ON THE REACTION OF DIORGANODIHYDROXYSILANES WITH (t-$Bu_2SnO)_3$. SYNTHESIS AND CHARACTERISATION OF A NOVEL STANNASILOXANE COMPLEX AND ITS DISSOCIATION IN SOLUTION

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Abstract

The complex $[Ph_2Si(OSn$*t*-$Bu_2)_2O\cdot$*t*-$Bu_2Sn(OH)_2]$ (**2**) was obtained in high yield by reaction of $Ph_2Si(OH)_2$ with (*t*-$Bu_2SnO)_3$ (**1**). Reaction of *t*-$Bu_2Si(OH)_2$ with **1** gave [t-$Bu_2Si(OSn$*t*-$Bu_2)_2O]$ (**4a**) instead. The compounds were investigated by means of NMR, IR, Mössbauer spectroscopy, and in case of **2** by X-ray analysis. In solution, **2** is in equilibrium with $[Ph_2Si(OSn$*t*-$Bu_2)_2O]$ (**2a**), **1**, and water. *t*-$Bu_2Sn(OH)_2$ (**3**) was prepared by controlled hydrolysis of *t*-$Bu_2Sn(OMe)_2$ and was shown to undergo condensation with formation of **1**. Mössbauer studies as well as ^{119}Sn CP MAS NMR including side band analysis suggest **3** to exhibit a dimeric structure with pentacoordinate tin. Similar studies on **1** suggest fast rotation of the molecule in the crystal lattice.

Introduction

In recent years there is increasing interest in the chemistry of stannasiloxanes [1] which, for instance, hold potential as models for mixed metal oxide surfaces [2]. We have shown that organohalosilanes such as *t*-$BuSiF_3$ and *t*-Bu_2SiX_2 (X = F, Cl) react with di-*tert*. butyltinoxide (*t*-$Bu_2SnO)_3$ under formation of well defined stannasiloxanes such as *t*-$Bu_2Sn[OSi(F)$*t*-$Bu_2]_2$, [*t*-$Bu_2Si(OSn$*t*-$Bu_2)_2O]$ (**4a**), and [*t*-$Bu_2SnOSi(R)$*t*-$BuO]_2$ (R = F, *t*-Bu) [3]. In continuation of these studies we report here on reactions of $R_2Si(OH)_2$ (R = Ph, *t*-Bu) with (*t*-$Bu_2SnO)_3$.

Results and Discussion

The reaction of (*t*-$Bu_2SnO)_3$ (**1**) with $Ph_2Si(OH)_2$ yields almost quantitativel y $[Ph_2Si(OSn$*t*-$Bu_2)_2O$ $\cdot$*t*-$Bu_2Sn(OH)_2]$ (**2**) as crystalline solid (eq 1). The molecular structure of **2** is shown in Figure 1.

$$\underset{\mathbf{1}}{(t\text{-}Bu_2SnO)_3} + Ph_2Si(OH)_2 \xrightarrow{\text{toluene, } 60°C,\ 1d} \underset{\mathbf{2}}{[Ph_2Si(OSn\,t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]} \quad (1)$$

Selected bond lengths and bond angles are listed in Table 1.
Compound **2** is readily soluble in common organic solvents such as toluene, chloroform and thf. It is stable against air-moisture. Formally, **2** consists of the six-membered ring $[Ph_2Si(OSn$*t*-$Bu_2)_2O]$ and *t*-$Bu_2Sn(OH)_2$ coordinated to it. All tin atoms are pentacoordinate and show distorted trigonal bi-pyramidal configurations. The *t*-butyl groups and O(3) are placed in equatorial positions while O(1), O(2), O(4), and O(5) are located in axial positions. The Sn_3O_3 cycle is almost planar, the strongest deviation being 0.165 Å. This arrangement is comparable with the structures found for [MesB(OSn*t*-$Bu_2)_2O\cdot$*t*-$Bu_2Sn(OH)_2]$ [4], [OC(OSn*t*-$Bu_2)_2O\cdot$*t*-$Bu_2Sn(OH)_2]$ [5], and $[Me_2Si(OSn$*t*-$Bu_2)_2O\cdot$*t*-$Bu_2Sn(OH)_2]$ [14]. Selected structural data of these compounds are compared in Table 2. The Sn_3O_3 structural motif within these compounds resembles that of the "three quarter" ladder postulated for [(*t*-$Bu_2SnCl_2)($*t*-$Bu_2SnO)_2]$ on the basis of ^{119}Sn NMR data [6].

The ^{119}Sn CP MAS NMR spectrum of **2** shows two signals at -265.7 and -273.7 ppm, respectively, with an integral ratio of 1:2 which is in line with the structure established by the X-ray measurement. The IR spectrum shows the presence of the OH groups by a (OH) of 3644 cm^{-1}.

