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Organotin-substituted organosiloxanes: synthesis and characterisation, including the crystal structure of 1,3-bis(triphenylstannoxy)-1,1,3,3-tetraphenyl-1,3-disiloxane

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Abstract

A series of linear 1,3-bis(triorganostannoxy)siloxanes $(R'_3SnO)R_2SiOSiR_2(OSnR'_3)$ ($R = Me, Ph$; $R' = Ph, {}^nBu, c\text{-}C_6H_{11}$) has been synthesised, and the compounds characterised by NMR (^1H, ^{13}C, ^{29}Si and ^{119}Sn) and Mössbauer spectroscopies. The structure of the homoleptic compound $R = R' = Ph$ has been determined by an X-ray diffraction study.

Key words: Siloxanes; Stannoxy; Mössbauer spectroscopy; Crystal structure

1. Introduction

The synthesis and structural chemistry of metallosiloxanes has been the subject of intensive research for many years. In the simplest cases, *e.g.* R_3SiOML_n, interest has focused on the role of the siloxide as a bulky OR ligand, while the technological importance of metals supported on silica or related bulk materials has been the driving force for both the synthetic and structural studies of cyclic and cage metallosiloxanes [1–4]. Surprisingly, while cyclic metallosiloxanes have been studied both structurally and as synthetic precursors to linear metallosiloxanes, the linear compounds themselves have been comparatively neglected. Thus, compounds which can act as models for fragments of polymeric $(\text{–M–O–Si–})_n$ chains are limited, a situation complicated by the fact that even the parent species, represented by compounds of general formula R_3SiOML_n, are often oligomeric. For example, $Et_2AlOSiMe_2Et$ is an *O*-bridged dimer, while $MeBeOSiMe_3$ is tetrameric and adopts a cubane structure [5,6]. Compounds with two (or more) –OSiR_3 groups include the slightly longer Si–O–M–O–Si moiety *e.g.* $(Ph_3SiO)_2CrO_2$ [7], $(Ph_3SiO)_2Cu(py)_2$ (py = pyridine) [8], $(Me_3SiO)_2V{\equiv}NPtMe(PEt_3)_2$ [9], and $(^tBu_3SiO)_3Ta{=}C{=}C{=}Ta(OSi^tBu_3)_3$ [10], but clearly the link between such species and $(\text{–M–O–Si–})_n$ is at best tenuous.

Our interest in the use of siloxane polymers as carriers for the controlled release of active boron and tin species for use in wood preservation has led us to synthesise materials with active groups as main-chain and side-arm functionalities. We, along with others, have studied the chemistry of cyclic borosiloxanes which can act as precursors to linear Si–O–B chains [2,3]. In this paper we report on the chemistry of linear Si–O–Sn compounds, both as part of the materials chemistry of such systems and in order to add to the scant knowledge of linear $(\text{–M–O–Si–})_n$ arrays in general. Despite the important role of organotin compounds as catalysts for the cross-linking of organosilanols and related species [11,12], compounds containing the Si–O–SnR_n fragment are rather rare, as indeed are similar species containing germanium and lead. The structures of $Ph_3GeOSiPh_3$ and $Ph_3PbOSiPh_3$ have been reported, but crystals of the analogous tin compound, $Ph_3SnOSiPh_3$, were found to be both partially disordered in terms of the metal/metalloid positions and unstable in the X-ray beam [13,14]. We have recently reported the synthesis and structure of $Bz_2[(Me_3Si)_3C]\text{-}SnOSiMe_3$ (Bz = benzyl) [15], which as far as we are

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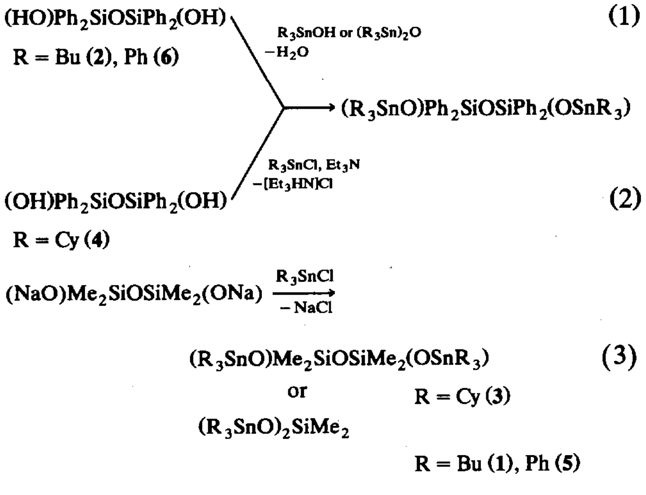
aware is the only organometallic Sn–O–Si compound for which unambiguous structural data exists, for although the structure of $[Me_2(Me_3SiO)Sn]_2O$ is available, only the Sn–O–Sn array has been discussed [16]. The reactions between Ph_3SnOH and either Ph_3SiOH or $Ph_2Si(OH)_2$ (catalysed by small amounts of $AlCl_3$) have been reported, though the products have not been characterised to any significant degree. The authors did, however, remark on a notable lowering of thermal stability compared with that of the parent siloxanes as Sn–O bonds increasingly replaced the Si–O moieties [17].

