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Hydrolysis of $(Me_3SiCH_2)PhSnCl_2$. Isomerisation of the dimeric tetraorganodistannoxane $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$

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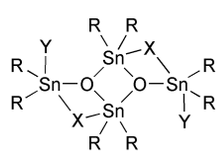
The hydrolysis of $(Me_3SiCH_2)PhSnCl_2$ (**1**) was studied under two different reaction conditions (*i*) by using an excess of aqueous NaOH in toluene at reflux temperature and (*ii*) by using small amounts of NEt_3 and water in CH_2Cl_2 at room temperature. For (*i*) the products $(Me_3SiCH_2)Ph_2SnOSnPh_2(CH_2SiMe_3)$ (**2**) and $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6](OH)_2$ (**3**) were isolated indicating that a phenyl group migration took place. For (*ii*) the dimeric tetraorganodistannoxane $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$ (**4**) was obtained. In solution, **4** exists as an equilibrium mixture of all five possible isomers **4a**–**4e**; in the solid state two of these isomers **4d** and **4e** co-crystallized in the same crystal modification. The observation of interconvertible isomers of **4** was attributed to the kinetic lability of the ladder-like $Sn_4O_2Cl_4$ structural motif. Compounds **1** and **4** were investigated by X-ray crystallography.

Introduction

Dimeric tetraorganodistannoxanes, $[R_2(X)SnOSn(Y)R_2]_2$ (R = alkyl, aryl; X, Y = F, Cl, Br, OH, OR, $OSiR_3$, O_3SCF_3) are commonly found hydrolysis products of diorganotin dihalides (Chart 1).[1] In the solid state, these compounds possess ladder-like structures containing almost planar $Sn_4O_2X_2Y_2$ structural motifs with pentacoordinate tin atoms. However, in solution these dimeric tetraorganodistannoxanes appear to be kinetically labile. Thus, molecular weight determinations suggest the presence of monomer–dimer equilibria, particularly at low concentrations.[1a,2] Furthermore, ^{119}Sn NMR spectroscopy indicates occurrence of rapid ligand exchange when different dimeric tetraorganodistannoxanes are reacted in solution.[3]



R = alkyl, aryl; X, Y = F, Cl, Br, OH, OR, $OSiR_3$, O_3SCF_3

Chart 1

In preceding studies, we and others have described the synthesis of dimeric tetraorganodistannoxanes, $[R_2(X)SnOSn(Y)R'_2]_2$ (R ≠ R′ = Me, Bu, Pr, CH_2SiMe_3, *t*-Bu; X, Y = OH, F, Cl), having different organic substituents bound to the endocyclic and exocyclic tin atoms.[4] In solution, these compounds are involved in various equilibria with other diorganotin species such as $t\text{-}Bu_2Sn(OSn(t\text{-}Bu)_2Cl)_2$. By contrast, we are aware of only one example of a dimeric tetraorganodistannoxane $[RR'(Cl)SnOSn(Cl)RR']_2$ (R = CH_2SiMe_3, R′ = *t*-Bu) that has two different substituents bound at the same tin atom. However, this compound has not yet been characterized in solution.[1d]

In the present work, we report that the hydrolysis of $(Me_3SiCH_2)PhSnCl_2$ (**1**) under two different reaction conditions provides (*i*) $(Me_3SiCH_2)Ph_2SnOSnPh_2(CH_2SiMe_3)$ (**2**) and the organotin–oxo cluster $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6](OH)_2$ (**3**), and (*ii*) the dimeric tetraorganodistannoxane $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$ (**4**).

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Discussion

The reaction of $(Me_3SiCH_2)SnPh_3$ with two equivalents of $HgCl_2$ afforded $(Me_3SiCH_2)PhSnCl_2$ (**1**) in very high yields (Eqn. 1).

$$(Me_3SiCH_2)SnPh_3 \xrightarrow[-\ 2\ PhHgCl]{2\ HgCl_2} \underset{\mathbf{1}}{(Me_3SiCH_2)PhSnCl_2} \quad (1)$$

