pr}_3\text{-C}_6\text{H}_2)_2\text{SnO}]_3 + (t\text{-Bu}_2\text{SnO})_3 \nrightarrow \text{no mixed oxides} \quad (2)$$

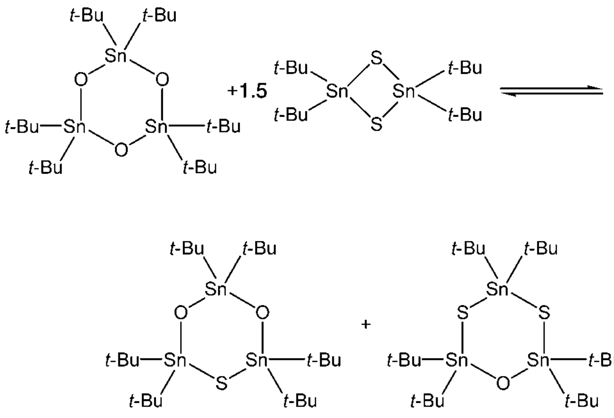
1

The reaction of *cyclo*-$(t\text{-Bu}_2\text{SnO})_3$ with various amounts of $t\text{-Bu}_2\text{SiCl}_2$ provided a number of cyclic and open-chain stannasiloxanes, such as *cyclo*-$t\text{-Bu}_2\text{Si}(\text{OSn}t\text{-Bu}_2)_2\text{O}$, *cyclo*-$(t\text{-Bu}_2\text{SiOSn}t\text{-Bu}_2\text{O})_2$, and $t\text{-Bu}_2\text{Si}(\text{OSn}t\text{-Bu}_2\text{SnCl})_2$ [25]. This reaction is irreversible with the thermodynamic driving force being the formation of energetically favored Si–O bonds. In contrast, the analogous reaction of **1** with $t\text{-Bu}_2\text{SiCl}_2$ in [D_8]toluene after 6 d heating at reflux failed. No reaction was observed even after prolonged heating of the pure reactants at 220 °C for 6 d. The ^{119}Sn and ^{29}Si NMR spectra ([D_8]toluene) of the reaction mixtures exclusively showed signals for the starting materials at –128.4 ppm ($^2J(^{119}\text{Sn–O–}^{117}\text{Sn})$ 501 Hz; **1**) and 35.6 ppm ($t\text{-Bu}_2\text{SiCl}_2$), respectively.

The reaction of **1** with the sterically less crowded Ph_2SiCl_2 in [D_8]toluene resulted indeed in oxide transfer from the organotin oxide to the organosilicon species. After 30 min at 90 °C, the ^{119}Sn NMR spectrum displayed resonances at –128.0 ppm ($^2J(^{119}\text{Sn–O–}^{117}\text{Sn})$ 501 Hz, integral 84%) belonging to the organotin oxide **1** and at –66.6 ppm (integral 16%) assigned to $(2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{SnCl}_2$. The ^{29}Si NMR spectrum of the same reaction mixture displayed a major resonance at 6.1 ppm (integral 88%; Ph_2SiCl_2) and two minor resonances at –21.8 (integral 4%) and –30.2 ppm (integral 7%). The oxide transfer is almost complete after 115 h at 90 °C. The ^{119}Sn NMR spectrum displayed a major resonance at –66.6 ppm (integral 97%) belonging to the diorganotin dichloride and a minor resonance at –128.0 ppm (integral 3%) belonging to compound **1**. The ^{29}Si NMR spectrum of this reaction mixture showed six major resonances at 6.0 ppm (integral 8%, Ph_2SiCl_2), –37.0 ppm (integral 17%), –37.3 ppm (integral 17%), –45.0 ppm (integral 30%), –45.2 ppm (integral 11%), and –45.6 ppm (integral 6%), and five minor resonances (total integral 11%) at –21.8 ppm, –35.2 ppm, –42.4 ppm (*cyclo*-$(\text{Ph}_2\text{SiO})_4$, identity confirmed by addition of an authentic sample), –43.0 ppm, and –46.8 ppm. Most of these signals could not be assigned but they might belong to open-chain chlorosiloxanes such as $\text{Ph}_2\text{ClSiOSiClPh}_2$, $\text{Ph}_2\text{Si}(\text{OSiClPh}_2)_2$, $\text{O}(\text{SiPh}_2\text{OSiClPh}_2)_2$, and/or $\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{OSiClPh}_2)_2$. It is interesting to note that along the reaction (i) no stannasiloxanes were detected and (ii) that only trace amounts of *cyclo*-$(\text{Ph}_2\text{SiO})_4$ are formed.