Organotin compounds have been widely used in the field of wood preservation, primarily but not exclusively $(Bu_3Sn)_2O$ (TBTO) [18–20]. Controlled release formulations have been effective in organotin anti-fouling paints [21,22], and the use of uncharacterised organotin–silicon hybrid materials (from the reactions of ethyl orthosilicate and organotin acetates) has been patented [23,24]. In this paper we report the synthesis of six compounds of the type $R'_3SnO(R_2SiO)_2SnR'_3$, including the crystal structure of the compound with R = R′ = Ph.

2. Results and discussion

A series of linear 1,3-bis(triorganostannoxy)siloxanes $(R'_3SnO)R_2SiOSiR_2(OSnR'_3)$ has been synthesised by one or more of the three routes shown below:



In addition, the product isolated from the reaction of $(NaO)Me_2SiOSiMe_2(ONa)$ with two equivalents of Cy_3SnCl has been identified from ^1H NMR data as 1,1-bis(tricyclohexylstannoxy)dimethylsilane.

Most of the products were undistillable oils, only **3**, **4** and **6** being solids. These latter compounds were obtained in better than 90% yields after recrystallisation. The oils were of satisfactory purity after solvent evaporation. The compounds are characterised by a single ^{29}Si NMR resonance at about −19 ppm for Me_2Si or about −45 ppm for Ph_2Si centres. The R_3Sn sites give signals in the ^{119}Sn NMR spectra at around 80, −15 or −110 ppm for R = ^nBu, c-Cy and Ph respectively. $^1J(^{119}Sn-^{13}C)$ couplings around 370 Hz, observable in the spectra of **1–3**, are typical of a tetrahedral environment about the metal. All six compounds have Mössbauer isomer shifts consistent with tin in the +4 oxidation state (1.10–1.31 mm s^{-1}), and quadrupole splittings associated with a four-coordinate metal (1.76–2.29 mm s^{-1}).

It is, however, apparent from the ^{29}Si and ^{119}Sn NMR spectra of a wider range of compounds that we have attempted to prepare, that despite the relatively mild conditions under which the syntheses were performed (reactions 2 and 3 were carried out under ambient conditions), many of the products so obtained are unstable, particularly those with small substituents on tin and/or silicon, *e.g.* $(R'_3SnO)R_2SiOSiR_2(OSnR'_3)$, R = Me, Ph; R′ = Me, ^nPr. Data for $(Me_3SnO)Me_2SiOSiMe_2(OSnMe_3)$ will serve to illustrate this point, as other unstable analogues show similar characteristics. While the analytical data of freshly prepared materials are reasonable for the formulation given [Anal. Found: C, 25.1; H, 6.5. calc.: C, 24.4; H, 6.1%] the ^1H NMR spectrum clearly shows two $(CH_3)_3Sn$ signals with their associated satellites, and at least four other singlets around 0.0 ppm that can be ascribed to Me_2Si units. The ^{119}Sn and ^{29}Si NMR spectra are more complex, revealing four distinct tin environments (approximate intensities 1:1:2:3; range 106 ppm to 114 ppm) and 12 silicon resonances (four major signals; range −12 ppm to −24 ppm). The Mössbauer spectrum of the neat oil (IS, QS: 1.13, 2.12 mm s^{-1}) is similar to those of **1–6**, though the linewidths are marginally broader (0.94, 0.98 mm s^{-1}). Clearly, the NMR data indicate the formation of a mixture of average composition corresponding to the formula given, in which the greater complexity of the silicon spectrum suggests a growing $(Me_2SiO)_n$ (n = 1, 2, 3 *etc*) chain. Such mixtures could be formed either during the preparation, or from a pure product on standing in solution following exposure to air. It has been noted previously that Si–O–Sn bonds are readily cleaved by protic reagents [25], and that the siloxane bridge on a silanol-terminated poly(dialkylsiloxane) is weaker than the other analogous bridges within the linear polymer [26]. Thus, residual unchanged silanol groups (routes 1 and 2) or traces of water present in the reaction mixtures (route 3) would facilitate redistribution reactions, particularly for Me–Si compounds, so yielding siloxanols of various chain lengths which may be end-capped by organotin moieties:

$$\mathrm{R'_3SnO(R_2SiO)_nSnR'_3} \rightleftharpoons \mathrm{R'_3SnOH + R_2Si(OH)_2 + HO(R_2SiO)_{n-1}SnR'_3}$$

$$\mathrm{R_2Si(OH)_2 + HO(R_2SiO)_{n-1}SnR'_3} \rightleftharpoons \mathrm{HO(R_2SiO)_nSnR'_3}$$

$$\left.\begin{array}{c}\mathrm{R_2Si(OH)_2}\\ + \\ \mathrm{R'_3Sn(OSiR_2)_nOH}\\ + \\ \mathrm{R'_3Sn(OSiR_2)_{n-1}OH}\end{array}\right\} \xrightarrow{\mathrm{R'_3SnOH}} \begin{array}{c}\mathrm{R'_3SnO(R_2SiO)_mSnR'_3}\\ m = 1, 2, 3\ etc.\end{array}$$

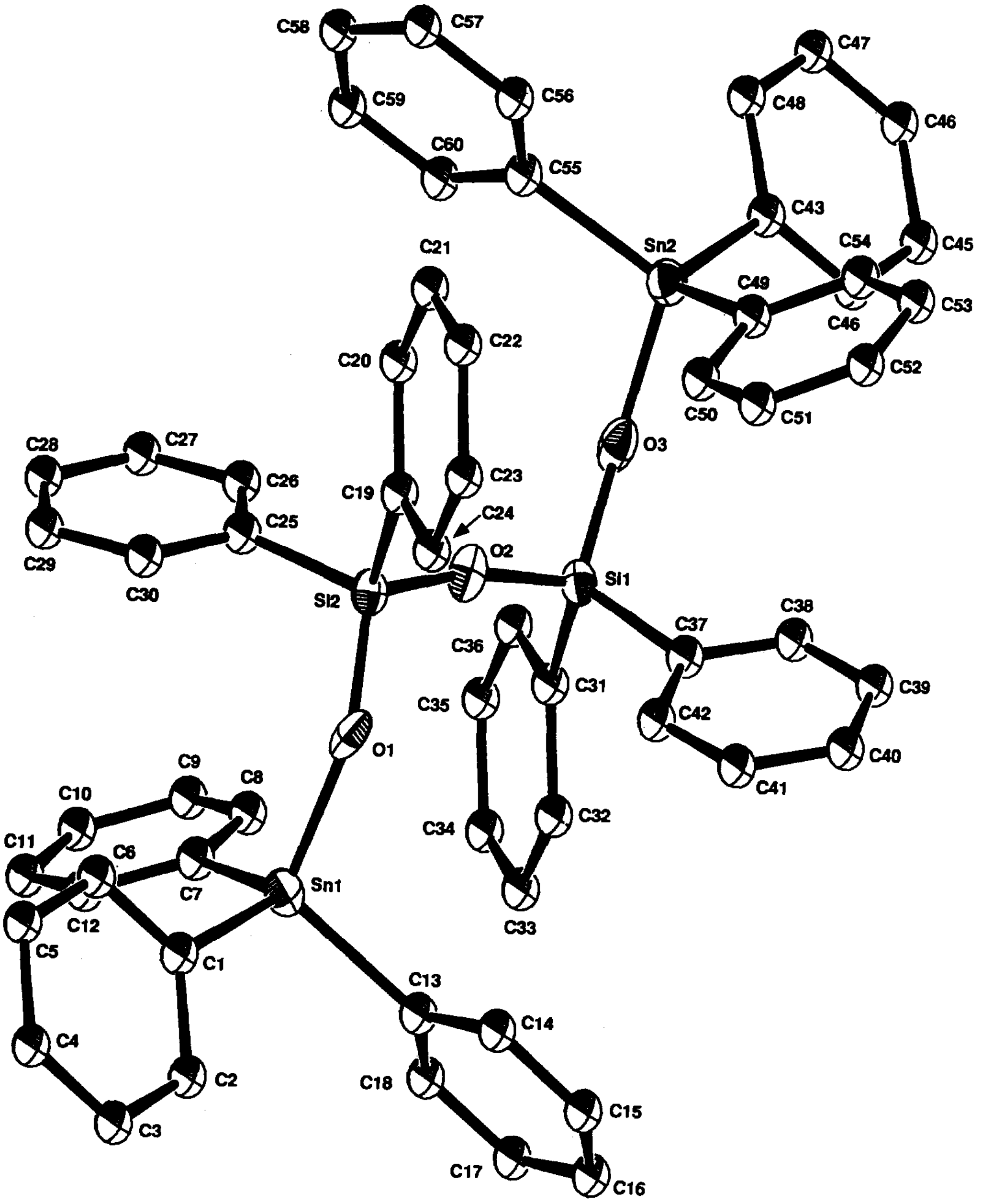
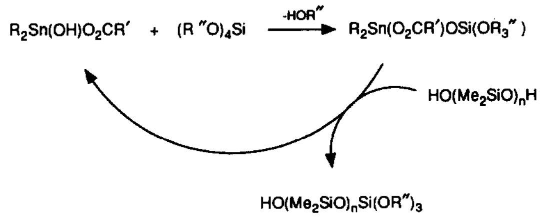