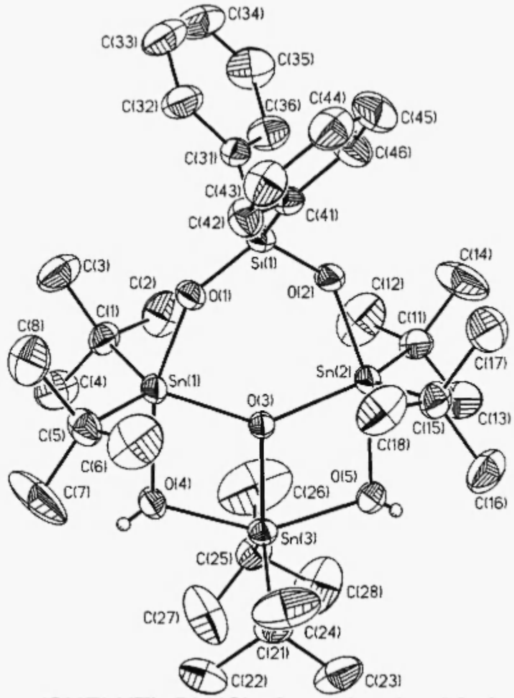
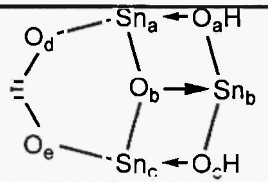


Figure 1. General view (SHELXTL-PLUS) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Selected bond lengths [Å] and bond angles [°] for **2**.

Sn(1)-O(1)	2.020(2)	Sn(2)-C(11)	2.177(4)	Sn(3)-C(21)	2.171(5)
Sn(1)-O(3)	2.092(2)	Sn(2)-C(15)	2.182(5)	Si(1)-O(1)	1.604(2)
Sn(1)-C(5)	2.171(4)	Sn(2)-O(5)	2.264(3)	Si(1)-O(2)	1.605(2)
Sn(1)-C(1)	2.189(5)	Sn(3)-O(3)	2.091(2)	Si(1)-C(31)	1.871(4)
Sn(1)-O(4)	2.261(3)	Sn(3)-O(5)	2.103(3)	Si(1)-C(41)	1.876(4)
Sn(2)-O(2)	2.018(3)	Sn(3)-O(4)	2.106(3)	O(4)-H(4)	0.66(3)
Sn(2)-O(3)	2.093(2)	Sn(3)-C(25)	2.166(5)	O(5)-H(5)	0.63(3)
O(1)-Sn(1)-O(3)	92.28(9)	O(2)-Sn(2)-O(5)	161.9(1)	O(2)-Si(1)-C(31)	108.5(2)
O(1)-Sn(1)-C(5)	93.1(2)	O(3)-Sn(2)-O(5)	70.1(1)	O(1)-Si(1)-C(41)	107.8(2)
O(3)-Sn(1)-C(5)	124.1(2)	C(11)-Sn(2)-O(5)	92.2(2)	O(2)-Si(1)-C(41)	112.3(2)
O(1)-Sn(1)-C(1)	99.0(1)	C(15)-Sn(2)-O(5)	93.5(2)	C(31)-Si(1)-C(41)	103.6(2)
O(3)-Sn(1)-C(1)	112.9(1)	O(3)-Sn(3)-O(5)	73.4(1)	Si(1)-O(1)-Sn(1)	138.4(1)
C(5)-Sn(1)-C(1)	121.1(2)	O(3)-Sn(3)-O(4)	73.2(1)	Si(1)-O(2)-Sn(2)	138.5(1)
O(1)-Sn(1)-O(4)	160.8(1)	O(5)-Sn(3)-O(4)	146.5(1)	Sn(3)-O(3)-Sn(1)	111.7(1)
O(3)-Sn(1)-O(4)	70.0(1)	O(3)-Sn(3)-C(25)	122.9(2)	Sn(3)-O(3)-Sn(2)	111.6(1)
C(5)-Sn(1)-O(4)	91.1(2)	O(5)-Sn(3)-C(25)	99.8(2)	Sn(1)-O(3)-Sn(2)	136.7(1)
C(1)-Sn(1)-O(4)	94.8(2)	O(4)-Sn(3)-C(25)	96.4(2)	H(4)-O(4)-Sn(3)	130(4)
O(2)-Sn(2)-O(3)	92.34(9)	O(3)-Sn(3)-C(21)	120.2(2)	H(4)-O(4)-Sn(1)	119(4)
O(2)-Sn(2)-C(11)	93.6(1)	O(5)-Sn(3)-C(21)	97.2(2)	Sn(3)-O(4)-Sn(1)	104.8(1)
O(3)-Sn(2)-C(11)	122.1(2)	O(4)-Sn(3)-C(21)	101.3(2)	H(5)-O(5)-Sn(3)	125(4)
O(2)-Sn(2)-C(15)	97.9(2)	C(25)-Sn(3)-C(21)	117.0(2)	H(5)-O(5)-Sn(2)	125(4)
O(3)-Sn(2)-C(15)	114.0(2)	O(1)-Si(1)-O(2)	111.9(1)	Sn(3)-O(5)-Sn(2)	104.8(1)
C(11)-Sn(2)-C(15)	121.9(2)	O(1)-Si(1)-C(31)	112.5(2)		

Table 2. Comparison of selected structural parameters of **2** and related derivatives [E(OSnt-Bu$_2$)$_2$O t-Bu$_2$Sn(OH)$_2$], (E = MesB, OC, Me$_2$Si). Δ refers to deviation of the atom from the plane defined by the three tin atoms.