The inertness of *cyclo*-$[2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{SnO}]_3$ (**1**) in its reaction with $t\text{-Bu}_2\text{SiCl}_2$ can be interpreted in terms of an enhanced kinetic stability of the Sn–O bonds. The synthesis and complete characterization of the four-membered ring *cyclo*-$\text{O}[(2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{Sn}]_2\text{S}$ [19] supports this interpretation as it is stable and does not rearrange to give *cyclo*-$[2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{SnS}]_2$ [18, 19] and *cyclo*-$[2,4,6\text{-}i\text{-Pr}_3\text{-C}_6\text{H}_2)_2\text{SnO}]_3$ (**1**).

Diorganotin oxysulphides other than *cyclo*-$\text{O}[(2,4,6\text{-}i\text{-Pr}_3\text{–C}_6\text{H}_2)_2\text{Sn}]_2\text{S}$ are not known so far. However, the six-membered rings *cyclo*-$t\text{-Bu}_2\text{Sn}(\text{OSn}t\text{-Bu}_2)_2\text{S}$ (**2a**) and *cyclo*-$t\text{-Bu}_2\text{Sn}(\text{SSn}t\text{-Bu}_2)_2\text{O}$ (**2b**) were generated *in situ* by heating at reflux for 12 h a mixture in chloroform of *cyclo*-$(t\text{-Bu}_2\text{SnO})_3$ and *cyclo*-$(t\text{-Bu}_2\text{SnS})_2$ in a ratio of 2 : 3 (Eq. (3)).



(3)

2a

2b

The ^{119}Sn NMR spectrum (CHCl_3, D_2O-capillary) showed six signals belonging to *cyclo*-$(t\text{-Bu}_2\text{SnO})_3$ (δ –84.5, $^2J(^{119}\text{Sn–O–}^{117}\text{Sn})$ 365 Hz; integral 30%), *cyclo*-$(t\text{-Bu}_2\text{SnS})_2$ (δ 123.9, $^2J(^{119}\text{Sn–S–}^{117}\text{Sn})$ 112 Hz; integral 40%), *cyclo*-$t\text{-Bu}_2\text{Sn}(\text{OSn}t\text{-Bu}_2)_2\text{S}$ (**2a**; δ 13.4, $^2J(^{119}\text{Sn–O–}^{119/117}\text{Sn})$ 520 Hz, δ –99.5, $^2J(^{119}\text{Sn–O–}^{119/117}\text{Sn})$; ratio 2 : 1; total integral 23%) and *cyclo*-$t\text{-Bu}_2\text{Sn}(\text{SSn}t\text{-Bu}_2)_2\text{O}$ (**2b**; δ 86.2, $^2J(^{119}\text{Sn–S–}^{119/117}\text{Sn})$ 69 Hz, δ –6.0, $^2J(^{119}\text{Sn–O–}^{119/117}\text{Sn})$ 672 Hz, $^2J(^{119}\text{Sn–S–}^{119/117}\text{Sn})$ 65 Hz; ratio 1 : 2; total integral 7%). Further heating for 24 h did not change the integral ratio indicating that the reaction mixture had reached equilibrium. Slow evaporation of the solvent from the reaction mixture afforded a microcrystalline solid from which a ^{119}Sn MAS NMR spectrum was recorded (Figure 2). It shows six center bands with ac-