Fig. 1. The asymmetric unit of $\mathrm{(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)}$, showing the labelling scheme used in the text and tables. Thermal ellipsoids for the Sn, Si and O atoms are at the 30% probability level.

Such a process is probably responsible for the formation of $(Cy_3SnO)_2SiMe_2$ noted earlier, and is also believed to be the key step in the cross-linking of siloxanols by diorganotin carboxylates, $R_2Sn(O_2CR')_2$, which are themselves converted *in situ* into $R_2Sn(O_2CR')(OH)$ [27]:



2.1. The structure of $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$ (6)

The structure of the title compound is shown in Fig. 1. Geometric data for the Sn–O–Si skeleton are given in Table 1. The molecule adopts a staggered configuration about the vector joining Si1–Si2, as shown in Fig. 2. The dihedral angles across this vector, *i.e.* O1–Si2–Si1–O3, C25–Si1–Si2–C37 and C19–Si1–Si2–C31, are 174.8, 180.0 and 179.4° respectively. The geometry about each tin and silicon is close to regular tetrahedral, though in the case of tin the angles involving oxygen, save O1–Sn1–C7 [110.4(5°)], are all consistently lower [103.2(6)–105.9(5)°] than angles involving only the less electronegative carbon [111.3(5)–113.5(5)°], in keeping with Bent's ideas of iso-valent rehybridisation [28]. The seven-atom $Sn_2Si_2O_3$ chain is, however, distorted about the oxygen centres. Thus, the angles Sn–O–Si are opened to values [140.0(8)°; 142.7(9)°] which can be compared with a Si–O–Sn angle of 144.2° in $Ph_3SnOSiPh_3$ [14] and 159.2(7)° in the more hindered $Bz_2[(Me_3Si)_3C]SnOSiMe_3$ [15]. More significant is the opening of the angle about the central oxygen, O2 [Si1–O2–Si2: 165.4(10)°]. Although Si–O–Si angles range from 109° to 180° in siloxanes [29,30], the angle of 165.4° observed in the title compound is still towards the high end of the range. Moreover, we have noted before that as the Si–O–Si angle opens, the Si–O bonds shorten [2]. Both points are exemplified in the structure of the precursor siloxane, $(HO)Ph_2SiOSiPh_2(OH)$, which crystallises as a

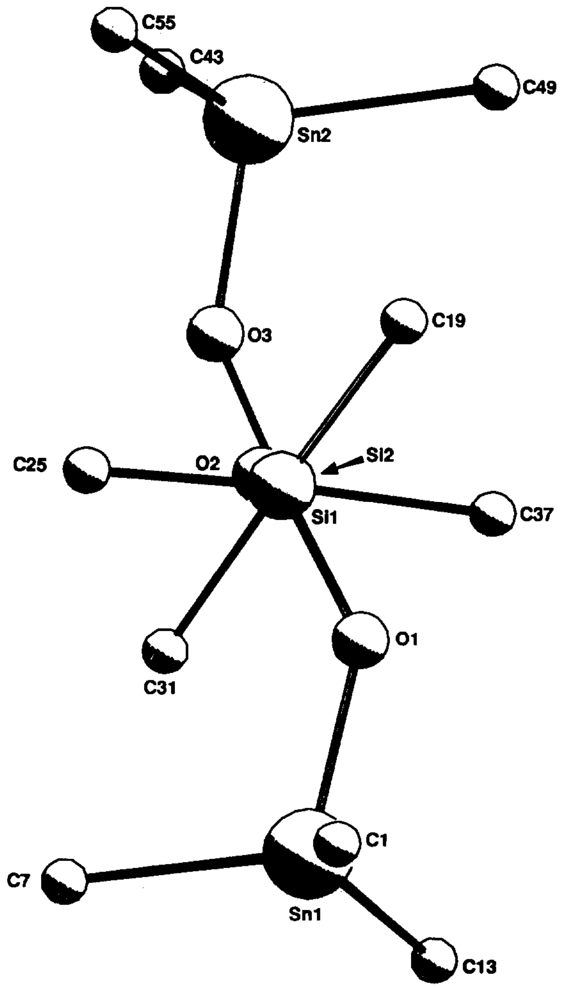


Fig. 2. A view of $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$ along the Si(1)–Si(2) vector. Only the α-carbons of the phenyl groups are shown for clarity.