$(Me_3SiCH_2)PhSnCl_2$ (**1**) is a low-melting solid that is soluble in most common organic solvents. The structure of **1** features a distorted tetrahedral Sn atom within a C_2Cl_2 donor set as shown in Fig. 1; crystal data and selected bond parameters are collected in Tables 1 and 2. Owing to the steric repulsion of the bulky organic substituents the distortion is most pronounced in the C–Sn–C angle of 125.66(14)° as is usually found in the case of diorganotin halides.[5] The Sn–Cl bond lengths at 2.3428(10) Å and 2.3489(11) Å are very similar and closely resemble those reported for $t\text{-}Bu_2SnCl_2$, $i\text{-}Pr_2SnCl_2$ and Ph_2SnCl_2.[5] The structure of **1** is essentially molecular with the closest intermolecular Sn ··· Cl contact being marginally greater than 4 Å. This interaction serves to link the molecules into a chain aligned along the crystallographic *b*-axis.[5]

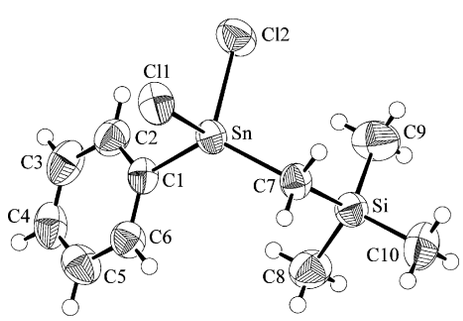

Fig. 1 Molecular structure of **1** showing the crystallographic numbering scheme and 50% probability displacement ellipsoids.

The hydrolysis of $(Me_3SiCH_2)PhSnCl_2$ (**1**) with an excess of aqueous NaOH in toluene at reflux temperature afforded a separable mixture of $(Me_3SiCH_2)Ph_2SnOSnPh_2(CH_2SiMe_3)$ (**2**) and $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6](OH)_2$ (**3**) in high yields (Eqn. 2).

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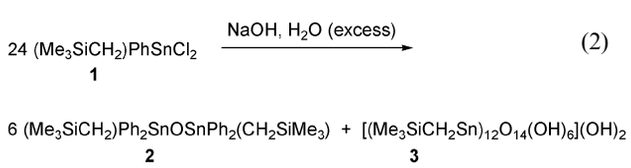
Table 1 Crystal data and refinement details for **1** and **4**

	1	**4**
Formula	$C_{10}H_{16}Cl_2SiSn$	$C_{40}H_{64}Cl_4O_2Si_4Sn_4$
Formula weight	353.91	1305.91
Crystal size/mm	0.05 × 0.10 × 0.40	0.13 × 0.18 × 0.31
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.4395(9)	12.203(2)
b/Å	6.3518(5)	27.565(12)
c/Å	19.9575(15)	12.138(6)
α/°	90	91.26(5)
β/°	94.342(1)	100.37(3)
γ/°	90	93.14(4)
V/Å^3	1445.98(19)	4008(3)
Z	4	3
ρ_{calcd}/Mg m^{-3}	1.626	1.623
T/K	293	173
μ/mm^{-1}	2.186	2.167
F(000)	696	1932
θ range/deg	2.0 to 27.6	3.1 to 27.5
No. of reflns collcd	12019	19237
No. of ind. reflns/R_{int}	3306	18375
No. of reflns obsd with $I > 2\sigma(I)$	2734	13001
No. refined params	127	730
GoF (F^2)	1.12	1.01
$R1$ (F) ($I > 2\sigma(I)$)	0.032	0.033
a	0.0313	0.0273
b	0.9314	10.4804
$wR2$ (F^2) (all data)	0.078	0.088

Table 2 Selected geometric parameters (Å, °) for **1**

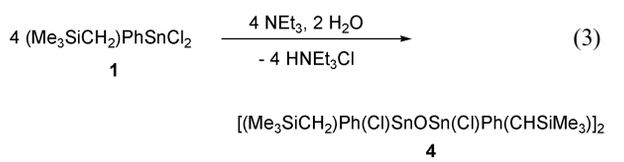
Sn–Cl1	2.3428(10)	Sn–Cl2	2.3489(11)
Sn–C1	2.120(3)	Sn–C11	2.105(3)
Cl1–Sn–C12	99.63(4)	Cl1–Sn–C1	106.73(9)
Cl1–Sn–C7	108.36(10)	Cl2–Sn–C1	104.48(10)
Cl2–Sn–C7	108.92(11)	C1–Sn–C7	125.66(14)