	E=Ph$_2$Si	E = Me$_2$Si [14]	E=MesB [4]	E=OC [5]
bond lengths (Å)				
Sn_a-O_a	2.264	2.281	2.33	2.123
Sn_b-O_b	2.091	2.092	2.10	2.106
Sn_c-O_c	2.262	2.288	2.33	2.137
Sn_a-O_b	2.092	2.094	2.06	2.043
Sn_b-O_a	2.102	2.111	2.17	2.115
Sn_c-O_b	2.092	2.097	2.06	2.023
Sn_b-O_c	2.106	2.114	2.17	2.155
bond angles (°)				
O_b-Sn_a-O_a	70.1	70.0	70.3	72.0
Sn_a-O_a-Sn_b	104.8	104.5	104.8	106.8
Sn_a-O_b-Sn_b	111.6	112.1	112.4	110.1
O_a-Sn_b-O_b	73.3	73.4	72.3	71.0
O_b-Sn_b-O_c	73.2	74.1	72.3	70.6
Sn_b-O_b-Sn_c	111.7	111.6	112.4	111.4
O_b-Sn_c-O_c	70.3	70.5	70.3	72.5
Sn_b-O_c-Sn_c	104.8	103.8	100.0	105.2
Sn_a-O_b-Sn_c	136.7	136.2	135	138.5
O_a-Sn_b-O_c	146.5	147.5	144.6	141.6
O_d-Sn_a-O_a	161.9	163.7	166	155.0
O_e-Sn_c-O_c	160.8	163.9	166	155.8
deviations from the plane defined by $Sn_aSn_bSn_c$				
Δ -O_a	0.091	0.0145	0.064	0.069
Δ -O_b	0.005	0.006	0.026	0.020
Δ -O_c	-0.165	-0.051	0.064	-0.165
Δ -O_d	-0.246	-0.028	0.006	-0.447
Δ -O_e	0.421	0.0118	0.006	0.580

The pentacoordinate configuration of the tin atoms in **2** is also reflected by its Mössbauer spectrum which shows an I.S. of 1.22 mm/s, a Q.S. of 2.38 mm/s and line widts of 0.86 and 0.86 mm/s. Owing to these narrow lines the method is unable to distinguish between the two different tin atoms in **2**. TGA measurements on **2** reveal loss of water between 93 - 166°C. Heating the sample for 15 min at 170°C resulted in a spectrum with an I.S. of 1.28 mm/s and a Q.S. of 1.96 mm/s (Γ_1 = 0.97 mm/s, Γ_2 = 0.88 mm/s) indicating change from penta- to tetracoordinate tins.

The compounds expected to be formed upon heating of **2** are **1** and [Ph$_2$Si(OSnt-Bu$_2$)$_2$O] (**2a**), as was shown at least for its solution (see Figure 2, eq 2). According to this assumption the Mössbauer spectrum observed after heating of **2** can be satisfactory fitted as a superposition of the spectra of one-third **1** (I.S. 1.26 mm/s, Q.S. 1.74 mm/s) and two-thirds of a new compound with Q.S. 2.40 mm/s and I.S. 1.33 mm/s, all the line widths being kept at 0.83 mm/s. One hypothesis is that this new compound is not six-membered **2a** but its polymer (Ph$_2$SiOSnt-Bu$_2$OSnt-Bu$_2$O)$_n$ (**2b**). This conclusion stems from the observation that completely characterized six-membered [t-Bu$_2$Si(OSnt-Bu$_2$)$_2$O] [3f] shows **a** Q.S. of 2.00 mm/s and a I.S. of1.28 mm/s whereas polymeric

$(Ph_2SiOSiPh_2OSn\textit{t}\text{-}Bu_2O)_n$ [1n] the tin atoms of which are also tetracoordinate exhibits a Q.S. of 2.45 mm/s and an I.S. of 1.35 mm/s. Further studies on this subject are in progress.

The solid state structure of **2** is preserved in thf. The ^{119}Sn NMR spectrum at room temperature of **2** in thf displays two signals with an integral ratio of 1:2 at -270.3 ppm ($^2J(^{119}Sn\text{-}O\text{-}^{117/119}Sn)$ 55 Hz, $^1J(^{119}Sn\text{-}^{13}C)$ 643 Hz) and -274.3 ppm ($^2J(^{119}Sn\text{-}O\text{-}^{117}Sn)$ 159 Hz, $^2J(^{119}Sn\text{-}O\text{-}^{117/119}Sn)$ 55 Hz, $^1J(^{119}Sn\text{-}^{13}C)$ 695 Hz), respectively. These values are comparable with the ^{119}Sn CP-MAS NMR data mentioned above and the ^{119}Sn chemical shifts of -260.3 and -278.5 ppm reported for $[MesB(OSn\textit{t}\text{-}Bu_2)_2O\textit{t}\text{-}Bu_2Sn(OH)_2]$ [4].