TABLE 1. Bond distances (pm) and angles (deg) for non-hydrogen atoms of $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$ (esds in parentheses) [a]

Bond lengths			
Sn1–O1	196(1)	Si1–O2	161(1)
Sn2–O3	193(2)	Si2–C25	187(2)
Sn1–C1	213(2)	Si1–O3	161(2)
Sn1–C7	213(2)	Si2–O1	159(1)
Sn1–C13	213(2)	Si2–O2	161(1)
Sn2–C43	212(2)	Si1–C31	187(2)
Sn2–C49	213(1)	Si1–C37	189(2)
Sn2–C55	213(2)	Si2–C19	190(1)
Bond angles			
O1–Sn1–C1	104.7(6)	O3–Sn2–C43	103.2(6)
O1–Sn1–C7	110.4(5)	O3–Sn2–C49	105.9(5)
O1–Sn1–C13	104.4(5)	O3–Sn2–C55	105.2(5)
C1–Sn1–C7	111.3(5)	C43–Sn2–C49	114.4(5)
C1–Sn1–C13	112.9(6)	C43–Sn2–C55	113.2(5)
C7–Sn1–C13	112.5(5)	C49–Sn2–C55	113.5(5)
O2–Si1–O3	110.3(8)	O1–Si2–O2	113.7(8)
O2–Si1–C31	107.4(8)	O1–Si2–C19	108.9(7)
O2–Si1–C37	108.7(7)	O1–Si2–C25	109.3(7)
O3–S11–C31	108.6(7)	O2–Si2–C19	108.5(7)
O3–Si1–C37	111.2(7)	O2–Si2–C25	108.0(7)
C31–Si1–C37	110.6(7)	C19–Si2–C25	108.3(7)
Sn1–O1–Si2	140.0(8)	Sn2–O3–Si1	142.7(9)
Si1–O2–Si2	165.4(10)		

[a] All phenyl rings refined as regular hexagons [C–C: 139.5 pm; C–C–C: 120°]

trimer in the presence of two moles of pyridazine. Of the three molecules, one Si–O–Si angle is constrained by symmetry to be 180° [Si–O: 160.1(4) pm], while the remaining analogous angles are only 144.5° [Si–O: 164.7(8) pm] [29]. The Si–O bonds in the stannasiloxane [average: 161(1) pm] are entirely consistent with this observation. The Sn–O(Si) bonds in the title compound [193(2), 196(1) pm] are in keeping with those found in $Bz_2[(Me_3Si)_3C]SnOSiMe_3$ [193(1) pm] [15].

3. Experimental details

Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), JEOL GX400 (^{29}Si, ^{119}Sn NMR). Details of our Mössbauer spectrometer and related procedures are given elsewhere [31]. NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature. ^{29}Si and ^{119}Sn chemical shifts are relative to Me_4Si and Me_4Sn respectively.

The 1,1,3,3-tetraorgano-1,3-dihydroxy-1,3-disiloxane (R = Me or Ph) and the di-sodium salt of the former were each prepared by a published method [32,33].

An example of each of the general synthetic methods is given.

3.1. Synthesis of 1,3-bis-(tributylstannoxy)-1,1,3,3-tetraphenyl-1,3-disiloxane (2)

A mixture of bis-(tributyltin)oxide (5.00 g, 8.4 mmol) and 1,1,3,3-tetraphenyl-1,3-dihydroxy-1,3-disiloxane (3.84 g, 8.4 mmol) in benzene (*caution*) was refluxed, and the liberated water was collected in a Dean and Stark apparatus. The solvent and all low molecular weight volatiles were removed by extended pumping *in vacuo* to leave the product as a colourless, undistillable oil (5.94 g 72%). The low yield in this case is probably a function of extended high-vacuum pumping, given the higher yield obtained in similar procedures (*vide infra*). Anal. Found: C, 58.3; H, 7.71. $C_{49}H_{74}Si_2Sn_2O_3$ calc.: C, 58.1; H 7.51%. ^1H NMR: 0.91 (t, 18H, CH_3); 1.00 (m, 12H, CH_3CH_2); 1.29 (m, 12H, $CH_3CH_2CH_2$); 1.50 (m, 12H, CH_2Sn); 7.22–7.72 (m, 20H, C_6H_5). ^{13}C NMR: 16.2, 27.7, 27.1, 13.6 ($SnCH_2CH_2CH_2CH_3$, respectively) [$^1J(^{13}C–^{117,119}Sn)$: 352.6, 370.2 Hz], 127.1, 128.7, 134.6, 139.3 (C_6H_5Si). ^{29}Si NMR: −45.3. ^{119}Sn NMR: 88.0 ppm. ^{119}Sn Mössbauer: IS = 1.25, QS = 2.26 mm s^{-1}.