(2)

$(Me_3SiCH_2)Ph_2SnOSnPh_2(CH_2SiMe_3)$ (**2**) is a colourless oil that was mainly characterized by NMR spectroscopy. The ^{119}Sn NMR spectrum ($CDCl_3$) revealed a signal at δ −11.5 ($^2J(^{119}Sn–O–^{117}Sn)$ 416 Hz). The magnitude of the coupling constant closely resembles those reported for $Me_3SnOSnMe_3$ (418 Hz), $Bu_3SnOSnBu_3$ (473 Hz) and $Ph_3SnOSnPh_3$ (440 Hz), respectively and allowed the estimation of the Sn–O–Sn angle to be approximately 134°.[6] ^{1}H NMR spectroscopy confirmed the presence of phenyl and Me_3SiCH_2 groups in a ratio of 2 : 1. $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6](OH)_2$ (**3**) is a high-melting solid that is only poorly soluble in common organic solvents. It comprises a member of the well-established class of organotin–oxo clusters $[(RSn)_{12}O_{14}(OH)_6]X_2$ (R = *i*-Pr, X = Cl; R = Bu, X = Cl, OH; R = CH_2SiMe_3, X = Cl).[7] Thus, the ^{119}Sn NMR spectrum ($CDCl_3$) of **3** displayed two equally intense signals at δ −265.9 ($^2J(^{119}Sn–O–^{117/119}Sn)$ 384 Hz) and −439.7 ($^2J(^{119}Sn–O–^{117/119}Sn)$ 384 Hz), which are unambiguously assigned to the penta- and hexacoordinate tin sites in the dication $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6]^{2+}$.[7d] The ^{119}Sn NMR chemical shifts differ from those reported previously but this can be explained by the change in counterions from Cl^- to OH^-. The identity of the dicationic cluster $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6]^{2+}$ was also confirmed by ESI MS spectrometry which showed in the positive detection mode a doubly charged mass cluster centred at 1398 Da. Considering the products at hand, a clean phenyl group migration must have taken place to account for the formation of **2** and **3**. While phenyl group migrations are commonplace in organotin chemistry this redistribution of a diorganotin species into a monoorganotin and a triorganotin compound appears to be a rare example of an inverse Kocheshkov reaction.

The hydrolysis of $(Me_3SiCH_2)PhSnCl_2$ (**1**) with small amounts of triethylamine and water in CH_2Cl_2 provided $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$ (**4**) in high yields (Eqn. 3).



(3)

Compound **4** is a high-melting crystalline solid that is reasonably soluble in slightly polar solvents such as toluene or $CHCl_3$. The ^{119}Sn NMR spectrum ($CDCl_3$) of an analytically pure, crystalline sample of **4** showed two sets of six signals, in the range between δ −135 and −145 and between δ −205 and −220 which were unambiguously assigned to the exocyclic and endocyclic tin sites, respectively, of five dimeric tetraorganodistannoxane isomers **4a**–**4e**, each having four magnetically equivalent chlorine atoms (Chart 2).[8]

The connectivity and partial assignment of these twelve signals was established by a 2D ^{119}Sn–^{119}Sn INADEQUATE NMR spectrum ($CDCl_3$), as shown in Fig. 2. Thus, the signals at δ −139.2 ($^2J(^{119}Sn–^{119}Sn)$ 83/99 Hz), −207.8 ($^2J(^{119}Sn–^{119}Sn)$ 99 Hz) and −219.3 ($^2J(^{119}Sn–^{119}Sn)$ 83 Hz) (integral ratio 2 : 1 : 1; total integral 23%) and the signals at δ −136.0 ($^2J(^{119}Sn–^{119}Sn)$ 88 Hz), −143.7 ($^2J(^{119}Sn–^{119}Sn)$ 99 Hz) and −216.0 ($^2J(^{119}Sn–^{119}Sn)$ 88 / 99 Hz) (integral ratio 1 : 1 : 2; total integral 26%) were unambiguously assigned to the isomers **4c** and **4b**, respectively. By contrast, for the signals at δ −142.9 ($^2J(^{119}Sn–^{119}Sn)$ 87 Hz) and −213.3 ($^2J(^{119}Sn–^{119}Sn)$ 87 Hz) (integral ratio 1 : 1; total integral 7%), at δ −135.3 ($^2J(^{119}Sn–^{119}Sn)$ 87 Hz) and −217.1 ($^2J(^{119}Sn–^{119}Sn)$ 87 Hz) (integral ratio 1 : 1; total integral 24%) and at δ −139.1 ($^2J(^{119}Sn–^{119}Sn)$ 90 Hz) and −215.2 ($^2J(^{119}Sn–^{119}Sn)$ 90 Hz) (integral ratio 1 : 1; total integral 20%) only a non-specific assignment to the remaining isomers **4a**, **4d** and **4e** could be made, *i.e.* without conclusive information about the stereochemistry. In view of the fact that only isomers **4d** and **4e**