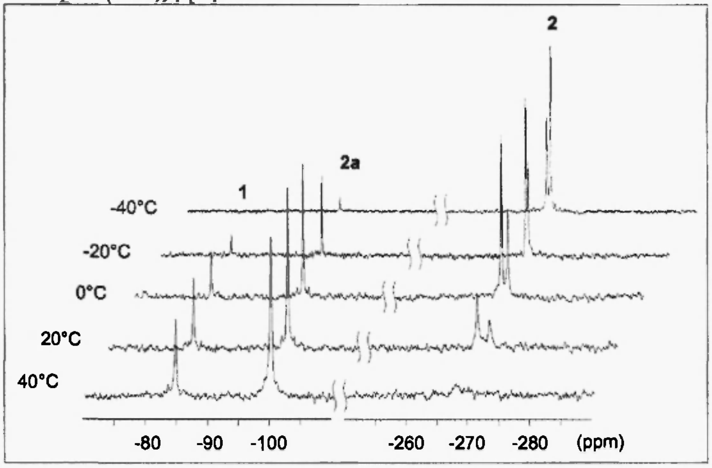


Figure 2. Temperature dependent ^{119}Sn NMR spectra of **2** in $CDCl_3$.

The ^{29}Si NMR spectrum of the same solution shows a signal at 42.7 ppm with a $^2J(^{29}Si\text{-}O\text{-}^{117/119}Sn)$ of 59 Hz. The signal-to-satellite integral ratio [7a,b] of about 16:68:16 confirms the connectivity within the six-membered ring of **2**.

The reversible temperature dependent ^{119}Sn NMR spectra of **2** in $CDCl_3$ (Figure 2) indicate an equilibrium between **2**, $[Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O]$ (**2a**), **1** and H_2O (eq 2) with **2** dominating at -40 °C and **2a** dominating at +40 °C.

$$\underset{\mathbf{2}}{[Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O\cdot\textit{t}\text{-}Bu_2Sn(OH)_2]} \xrightleftharpoons{CDCl_3} \underset{\mathbf{2a}}{[Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O]} + 1/3\ \mathbf{1} + H_2O \quad (2)$$

The signal at about -100 ppm is assigned to **2a** whereas that at about -83 ppm belongs to **1**. The latter was unambiguously confirmed by an increase of the signal integral ratio upon addition of authentic **1** to the $CDCl_3$ solution of **2**. The temperature dependent formation constants calculated from the populations of **2**, **2a** and **1** follow a van't Hoff behaviour and allow the estimation of the enthalpy of H ~ 52 kJ/mol for the equilibrium in eq (2).

The formation of **1** in the equilibrium according to eq (2) results from immediate self-condensation of $\textit{t}\text{-}Bu_2Sn(OH)_2$ (**3**), which is supposed to be the initial product of the dissociation of **2**. That **3** can be prepared at all was shown in a control experiment according to eq (3).

$$\textit{t}\text{-}Bu_2Sn(OMe)_2 + 2H_2O \longrightarrow \underset{\mathbf{3}}{\textit{t}\text{-}Bu_2Sn(OH)_2} + 2MeOH \quad (3)$$

Its synthesis was claimed earlier but the compound was not completely characterised [7c]. Compound **3** is an amorphous solid. Its IR spectrum shows a sharp (OH) at 3653 cm^{-1} proving the presence of hydroxy groups. The ^{119}Sn CP MAS NMR spectrum shows a single resonance at -276.3 ppm which is very close to the chemical shift of Sn(3) in **2** and which is indicative of pentacoordinate tin [6]. Further support for pentacoordination stems from ^{119}Sn Mössbauer measurements (I.S. 1.18 mm/s, Q.S. 2.32 mm/s). Very likely, compound **3** adopts a dimeric structure (Figure 3) comparable with [*t*-$Bu_2Sn(OH)X]_2$ (X = F, Cl, Br) [8]. This view is further supported by a careful sideband analysis of the ^{119}Sn CP MAS NMR spectrum of **3** (Figure 4) according to the method of Herzfeld and Berger [9] using the convention of Haeberlen [10].

The parameters obtained (anisotropy $\Delta\sigma$ = -598.6 ppm, asymmetry η = 0.69) are in favour of the proposed structure (Figure 3) with the *t*-butyl groups in equatorial positions. The alternative asymmetric structure lacking a local C_3 axis with one *t*-butyl group in axial position of a trigonal bipyramid is much less favoured because of the polarity rule [11].

TGA studies on **3** indicate loss of water between 88 - 154°C. Heating a sample of **3** for 15 min at 160°C resulted in loss of water and formation of **1** as evidenced by the Mössbauer spectrum (Q.S. 1.74 mm/s, I.S. 1.25 mm/s) being identical with that of an authentic sample of **1**.

The side band analysis of the ^{119}Sn CP MAS NMR spectrum of **1** gives $\Delta\sigma$ -214.8 ppm and η = 0.0. In view of the established molecular structure of **1** [12] with tetrahedral configurated tins and their C_2SnO_2 substituent patterns an asymmetry of zero can only be explained by assuming a rotation of **1** around its C_3 axis. This rotation must be fast on the ^{119}Sn CP MAS NMR time scale.