3.2. 1,3-bis-(triphenylstannoxy)-1,1,3,3-tetraphenyl-1,3-disiloxane (6)

This complex was prepared by the same method as 3.1. A white solid, recrystallised from 60–80 petrol (90%, m.p. 122°C). Anal. Found: C, 64.8; H, 4.50. $C_{60}H_{50}Si_2Sn_2O_3$ calc.: C, 64.8; H, 4.53%. ^1H NMR: 6.94–7.51 (m, 50H, C_6H_5). ^{13}C NMR: 127.1, 128.8, 134.7 (C_6H_5Si); 128.6, 129.7, 136.3 (C_6H_5Sn) (*ipso*-carbon not resolved). ^{29}Si NMR: −43.0. ^{119}Sn NMR: −106.5 ppm. ^{119}Sn Mössbauer: IS = 1.13, QS = 1.91 mm s^{-1}.

3.3. Synthesis of bis-(tricyclohexylstannoxy)dimethylsilane (3)

A mixture of tricyclohexyltin chloride (1.85 g, 4.6 mmol) and the di-sodium salt of 1,1,3,3-tetramethyl-1,3-dihydroxy-1,3-disiloxane (0.69 g, 2.3 mmol) in diethyl ether (50 ml) was stirred for 4 h at room temperature. The sodium chloride formed was filtered off, and the solvent evaporated to leave the product as a white solid (1.97 g, 95%; m.p. 140–142°C). Anal. Found: C, 55.2; H, 8.96. $C_{38}H_{72}SiSn_2O_2$ calc.: C, 55.2; H, 8.80%. ^1H NMR: 0.00 (s, 6H, CH_3Si); 1.38–2.20 (m, 66H, C_6H_{11}). ^{13}C NMR: 3.37 (CH_3Si); 32.4, 31.2, 29.4, 27.1 (C_{1-4}, C_6H_{11}) [$^1J(^{13}C–^{117,119}Sn)$: 352.6, 370.2; $^{2,3}J(^{13}C–Sn)$: 13.2, 63.9 Hz unresolved]. ^{29}Si NMR: −19.0. ^{119}Sn NMR: −23.6 ppm. ^{119}Sn Mössbauer: IS = 1.31, QS = 2.06 mm s^{-1}.

3.4. 1,3-bis-(tributylstannoxy)-1,1,3,3-tetramethylyl-1,3-disiloxane (1)

This was prepared by the same method as in 3.3.

Colourless oil (95%). Anal. Found: C, 45.4; H, 9.20. $C_{28}H_{66}Si_2Sn_2O_3$ calc.: C, 45.2; H, 8.94%. ^1H NMR: −0.02 (s, 12H, CH_3Si); 0.90 (t, 18H, CH_3); 1.07 (m, 12H, CH_3CH_2); 1.36 (m, 12H, $CH_3CH_2CH_2$); 1.60 (m, 12H, CH_2Sn). ^{13}C NMR: 2.24 (CH_3Si); 15.9, 27.2, 27.1, 13.6 ($SnCH_2CH_2CH_2CH_3$, respectively) [$^1J(^{13}C–^{117,119}Sn)$: 357.0, 374.6 Hz]. ^{29}Si NMR: −19.9. ^{119}Sn NMR: 78.5 ppm. ^{119}Sn Mössbauer: IS = 1.23, QS = 2.02 mm s^{-1}.

3.5. 1,3-bis-(triphenylstannoxy)-1,1,3,3-tetramethyl-1,3-disiloxane (5)

Colourless oil (94%). Anal. Found: C, 56.0; H, 4.81. $C_{40}H_{42}Si_2Sn_2O_3$ calc.: C, 55.6; H, 4.90%. ^1H NMR: 0.06 (s, 12H, CH_3Si); 7.42–7.90 (m, 30H, C_6H_5). ^{13}C NMR: 2.20 (CH_3Si); 128.7, 129.0, 136.3 (C_6H_5Sn) (*ipso*-carbon not resolved). ^{29}Si NMR: −17.0. ^{119}Sn NMR: −110.7 ppm. ^{119}Sn Mössbauer: IS = 1.10, QS = 1.76 mm s^{-1}.