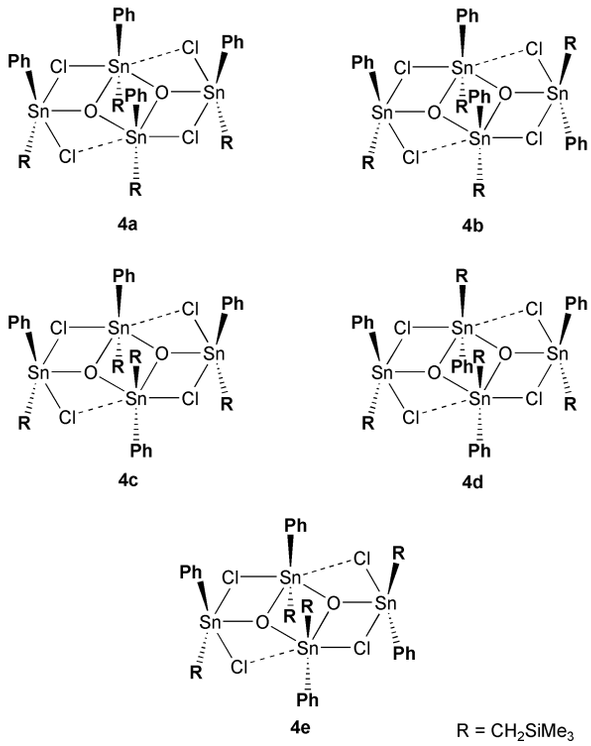


Chart 2

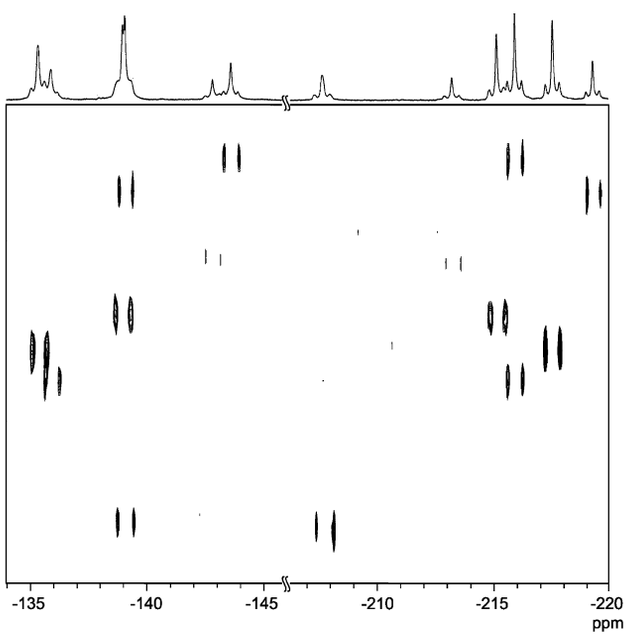


Fig. 2 2D ^{119}Sn–^{119}Sn INADEQUATE NMR spectrum (149.07 MHz, $CDCl_3$) of **4**.

are isolated in the crystal, the ^{119}Sn NMR spectrum can be best explained by postulating a dynamic equilibrium between the five principal isomers. This equilibrium is (*i*) fast on the laboratory time scale, but slow on the ^{119}Sn NMR time scale and (*ii*) has a non-statistical population of the isomers **4a**–**4e**, the integral ratio being 26 : 24 : 23 : 20 : 7. Crystals of **4** were obtained by evaporation of a hexane solution containing all five isomers, however the crystal chosen for the X-ray diffraction study contained only two of these isomers, namely **4d** and **4e**, the molecular structures of which are illustrated in Fig. 3 and 4; crystal data and selected bond parameters are collected in Tables 1 and 3. Whilst no crystallographic symmetry is found in the molecular structure of **4d**, the molecular structure of **4e** is disposed about a centre of inversion so that there are a total of three molecules in the triclinic unit cell with two of these being **4d**.