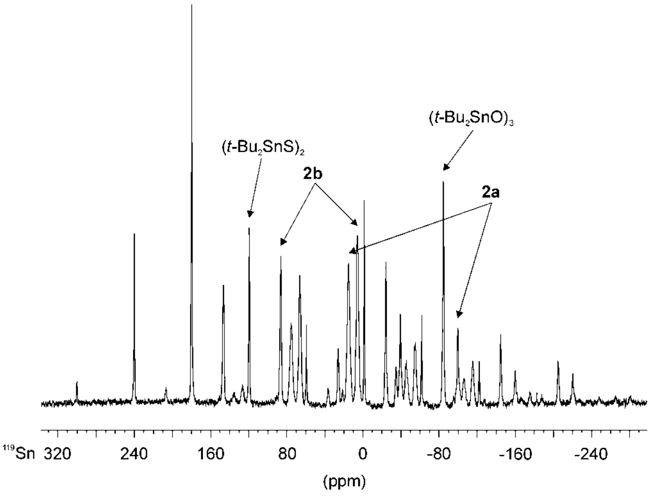


Fig. 2 ^{119}Sn MAS NMR spectrum (149.21 MHz) of a reaction mixture according Equation 4 (Spin frequency 9 KHz; 10000 transitions). Center bands are indicated by arrows.

companying sets of spinning sidebands, which are unambiguously assigned to *cyclo*-(*t*-Bu$_2$SnO)$_3$ (δ –84.3; integral 28%), [29] *cyclo*-(*t*-Bu$_2$SnS)$_2$ (δ 126.1; integral 36%), *cyclo*-*t*-Bu$_2$Sn(OSn*t*-Bu$_2$)$_2$S (**2a**; δ 14.7, –99.5; ratio 2 : 1; total integral 26%) and *cyclo*-*t*-Bu$_2$Sn-(SSn*t*-Bu$_2$)$_2$O (**2b**; δ 86.0, 5.6; ratio 1 : 2; total integral 10%). It is worth mentioning that the ^{119}Sn MAS NMR chemical shift measured for *cyclo*-(*t*-Bu$_2$SnS)$_2$ (δ 126.1) differs from that previously reported by *Harris* and *Sebald* (δ 119.4, 117.3) [30] which is tentatively attributed to the presence of different polymorphs. Indeed, monoclinic (α-form) and triclinic (β-form) modifications have been reported for (*t*-Bu$_2$SnS)$_2$ [31]. However, both ^{119}Sn MAS chemical shifts are consistent with the respective value of *cyclo*-(*t*-Bu$_2$SnS)$_2$ in CDCl$_3$ solution (δ 124.1) [27]. The graphical integration of the signals was achieved by taking into account the intensity of the center bands and all spinning sidebands belonging to them. However, the integration has to be considered as an estimate because errors may arise from poor signal-to-noise ratio and disparate applying cross polarization. It is very likely that *cyclo*-(*t*-Bu$_2$SnO)$_3$, **2a**, and **2b** realize mixed crystals as the trimeric di-*tert*-butylelement oxides, *cyclo*-(*t*-Bu$_2$MO)$_3$ (M = Si, Ge, Sn), [3, 4, 32, 33] *cyclo*-*t*-Bu$_2$M-(OSn*t*-Bu$_2$)$_2$O (M = Si, Ge), [2, 29] and di-*tert*-butylelement imines *cyclo*-(*t*-Bu$_2$MNH)$_3$ (M = Si, Sn) [34, 35] all crystallize in the trigonal space group R-3c.

Conclusion

Bis(2,4,6-tri*iso*propylphenyl)tin oxide, *cyclo*-[(2,4,6-*i*-Pr–C$_6$H$_2$)$_2$SnO]$_3$ (**1**), was prepared in high yield as a cyclic trimer by the hydrolysis of (2,4,6-*i*-Pr–C$_6$H$_2$)$_2$-SnBr$_2$ under basic conditions. The molecular structure of **1** shows no significant difference from those of other trimeric diorganotin oxides. The six-membered ring is retained in solution, and no evidence was found for the formation of a dimer, *cyclo*-[(2,4,6-*i*-Pr–C$_6$H$_2$)$_2$SnO]$_2$. Redistribution reactions with *cyclo*-(*t*-Bu$_2$SnO)$_3$ and *t*-Bu$_2$SiCl$_2$ failed and reveal an enhanced kinetic inertness of the Sn–O bonds in **1** as compared to other trimeric diorganotin oxides such as *cyclo*-(*t*-Bu$_2$SnO)$_3$ which is attributed to the high shielding capacity of the 2,4,6-*iso*propylphenyl ligands [36]. The reaction of **1** with Ph$_2$SiCl$_2$ proceeds under oxygen transfer to give a mixture of open-chain chlorosiloxanes, but only traces of *cyclo*-diphenylsiloxanes. This is in contrast to the reaction in chloroform of (*t*-Bu$_2$SnO)$_3$ with Ph$_2$SiCl$_2$ which proceeds at lower temperature and gives *cyclo*-(Ph$_2$SiO)$_n$ (n = 3, 4) as major products [25].