3.6. Synthesis of 1,3-bis-(tricyclohexylstannoxy)-1,1,3,3-tetraphenyl-1,3-disiloxane (4)

A mixture of tricyclohexyltin chloride (0.80 g, 1.98 mmol) and 1,1,3,3-tetramethyl-1,3-dihydroxy-1,3-disiloxane (0.41 g, 0.99 mmol) in diethyl ether (50 ml) was stirred and triethylamine was added dropwise at room temperature. The triethylamine hydrochloride formed was filtered off, and the solvent evaporated, to give the product as a white solid which was recrystallised from

TABLE 2. Positional parameters and isotropic temperature factors (Å^2) for non-hydrogen atoms of $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$ (esds in parentheses)

Atom	x	y	z	U_{iso}
Sn1	0.2508(1)	0.2263(1)	0.0822(1)	0.0492(9) [a]
Sn2	0.8385(1)	0.2866(1)	0.0093(1)	0.0474(9) [a]
Si1	0.5877(4)	0.2754(3)	−0.0220(3)	0.042(3) [a]
Si2	0.4999(4)	0.2335(3)	0.1172(3)	0.042(3) [a]
O1	0.3992(10)	0.2002(6)	0.1014(6)	0.052(9) [a]
O2	0.5513(11)	0.2625(7)	0.0521(7)	0.060(9) [a]
O3	0.7000(11)	0.3066(7)	−0.0184(6)	0.056(9) [a]
C1	0.1683(12)	0.1698(8)	0.1511(7)	0.060(6)
C2	0.0855(12)	0.1318(8)	0.1270(7)	0.066(7)
C3	0.0253(12)	0.0987(8)	0.1715(7)	0.092(9)
C4	0.0479(12)	0.1037(8)	0.2401(7)	0.095(9)
C5	0.1308(12)	0.1417(8)	0.2642(7)	0.123(12)
C6	0.1910(12)	0.1748(8)	0.2197(7)	0.102(10)
C7	0.2324(11)	0.3318(8)	0.0964(7)	0.053(6)
C8	0.2827(11)	0.3787(8)	0.0586(7)	0.068(7)
C9	0.2650(11)	0.4474(8)	0.0667(7)	0.083(8)
C10	0.1970(11)	0.4693(8)	0.1127(7)	0.089(9)
C11	0.1466(11)	0.4223(8)	0.1505(7)	0.087(8)
C12	0.1643(11)	0.3536(8)	0.1424(7)	0.058(6)
C13	0.2189(11)	0.1964(7)	−0.0188(7)	0.064(6)
C14	0.2427(11)	0.1320(7)	−0.0412(7)	0.071(7)
C15	0.2206(11)	0.1142(7)	−0.1077(7)	0.089(8)
C16	0.1747(11)	0.1608(7)	−0.1519(7)	0.082(8)
C17	0.1509(11)	0.2251(7)	−0.1295(7)	0.067(7)
C18	0.1730(11)	0.2429(7)	−0.0630(7)	0.061(6)
C19	0.5877(10)	0.1682(5)	0.1582(7)	0.045(5)
C20	0.6804(10)	0.1885(5)	0.1881(7)	0.055(6)
C21	0.7496(10)	0.1404(5)	0.2128(7)	0.075(7)
C22	0.7262(10)	0.0720(5)	0.2076(6)	0.075(7)
C23	0.6336(10)	0.0517(5)	0.1776(7)	0.067(7)
C24	0.5643(10)	0.0998(5)	0.1529(7)	0.063(6)
C25	0.4872(11)	0.3048(6)	0.1772(7)	0.053(6)
C26	0.4324(11)	0.2924(6)	0.2332(7)	0.056(6)
C27	0.4095(11)	0.3453(6)	0.2756(7)	0.082(8)
C28	0.4413(11)	0.4106(6)	0.2619(7)	0.103(10)
C29	0.4961(11)	0.4230(6)	0.2058(7)	0.120(11)
C30	0.5190(11)	0.3701(6)	0.1634(7)	0.106(10)
C31	0.4990(11)	0.3382(6)	−0.0632(7)	0.047(5)
C32	0.4074(11)	0.3185(6)	−0.0951(7)	0.059(6)
C33	0.3384(11)	0.3671(6)	−0.1191(7)	0.085(8)
C34	0.3609(11)	0.4354(6)	−0.1112(7)	0.085(8)
C35	0.4525(11)	0.4551(6)	−0.0792(7)	0.076(7)
C36	0.5215(11)	0.4065(6)	−0.0553(7)	0.063(6)
C37	0.5826(11)	0.1929(6)	−0.0692(7)	0.052(6)
C38	0.6391(11)	0.1863(6)	−0.1254(7)	0.064(6)
C39	0.6425(11)	0.1246(6)	−0.1585(7)	0.080(8)
C40	0.5894(11)	0.0694(6)	−0.1354(7)	0.078(7)
C41	0.5329(11)	0.0760(6)	−0.0792(7)	0.088(8)
C42	0.5295(11)	0.1377(6)	−0.0461(7)	0.069(7)
C43	0.9220(11)	0.3459(7)	−0.0561(8)	0.049(5)
C44	0.9052(11)	0.3392(7)	−0.1251(8)	0.071(7)
C45	0.9619(11)	0.3771(7)	−0.1680(8)	0.088(8)
C46	1.0354(11)	0.4217(7)	−0.1419(8)	0.093(9)
C47	1.0522(11)	0.4283(7)	−0.0730(8)	0.090(9)
C48	0.9955(11)	0.3904(7)	−0.0301(8)	0.067(7)
C49	0.8555(10)	0.1804(6)	−0.0029(7)	0.047(5)
C50	0.9286(10)	0.1557(6)	−0.0439(7)	0.053(6)
C51	0.9385(10)	0.0863(6)	−0.0532(7)	0.067(7)
C52	0.8753(10)	0.0418(6)	−0.0215(7)	0.075(7)