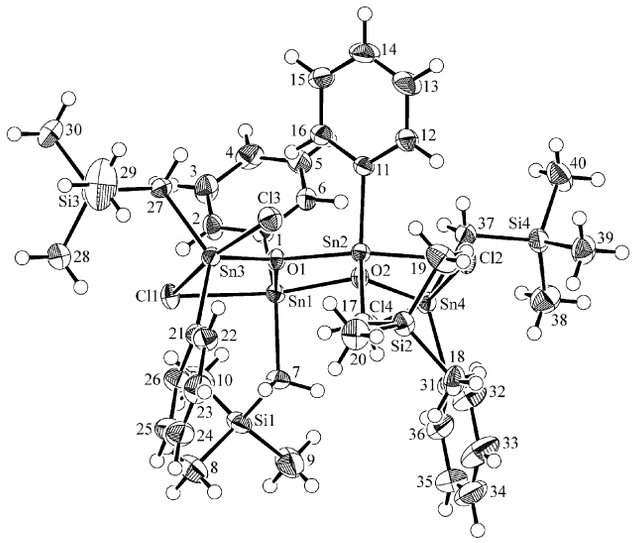


Fig. 3 Molecular structure of **4d** showing the crystallographic numbering scheme and 50% probability displacement ellipsoids. Atoms otherwise not indicated are carbons. The Cl4 atom is largely obscured by C17.

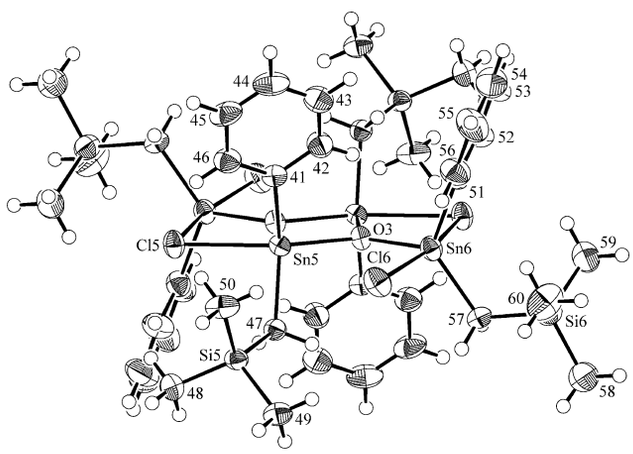


Fig. 4 Molecular structure of **4e** showing the crystallographic numbering scheme and 50% probability displacement ellipsoids. Atoms otherwise not indicated are carbons. The symmetry operation required to generate the remaining atoms is $1 - x$, $1 - y$, $1 - z$.

The common feature of both molecules comprising the asymmetric unit is the formation of a central (endocyclic) $R_4Sn_2O_2$ core to which are attached, *via* the μ_3-oxo atom, two (exocyclic) R_2SnCl_2 units. Each pair of exo- and endocyclic Sn atoms is bridged by a Cl that expectedly forms longer Sn–Cl bonds than the Cl atoms binding in a terminal fashion to the exocyclic Sn atoms. In this way, the molecular framework might be described as a ladder.[9] The Sn atoms uniformly exist in distorted trigonal bipyramidal geometries with the trigonal plane being defined by a C_2O donor set in each case. The greatest deviations within the trigonal plane are seen in the C–Sn–C angles that range from 132.27(17) to 141.61(18)°, presumably so as to minimise steric hindrance between the organic substituents. For the Sn1, Sn2 and S5 atoms, the axial positions are occupied by O and Cl donors whereas two Cl atoms define the axial sites for the remaining Sn atom geometries. The former set of axial angles deviate to a greater extent from the ideal angle of 180° (range 151.71(8) to 152.62(8)°) compared with the angles (162.45(5) to 163.73(4)°) subtended by the Cl atoms, an observation reflecting the longer Sn–Cl bond distances. The distinguishing feature of the molecules is found in the relative disposition of the Sn-bound organic substituents as discussed above. Thus, in **4d** the endocyclic Sn-bound phenyl groups lie to one side of the ladder framework and those bound to the exocyclic Sn atoms to the other side. By contrast, in **4e**, the phenyl groups of diagonally