Experimental Part

All operations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and freshly distilled prior to use. (2,4,6-*i*-Pr–C$_6$H$_2$)$_2$SnBr$_2$, [37] *cyclo*-(*t*-Bu$_2$SnO)$_3$, [4] and *cyclo*-(*t*-Bu$_2$SnS)$_2$ [31] were prepared according to literature procedures. *t*-Bu$_2$SiCl$_2$ was commercially obtained (Fluka) and used as supplied. Solution ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were recorded on a Bruker DRX 400 instrument at 400.13 (^{1}H), 100.31 (^{13}C), 79.49 (^{29}Si), and 149.20 MHz (^{119}Sn). ^{119}Sn{^{1}H} MAS NMR spectra were obtained from a Bruker MSL 400 spectrometer at 149.20 MHz using cross polarization and high power proton decoupling. Three different spinning speeds were applied in order to assign unambiguously the center bands. *c*-Hex$_4$Sn was used as a second reference (δ –97.35 ppm against Me$_4$Sn). The elemental analysis was determined on an instrument from Carlo Erba Strumentazione (Model 1106). The molecular weight was measured on a Knauer osmometer.

Synthesis of Hexakis(2,4,6-tri*iso*propylphenyl)*cyclo*tristannoxane (1). A solution of NaOH (0.85 g, 21.2 mmol) in water (20 mL) was slowly added to a solution of (2,4,6-*i*-Pr–C$_6$H$_2$)$_2$SnBr$_2$ (7.25 g, 10.5 mmol) in refluxing toluene (300 mL). After 3 h the mixture was allowed to cool to 40 °C, then the layers were separated, and the organic layer was dried over sodium sulphate. The solvent was reduced to approx. 100 mL. The crude product that crystallizied after 12 h at –10 °C was recrystallized from chloroform/hexane to give 4.6 g (8.5 mmol, 81%) of colorless crystals of **1**, mp. > 360 °C.

Anal. Calcd for C$_{90}$H$_{138}$O$_3$Sn$_3$ (1624.3): C, 66.6; H, 8.6. Found: C, 66.6; H, 9.2%.

^{1}H NMR (CDCl$_3$): δ = 6.89 (^4J($^{117/119}$Sn–^{1}H) 30 Hz, phenyl proton), 6.86 (^4J($^{117/119}$Sn–^{1}H) 28 Hz, phenyl proton), 3.72 (sept, 1 H, ^3J(^{1}H–^{1}H) 7 Hz, Me$_2$C*H*), 3.01 (sept, 1 H, ^3J(^{1}H–^{1}H) 7 Hz, Me$_2$C*H*), 2.78 (sept, 1 H, ^3J(^{1}H–^{1}H) 7 Hz, Me$_2$C*H*), 1.32 (d, 3 H, ^3J(^{1}H–^{1}H) 7 Hz, *Me*$_2$CH), 1.17 (d, 3 H, ^3J(^{1}H–^{1}H) 7 Hz, *Me*$_2$CH), 0.92 (d, 6 H, ^3J(^{1}H–^{1}H) 7 Hz, *Me*$_2$CH) 0.57 (d, 3 H, ^3J(^{1}H–^{1}H) 7 Hz, *Me*$_2$CH), 0.30 (d, 3 H, ^3J(^{1}H–^{1}H) 7 Hz, *Me*$_2$CH); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 155.1 (s, ^2J(^{13}C–$^{117/119}$Sn) 51 Hz, C$_o$), 153.9 (s, ^2J(^{13}C–$^{117/119}$Sn) 58 Hz, C$_o$), 149.8 (s, C$_p$), 143.0 (s, ^1J(^{13}C–^{119}Sn) 809 Hz, C$_i$), 121.9 (s, ^3J(^{13}C–$^{117/119}$Sn) 69 Hz, C$_m$), 121.0 (s, ^3J(^{13}C–$^{117/119}$Sn) 67 Hz, C$_m$), 37.4 (s, ^3J(^{13}C–^{119}Sn) 46 Hz, Me$_2$*C*H), 34.2 (s, Me$_2$*C*H), 33.9 (s, ^3J(^{13}C–^{119}Sn) 28 Hz, Me$_2$*C*H), 25.8 (s, *Me*$_2$CH), 25.3