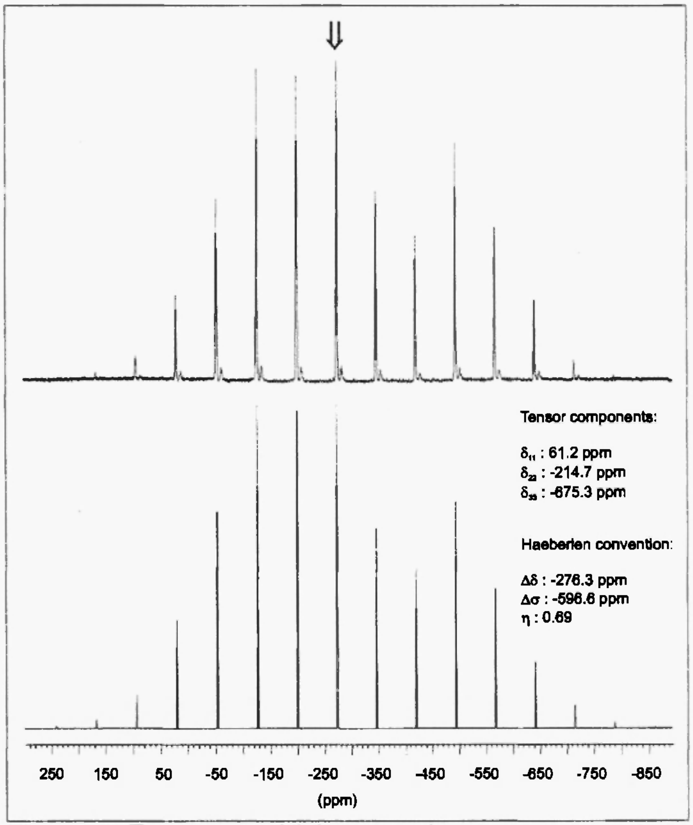


Figure 4. Experimental (above) and computer simulated (below) ^{119}Sn CP MAS NMR spectrum of *t*-$Bu_2Sn(OH)_2$ (**3**)
(MAS frequency 11 kHz). Centerband position in the experimental spectrum is indicated by an arrow.

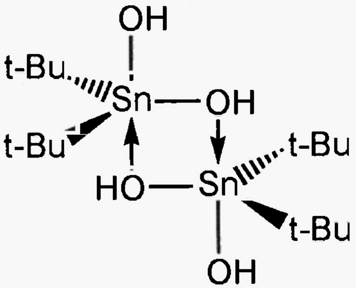


Figure 3. Proposed structure of *t*-$Bu_2Sn(OH)_2$ (**3**).

Upon dissolution of **3** in $CDCl_3$ condensation takes place under formation of **1** and water as is evidenced by the ^{119}Sn NMR signal at -83.1 ppm. The line width $W_{1/2}$ of 50 Hz of this signal is a hint for an exchange process taking place between **1** and **3** or related species such as [*t*-$Bu_2(OH)Sn]_2O$ with the two latter species not being visible in the ^{119}Sn NMR spectrum. In the absence of water pure **1** shows a ^{119}Sn NMR resonance in $CDCl_3$ at -83.5 ppm with $W_{1/2}$ = 5 Hz. The same arguments hold for **2**a. When generated according to eq (2) the ^{119}Sn NMR signal of **2**a shows $W_{1/2}$ = 30 Hz indicating exchange. When generated under water-free conditions by reaction of (*t*-$Bu_2SnOSiPh_2SnO)_2$ [13] with **1** (eq 4) **2a** displays a ^{119}Sn resonance at -98.6 ppm ($^2J(^{119}Sn$-O-$^{117}Sn)$ 298 Hz) with a line width $W_{1/2}$ = 5 Hz.

$$(t\text{-}Bu_2SnOSiPh_2O)_2 + 2/3\ \mathbf{1} \longrightarrow 2\ [Ph_2Si(OSn t\text{-}Bu_2)_2O] \qquad (4)$$

2a

In contrast to $Ph_2Si(OH)_2$, the reaction of t-$Bu_2Si(OH)_2$ with **1** exclusively gives [t-$Bu_2Si(OSnt$-$Bu_2)_2O$] [**4a**] (eq 5).

$$2/3\ \mathbf{1} + t\text{-}Bu_2Si(OH)_2 \longrightarrow [t\text{-}Bu_2Si(OSn t\text{-}Bu_2)_2O] + H_2O \qquad (5)$$