Table 3 Selected geometric parameters (Å, °) for **4d** and **4e**[a]

Sn1–Cl1	2.6670(17)	Sn1–O1	2.055(3)
Sn1–O2	2.129(3)	Sn1–C1	2.117(4)
Sn1–C7	2.104(4)	Sn2–Cl2	2.6483(16)
Sn2–O1	2.124(3)	Sn2–O2	2.054(3)
Sn2–C11	2.118(4)	Sn2–C17	2.114(4)
Sn3–Cl1	2.7785(15)	Sn3–Cl3	2.4335(15)
Sn3–O1	2.015(3)	Sn3–C21	2.140(4)
Sn3–C27	2.110(4)	Sn4–Cl2	2.8147(16)
Sn4–Cl4	2.4274(14)	Sn4–O2	2.024(3)
Sn4–C31	2.142(5)	Sn4–C37	2.113(5)
Sn5–Cl5	2.6951(16)	Sn5–O3	2.053(3)^{i}
Sn5–O3	2.130(3)	Sn5–C41	2.130(5)
Sn5–C47	2.106(5)	Sn6–Cl5	2.6999(17)^{i}
Sn6–Cl6	2.4514(19)	Sn6–O3	2.013(3)
Sn6–C51	2.123(5)	Sn6–C57	2.134(5)
Cl1–Sn1–O2	151.71(8)	O1–Sn1–C1	111.38(15)
O1–Sn1–C7	109.45(15)	C1–Sn1–C7	138.65(18)
Cl2–Sn2–O1	152.62(8)	O2–Sn2–C11	112.02(15)
O2–Sn2–C17	108.24(15)	C11–Sn2–C17	139.61(17)
Cl1–Sn3–Cl3	163.73(4)	O1–Sn3–C21	112.57(15)
O1–Sn3–C27	112.51(15)	C21–Sn3–C27	132.27(17)
Cl2–Sn4–Cl4	163.14(4)	O2–Sn4–C31	110.90(15)
O2–Sn4–C37	110.03(16)	C31–Sn4–C37	136.62(18)
Cl5–Sn5–O3	152.02(9)	O3^{i}–Sn5–C41	108.30(16)
O3^{i}–Sn5–C47	108.93(16)	C41–Sn5–C47	141.61(18)
Cl5^{i}–Sn6–Cl6	162.45(5)	O3–Sn6–C51	111.43(18)
O3–Sn6–C57	121.61(17)	C51–Sn6–C57	125.2(2)

[a] Symmetry operation *i*: $1 - x$, $1 - y$, $1 - z$.

opposite endo- and exocyclic Sn atoms lie to one side of the ladder and the remaining phenyl groups to the other. The ^{119}Sn MAS NMR spectrum of **4** is essentially in accord with the crystal structure although only four of required six signals were detected at δ −129.4 (32%), −143.7 (17%) (exocyclic tin sites) −212.7 (33%) and −230.4 (18%) ppm (endocyclic tin sites). Apparently, the differences in the exocyclic and endocyclic tin sites of the non-centrosymmetric isomer **4d** are too small to be resolved by ^{119}Sn MAS NMR spectroscopy. Integration of the spinning side-band manifolds confirms the presence of two molecules of **4d** and one of **4e** in the unit cell. When crystals of **4** were re-dissolved in $CDCl_3$, the ^{119}Sn NMR spectrum was identical to that described above.