(s, *Me*$_2$CH), 25.1 (s, *Me*$_2$CH), 24.4 (s, *Me*$_2$CH), 24.0 (s, *Me*$_2$CH), 23.9 (s, *Me*$_2$CH); ^{119}Sn{^{1}H} NMR (CDCl$_3$): $\delta = -128.4$ (s, $^1J(^{119}\text{Sn}-^{13}\text{C}_i)$ 806 Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ 501 Hz, $^2J(^{119}\text{Sn}-^{13}\text{C}_o)$ 51 Hz, $^3J(^{119}\text{Sn}-^{13}\text{C}_m)$ 69 Hz); ^{119}Sn{^{1}H} MAS NMR: $\delta = -128.6$. Molecular weight determination (10 mg · ml^{-1}, CHCl$_3$): 1674 g · mol^{-1}.

Attempted reaction of 1 with *cyclo*-(*t*-Bu$_2$SnO)$_3$. A solution of **1** (54.1 mg, 0.033 mmol) and (*t*-Bu$_2$SnO)$_3$ (24.9 mg, 0.033 mmol) in [D$_8$]toluene (300 µL) was heated at reflux for 6 d. A ^{119}Sn NMR spectrum was recorded which is discussed in the text.

Attempted reaction of 1 with *t*-Bu$_2$SiCl$_2$. (i) A solution of **1** (54.1 mg, 0.033 mmol) and *t*-Bu$_2$SiCl$_2$ (21.3 mg, 0.1 mmol) in [D$_8$]toluene (300 µL) was heated at reflux for 6 d, and, (ii) a neat mixture of **1** (108.2 mg, 0.066 mmol) and *t*-Bu$_2$SiCl$_2$ (42.6 mg, 0.2 mmol) was heated 6 d at 220 °C, then [D$_8$]-toluene (300 µL) was added. ^{119}Sn and ^{29}Si NMR spectra were recorded which are discussed in the text.

Reaction of 1 with Ph$_2$SiCl$_2$. A solution of **1** (319 mg, 0.588 mmol) and Ph$_2$SiCl$_2$ (149 mg, 0.588 mmol) in [D$_8$]-toluene (300 µL) was kept at 90 °C. ^{29}Si and ^{119}Sn NMR spectra were recorded after 30 min, 91 h, and 115 h.

Reaction of *cyclo*-(*t*-Bu$_2$SnO)$_3$ with *cyclo*-(*t*-Bu$_2$SnS)$_2$. A mixture of *cyclo*-(*t*-Bu$_2$SnO)$_3$ (249 mg, 0.33 mmol) and *cyclo*-(*t*-Bu$_2$SnS)$_2$ (265 mg, 0.5 mmol) in CHCl$_3$ (5 mL) was heated to reflux for 12 h. A ^{119}Sn NMR (CHCl$_3$; D$_2$O-capillary) spectrum was recorded which is discussed in the text. Then, the solvent was slowly evaported on exposure to air leaving a colorless microcrystalline solid. A ^{119}Sn MAS NMR spectrum was recorded which is discussed in the text.

X-ray Crystal Structure Determination of ***1***

Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoKα (0.71069 Å) radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 20 s per frame. The crystal-to-detector distance was 2.7 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. Analysis of the duplicate reflections revealed no indication of any decay. The structures were solved by direct methods SHELXS97 [38] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97 [39]. The H atoms were placed in geometrically calculated positions using a riding model and refined with common isotropic temperature factors for different C–H types (C–H$_{\text{prim.}}$ 0.96 Å, C–H$_{\text{tert.}}$ 0.98 Å U$_{\text{iso}}$ 0.260(3); C–H$_{\text{aryl}}$ 0.93 Å, U$_{\text{iso}}$ 0.053(5) Å^2).

A disordered iso-propyl group was found with occupancies of 0.5 (C(28′), C(28″), C(28 a), C(28 b)).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography [40]. The figures were created by SHELXTL [41]. Selected bond distances and angles are listed in Table 1. Crystallographic data are given in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 1566301 (**1**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-(0)12 23-33 60 33 or e-mail: deposit@ccdc.cam.ac.uk).

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