TABLE 2 (continued)

Atom	x	y	z	U_{150}
C53	0.8022(10)	0.0666(6)	0.0194(7)	0.081(8)
C54	0.7923(10)	0.1359(6)	0.0287(7)	0.064(6)
C55	0.8557(12)	0.3187(7)	0.1106(8)	0.061(6)
C56	0.9094(12)	0.2776(8)	0.1566(8)	0.075(7)
C57	0.9229(12)	0.2974(7)	0.2232(8)	0.090(8)
C58	0.8826(12)	0.3584(7)	0.2439(8)	0.103(10)
C59	0.8289(12)	0.3995(7)	0.1979(8)	0.117(11)
C60	0.8155(12)	0.3797(7)	0.1313(8)	0.087(8)

[a] Atom refined anisotropically, U_{eq} given.

acetonitrile (1.08 g, 95%; m.p. 163–164°C) Anal. Found: C, 62.8; H, 7.55. $C_{60}H_{86}SiSn_2O_2$ calc.: C, 62.7; H, 7.54%. ^{1}H NMR: 1.14–1.73 (m, 66H, C_6H_{11}); 7.10–7.64 (m, 20H, C_6H_5Si). ^{13}C NMR: 32.9, 30.9, 28.9, 26.9 (C_{1-4}, C_6H_{11}) [$^1J(^{13}C–Sn)$: 348, $^{2,3}J(^{13}C–Sn)$: 13.2, 63.9 Hz, unresolved]. ^{29}Si NMR: −46.7. ^{119}Sn NMR: −10.4 ppm. ^{119}Sn Mössbauer: IS = 1.10, QS = 2.29 mm s^{-1}.

3.7. *The structure of $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$ (6)*

Recrystallisation from 60–80 petrol yielded crystals suitable for diffraction studies. A crystal of approximate dimensions 0.3 mm × 0.3 mm × 0.25 mm was used for data collection. *Crystal data*: $C_{60}H_{50}O_3Si_2Sn_2$, $M = 1112.6$ monoclinic, $a = 13.249(2)$, $b = 19.838(3)$, $c = 20.050(5)$ Å, $\beta = 93.28(2)$, $U = 5265.5$, space group $P2_1/n$, $Z = 4$, $D_c = 1.40$ g cm^{-3}, μ(Mo-Kα) = 9.41 cm^{-1}, $F(000) = 2248$. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 \leq \theta \leq 22°$. 8417 reflections were collected of which 4095 were unique with $I \geq 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and also for absorption [34]. Maximum and minimum absorption factors after correction were 1.30 and 0.97 respectively. The structure was solved by Patterson methods and refined using the SHELX [35,36] suite of programs. Scattering factors were taken from the usual sources [37–39]. In the final least squares cycles the tin, silicon, and oxygen atoms were allowed to vibrate anisotropically. All other atoms were treated isotropically, and the phenyl groups were refined as rigid hexagons. Hydrogen atoms were included at calculated positions (C–H: 108 pm) with fixed isotropic temperature factors ($U = 0.05$ Å^2). Final residuals after eight cycles of least squares were $R = R_w = 0.0955$, for unit weights. Maximum final shift/esd was 0.004. Residual densities were 0.88 e Å^{-3} and −0.65 e Å^{-3} in the region of the tin atoms, and as such have no chemical significance. Bond distances and angles and final fractional atomic coordinates and isotropic thermal parameters, are given in Tables 1 and 2 respectively. Tables of anisotropic temperature factors and hydrogen atom positions have been deposited with Cambridge Crystallographic Data Centre. The asymmetric unit is shown in Fig. 1, along with the labelling scheme used.

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