Experimental

$(Me_3SiCH_2)SnPh_3$ was prepared according to a literature procedure.[10] The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in $CDCl_3$ using a Jeol Eclipse Plus 400 spectrometer and were referenced to $SiMe_4$ (^{1}H, ^{13}C) and $SnMe_4$ (^{119}Sn). The 2D ^{119}Sn–^{119}Sn INADEQUATE NMR spectrum was collected using a standard pulse sequence and a coupling value of 90 Hz. The ^{119}Sn MAS NMR spectra were measured using cross polarization and high-power proton decoupling (conditions: 8 μs (90°) pulse, 5 ms contact time, 10 s recycle delay). Two experiments with spinning frequencies of 8 and 11 kHz were measured to unambiguously determine the isotropic chemical shifts. *c*-Hex_4Sn was used as secondary reference (δ(^{119}Sn) −97.35). The ESI MS spectrum was obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer *via* a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporisation nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approx. 200 mL min^{-1} and 20 mL min^{-1}, respectively. Pressure in the mass analyser region was usually about 4×10^{-5} mbar. Typically ten signal averaged spectra were collected. The IR spectra were recorded using a BioRad FTIR spectrophotometer. Microanalysis was performed by CMAS, Belmont, Australia.

Synthesis of $(Me_3SiCH_2)PhSnCl_2$ (1)

A solution of $HgCl_2$ (16.3 g, 60.0 mmol) in acetone (100 mL) was added dropwise to $Me_3SiCH_2SnPh_3$ (13.2 g, 30.0 mmol) in acetone (100 mL) at 0 °C. Stirring was continued for 1 h after complete addition. The acetone was removed in vacuum and hexane (50 mL) was added. After filtering to remove PhHgCl the filtrate was cooled at −20 °C overnight to give colourless crystals of **1** (9.7 g, 27.4 mmol, 91%), mp. 42–43 °C. ^{1}H NMR δ: 0.22 (9H, s, $SiMe_3$), 1.05 (2H, s, ^2J(^{1}H–^{119}Sn) 100 Hz; $SnCH_2$), 7.45–7.80 (5H, m; Ph); ^{13}C{^{1}H} NMR δ: 1.00 (^1J(^{13}C–^{29}Si) 52 Hz, ^3J(^{13}C–$^{117/119}$Sn) 28; $SiMe_3$), 10.28 (^1J(^{13}C–^{119}Sn) 355 Hz, ^1J(^{13}C–^{29}Si) 42 Hz; $SnCH_2$), 129.44 (^3J(^{13}C–^{119}Sn) 82 Hz; Ph_m), 131.37 (^4J(^{13}C–^{119}Sn) 17 Hz; Ph_p), 134.29 (^2J(^{13}C–^{119}Sn) 65 Hz; Ph_o), 139.98 (^1J(^{13}C–^{119}Sn) 725 Hz; Ph_i); ^{119}Sn {^{1}H} NMR δ: 61.2; Found: C, 33.8; H, 4.6. $C_{10}H_{16}Cl_2SiSn$ (353.9) requires C, 33.9; H, 4.6%.

Hydrolysis of $Ph(Me_3SiCH_2)SnCl_2$ (1). Method A

A solution of NaOH (1.60 g, 40.0 mmol) in water (40 mL) was added dropwise to a solution of **1** (3.54 g, 10.0 mmol) in refluxing toluene (80 mL) and the mixture stirred overnight. After cooling to room temperature the insoluble material was collected by vacuum filtration, washed with water (40 mL) and toluene (40 mL), and dried in vacuum to give $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6](OH)_2$ (**3**) as a colourless solid (1.13 g, 0.399 mmol, 96%; mp. > 350 °C). The organic layer of the filtrate was separated, washed with water (50 mL), dried over Na_2SO_4, filtered and the solvent removed in vacuum. Kugelrohr distillation gave $(Me_3SiCH_2)Ph_2SnOSnPh_2(CH_2SiMe_3)$ (**2**) as a colourless oil (1.58 g, 2.15 mmol, 86%; bp. 210 °C/10^{-2} Torr).