4a

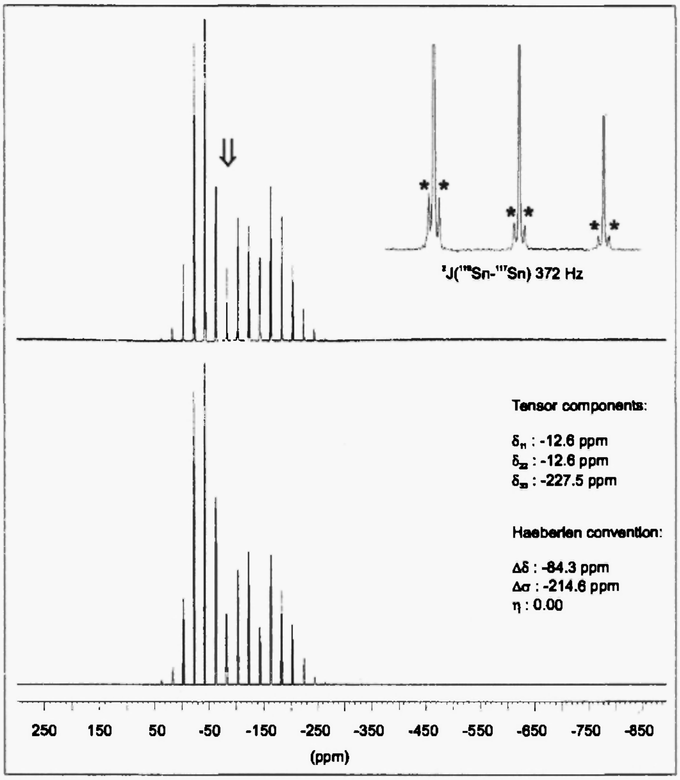


Figure 5. Experimental (above) and computer simulated ^{119}Sn CP MAS NMR spectrum (below) of (t-$Bu_2SnO)_3$ (**1**) (MAS frequency 3 kHz). Center-band position and satellites in the experimental spectrum are indicated by an arrow and by asterisks, respectively.

Regardless of the molar ratio of **1** and t-$Bu_2Si(OH)_2$, there is no indication for the formation of [t-$Bu_2Si(OSnt$-$Bu_2)_2O$-t-$Bu_2Sn(OH)_2$] (**4**), the analogue of **2**. Apparently, the organic substituents at silicon control the stability of complexes **2** and **4**, respectively. This view is supported by recent results of *Pannell* and co-workers who obtained [$Me_2Si(OSnt$-$Bu_2)_2O$-t-$Bu_2Sn(OH)_2$] by accident in a reaction of t-Bu_2SnCl_2, silicon grease and Mes_3PbLi [14].

Experimental

$Ph_2Si(OH)_2$ [15] and (t-$Bu_2SnO)_3$ [12] were prepared according to literature procedures. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over the appropriate desiccants.

Solution NMR spectra were recorded on a Bruker DRX 400 instrument and were referenced to $SiMe_4$ (^1H, ^{13}C, ^{29}Si) or $SnMe_4$ (^{119}Sn). ^{119}Sn MAS spectra were obtained from a Bruker MSL 400 spectrometer using cross-polarisation and high power proton decoupling. Cy_4Sn was used as a second reference (δ -97.35 ppm) and to optimise Hartmann-Hahn CP matching conditions. In order to obtain sufficient signal to noise ratios for spinning sideband analysis several thousand transients were accumulated (conditions: recycle delay 4.0 s, 90° pulse 5.0 us, contact time 3.5 ms.) MAS frequencies were estimated for about 15 intense sidebands suitable for Herzfeld - Berger analysis.

IR and Raman spectra were obtained from Bruker FTIR IFS 113v spectrometer and Jobin, Yvon T64000 spectrometer (Ar laser, ν_e 514.5 nm), respectively. The electron ionisation mass spectrum was recorded on a Finnigan MAT 8230 spectrometer. The ions showed the expected isotope pattern.
The Mössbauer spectra were recorded in constant-acceleration mode on a home-made instrument, designed and built by the Institut voor Kernen Stralingsfysica (IKS), Leuven. The isomer shifts refer to a source of $Ca^{119m}SnO_3$ from Amersham, UK, samples being maintained at 90 ± 2 K. The data were treated with a least-square iterative program deconvoluting the spectrum into a sum of lorentzians.
The TGA measurements were performed on a Mettler Instrument equipped with a PID Module 200. The density of single crystals of **2** was determined using a Micromeritics Accu Pyc 1330.

Synthesis of t-Bu$_2$Sn(OMe)$_2$ [16]

Sodium (0.92 g, 40 mmol) was dissolved in 50 mL dry methanol. *t*-Bu_2SnCl_2 (6.08 g, 20 mmol), dissolved in 30 mL methanol, was added dropwise under magnetical stirring. The reaction mixture was refluxed for 3 h. The precipitate of sodium chloride was filtered and the filtrate was evaporated *in vacuo*. Distillation of the residue afforded 3.2 g *t*-$Bu_2Sn(OMe)_2$ (10.8 mmol, 54 %) of b.p. 50 - 51°C (0.2 mm Hg). ^{119}Sn NMR ($CDCl_3$): -109 ppm.
Anal. Found: C, 40.28; H, 8.32 Calcd for $C_{10}H_{24}O_2Sn$ (M 295.00) C, 40.71; H, 8.20 %.