2: ^{1}H NMR δ: 0.15 (s, 9H; $SiMe_3$), 0.46 (s, 2H, ^2J(^{1}H–^{119}Sn) 86 Hz; $SnCH_2$), 7.40–7.80 (m, 5H; Ph); ^{13}C{^{1}H} NMR δ: 1.05 (^1J(^{13}C–^{119}Sn) 332 Hz, ^1J(^{13}C–^{29}Si) 46; $SnCH_2$), 1.52 [^1J(^{13}C–^{29}Si) 51 Hz, ^3J(^{13}C–$^{117/119}$Sn) 20 Hz; $SiMe_3$], 128.24 (^3J(^{13}C–^{119}Sn) 57, Ph_m), 128.99 (^4J(^{13}C–^{119}Sn) 12 Hz; Ph_p), 136.03 (^2J(^{13}C–^{119}Sn) 45 Hz; Ph_o), 143.06 (^1J(^{13}C–^{119}Sn) 579 Hz; Ph_i); ^{119}Sn {^{1}H} NMR δ: −11.5 (^2J(^{119}Sn–O–^{117}Sn) 416 Hz); Found: C, 52.1; H, 5.9. $C_{32}H_{42}OSi_2Sn_2$ (736.3) requires C, 52.2; H, 5.8%.

3: ^{1}H NMR δ: 0.05 (s, 9H; $SiMe_3$), 0.06 (s, 2H, ^2J(^{1}H–$^{117/119}$Sn) 156 Hz; $SnCH_2$), 0.17 (s, 9H; $SiMe_3$), 0.37 (s, 2H, ^2J(^{1}H–$^{117/119}$Sn) 135 Hz; $SnCH_2$). ^{13}C{^{1}H} NMR δ: 1.43 (^1J(^{13}C–^{29}Si) 52 Hz, ^3J(^{13}C–$^{117/119}$Sn) 34 Hz; $SiMe_3$); 1.73 (^1J(^{13}C–^{29}Si) 52 Hz, ^3J(^{13}C–$^{117/119}$Sn) 40 Hz; $SiMe_3$), 6.56 (^1J(^{13}C–^{119}Sn) 670 Hz; $SnCH_2$), 13.13 (^1J(^{13}C–^{119}Sn) 909 Hz; $SnCH_2$); ^{119}Sn {^{1}H} NMR δ: −265.9 (^2J(^{119}Sn–O–$^{117/119}$Sn) 384 Hz, ^2J(^{119}Sn–O–^{117}Sn) 215 Hz), −439.7 [^2J(^{119}Sn–O–$^{117/119}$Sn) 384 Hz, ^2J(^{119}Sn–O–^{117}Sn) 266 Hz); IR (KBr) ν(OH): 3415vbr, 3640sh cm^{-1}; Found: C, 19.9; H, 5.0; Cl, <0.1. $C_{48}H_{140}O_{22}Si_{12}Sn_{12}$ (2831.17) requires C, 20.4; H, 5.0%; ESI MS (pos. mode, 30 V) 1398 $[(Me_3SiCH_2Sn)O_{14}(OH)_6]^{2+}$.

Hydrolysis of $Ph(Me_3SiCH_2)SnCl_2$ (1). Method B

A solution of NEt_3 (1.01 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was slowly dropped into a solution of **1** (3.54 g, 10.0 mmol) in CH_2Cl_2 (40 mL) and water (180 mg, 10.0 mmol). An immediate precipitation of NEt_3HCl took place. The mixture was stirred for 2 h at room temperature before the precipitate was filtered. The solvent was removed in vacuum and the solid residue recrystallized from hexane to give $[(Me_3SiCH_2)Ph(Cl)SnOSn(Cl)Ph(CH_2SiMe_3)]_2$ (**4**) as colourless crystals (3.10 g, 2.37 mmol, 95%), mp. 147–151 °C.

4: ^{119}Sn NMR and ^{119}Sn MAS NMR details are discussed in the text; Found: C, 36.5; H, 5.1. $C_{40}H_{64}Cl_4O_2Si_4Sn_4$ (1305.93) requires C, 36.8; H, 4.9%.

Crystallography

Intensity data for **1** (**4**) were measured on a Bruker CCD area detector (Rigaku AFC7R diffractometer) at 293 K (173 K) employing MoKα radiation. The structures were refined with anisotropic displacement parameters, H atoms included in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ included. In **4**, the maximum residual electron density peak of 4.23 e $Å^{-3}$ was located 0.80 Å from the Sn6 atom, and as such probably reflects the inadequacy of the empirical absorption correction applied.[11] Crystal data are summarised in Table 1.

CCDC reference numbers 197520 (**1**) and 197521 (**4**).

See http://www.rsc.org/suppdata/dt/b2/b211070a/ for crystallographic data in CIF or other electronic format.

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