Synthesis of [(Ph$_2$SiO)(t-Bu$_2$SnO)$_2$·t-Bu$_2$Sn(OH)$_2$] (**2**)

$Ph_2Si(OH)_2$ (1.08 g, 5 mmol) and **1** (3.73 g, 5 mmol) in toluene (25 mL) were heated at 60°C for 1d. After cooling to -10°C, 4.3g (4.5 mmol, 90%) of **2** were obtained as colourless crystalline solid, m.p. 175°-190°C.
Crystals suitable for X-ray measurements were obtained from hexane/$CHCl_3$ at -10°C.
^{1}H NMR (THF-d8): δ 7.8-7.0 ppm (10H, Ph); 3.62 ppm (2H, OH); 1.46 ppm, $^{3}J(^{1}H-^{119}Sn)$ 100.0 Hz (18H, Sn-*t*-Bu); 1.40 ppm, $^{3}J(^{1}H-^{119}Sn)$ 103.1 Hz (36H, Sn-*t*-Bu). ^{13}C NMR (THF-d8): 144.7, 134.7, 126.9, 126.2 ppm (m-, p-, o-, i-C of Ph); 39.5 ppm, $^{1}J(^{13}C-^{119}Sn)$ 696 Hz (Sn-*C*Me$_3$); 37.5 ppm, $^{1}J(^{13}C-^{119}Sn)$ 642 Hz (Sn-*C*Me$_3$); 30.5 ppm (Sn-C*Me*$_3$); 30.3 ppm (Sn-C*Me*$_3$). ^{29}Si NMR (THF-d8): -42.7 ppm, $^{2}J(^{29}Si-^{119}Sn)$ 58.9 Hz. ^{119}Sn NMR (THF-d8): -270.3 ppm, $^{1}J(^{119}Sn-^{13}C)$ 643 Hz, $^{2}J(^{119}Sn-^{117}Sn)$ 55.2 Hz; -274.3 ppm, $^{1}J(^{119}Sn-^{13}C)$ 695 Hz, $^{2}J(^{119}Sn-^{117}Sn)$ 159 Hz, $^{2}J(^{119}Sn-^{117}Sn)/^{2}J(^{119}Sn-^{29}Si)$ 55.2 Hz. CP MAS ^{119}Sn NMR: -265.7 ppm (δ_{11} 114.6 ppm, δ_{22} -175.3 ppm, δ_{33} -736.5 ppm, $\Delta\sigma$ -706.2 ppm, η 0.61), -273.7 ppm (δ_{11} 77.8 ppm, δ_{22} -207.3 ppm, δ_{33} -691.6 ppm, $\Delta\sigma$ -625.9 ppm, η 0.68). Mössbauer spectroscopy: Q.S. 2.38 $mm \cdot s^{-1}$, I.S. 1.22 $mm \cdot s^{-1}$. MS (m/e): 836 (M-C_9H_{18} , 12 %), 639 (M-$C_{12}H_{29}O_2Sn$, 50%), 583 (M-$C_{16}H_{37}O_2Sn$, 48%), 391 ($C_6H_5O_3Sn_2Si$, 56%), 57 (C_4H_9, 100%). IR (KBr): 3644vs, 3064m, 2846vs, 1469vs, 1469m, 1391vs, 1165s, 1109vs, 1005s, 993vs, 953vs, 807m, 771s, 742m 704s, 632s, 577s, 511s cm^{-1}. Raman: 3649m, 3050s, 2853vs, 1570m, 1468m, 1445m, 1370m, 1172vs, 1002vs, 810vs, 510vs cm^{-1}. Anal. Found: C, 45.1; H, 7.0 Calcd for $C_{36}H_{66}O_5SiSn_3$ (M 963.21): C, 44.9; H, 6.9%. TGA: M-H_2O between 93-166°C.

NMR generation of [Ph$_2$Si(OSnt-Bu$_2$)$_2$O] (**2a**)

A mixture of [Ph_2SiOSn*t*-Bu_2O]$_2$ (89.4 mg, 0.1 mmol) and **1** (49.8 mg, 0.2/3 mmol) dissolved in $CDCl_3$ (250 µL) was refluxed for 2h to give a clear solution.
^{1}H NMR ($CDCl_3$): 7.8-7.3 ppm (10H, Ph), 1.41 ppm, $^{3}J(^{1}H-^{119}Sn)$ 96.6 Hz (36H, *t*-Bu). ^{13}C NMR ($CDCl_3$): 141.2, 134.3, 128.5, 127.1 ppm (m-, p-, o-, i-C of Ph); 39.4 ppm $^{1}J(^{13}C-^{119}Sn)$ 487 Hz (Sn-*C*Me$_3$), 30.1 ppm (Sn-C*Me*$_3$). ^{29}Si NMR ($CDCl_3$): -38.3 ppm, $^{2}J(^{29}Si-^{119/117}Sn)$ 35.7 Hz. ^{119}Sn NMR ($CDCl_3$): -98.6 ppm, $^{1}J(^{119}Sn-^{13}C)$ 488 Hz, $^{2}J(^{119}Sn-^{117}Sn)$ 298 Hz, $^{2}J(^{119}Sn-^{29}Si)$ 35.8 Hz.

Synthesis of t-Bu$_2$Sn(OH)$_2$ (**3**)

To a magnetically stirred solution of *t*-$Bu_2Sn(OMe)_2$ (2.95 g, 10 mmol) in MeOH (10 mL) was added dropwise at room temperature a mixture of water (100 µL) and MeOH (5 mL). After 2h the solvent was removed in vacuo to give an amorphous solid which was dried at air for 1d to give 2.52 g amorphous **3** (9.4 mmol, 94%).

^{119}Sn NMR ($CDCl_3$): -83.1 ppm (W_ = 50 Hz) assigned to **1**. CP MAS ^{119}Sn NMR: 276.3 ppm (δ_{11} 61.2 ppm, δ_{22} -214.7 ppm, δ_{33} -675.3 ppm, $\Delta\sigma$ -598.6 ppm ,η 0.69). Mössbauer spectroscopy: Q.S. 2.32 mm s^{-1}, I. S. 1.18 mm s^{-1}. IR (KBr): 3653s, 2848vs, 1468s, 1405s, 1362m, 1168s, 1015m, 941w, 808s, 558vs cm^{-1}. Raman: 3655m, 2854vs, 1468m, 1444m, 1369m, 1175vs, 1018m, 945m, 812vs, 587m, 511s cm^{-1}.
Anal. Found: C, 36.2; H, 7.6 Calcd for $C_8H_{20}O_2Sn$ (M 266.98): C, 36.0; H, 7.6. TGA: M-H_2O between 88-154°C.

*Synthesis of [t-$Bu_2Si(OSnt$-$Bu_2)_2O$] (**4a**)*

t-$Bu_2Si(OH)_2$ (352.6 mg, 2 mmol) and (t-$Bu_2SnO)_3$ (995.6 mg, 4/3 mmol) were heated in 20 ml toluene in a Dean-Stark apparatus. Colourless crystals of **4a** (1.15g, 88%) were obtained upon cooling, m.p. 242°C.
^{1}H NMR ($CDCl_3$): 1.49 ppm $^3J(^1H$-$^{119}Sn)$ 94.7 Hz (36H, Snt-Bu), 1.16 ppm (18H, Snt-Bu).
^{13}C NMR ($CDCl_3$): 39.7 ppm $^1J(^{13}C$-$^{119}Sn)$ 497 Hz (Sn-CMe_3), 30.6 ppm (Sn-CMe_3), 29.2 ppm (Si-CMe_3), 22.2 ppm (Si-CMe_3). ^{29}Si NMR ($CDCl_3$): -17.9 ppm, $^2J(^{29}Si$-$^{119}Sn)$ 50.9 Hz.
^{119}Sn NMR ($CDCl_3$): -107.2 ppm, $^1J(^{119}Sn$ - $^{13}C)$ 498 Hz, $^2J(^{119}Sn$-$^{117}Sn)$ 292 Hz, $^2J(^{29}Si$-$^{119}Sn)$ 50.9 Hz.
Mössbauer spectroscopy: Q.S 1.99 mm s^{-1}, I. S. 1.28 mm s^{-1}.
Anal. Found: C, 43.8; H, 8.6 Calcd for $C_{24}H_{54}O_3SiSn_2$ (M 656.25): C, 43.9; H, 8.3%.

Crystallography

Intensity data for the colourless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoK radiation. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation (Δ/ω = 1°) at two times 5s 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, analysing the duplicate reflections and was not detected. The structure was solved by direct methods SHELXS86 [17] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL93 [18].
H(4) and H(5) were located in the difference Fourier map and refined isotropically (H(4), U_{iso} 0.054(17) Å^2; H(5), U_{iso} 0.044(16) Å^2). The other H atoms were placed in geometrically calculated positions and refined with different isotropic temperature factors for alkyl and aryl H atoms (H_{alkyl} C-H 0.96 Å, U_{iso} 0.161(4) Å^2; H_{aryl} C-H 0.93 Å, U_{iso} 0.103(4) Å^2). Disordered C-Atoms were found in one t-Bu-group C(27) and C(27') (s.o.f. 0.5). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X–ray Crystallography* [19]. The figures were created by SHELXTL-Plus [20]. Crystallographic data are given in Table 3.

Table 3. Crystallographic Data for **2**.

Empirical formula	$C_{36}H_{66}O_5SiSn_3$ (**1**)	Crystal size	0.20 x 0.18 x 0.18 mm
Formula weight	963.05	range for data collection	4.76 to 25.69°
Temperature	291(1) K	Data/ restraints / parameters	8043 / 0 / 425
Wavelength	0.71069 Å	Reflections collected	58727
Crystal system	Monoclinic	Independent reflections	8043 / [R(int) = 0.048]
Space group	$P2_1/c$	Reflections obs. ($I > 2\sigma(I)$)	4786
Unit cell dimensions	a = 12.715(1) Å	Index ranges	$-15 < h \leq 15$
	b = 19.518(1) Å		$-23 < k < 23$
	c = 17.742(1) Å		$-21 < l \leq 21$
	β = 100.968(1)°	Completeness to = 25.69	98.2 %
Volume	4322.6(5) Å^3	Goodness-of-fit on F^2	0.921
Density (calculated)	1.480 Mg/m^3	R indices ($I > 2\sigma(I)$)	R1 = 0.0339 (F);
Density (measured)	1.48(1) Mg/m^3	(all Data)	wR2 = 0.0648 (F^2)
Z	4	$(\Delta/\sigma)_{max.}$	0.001
Absorption coefficient	1.782 mm^{-1}	Largest diff. Peak and hole	0.423 and -0.404 e Å^3
F(000)	1944		

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