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Synthesis and crystal structures of the cyclosiloxytin(IV) complexes $[Cl_2Sn\{O(SiPh_2O)_2\}_2]$-$\mu$-$(Li(THF)_2)_2]$ and $[THF_2Sn\{(OSiPh_2)_3O\}_2]\cdot$toluene

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Abstract

The reaction between the lithium compound $[\{Ph_2SiOLi\}_2O]$ and $SnCl_4$ gave the lithium-bridged chlorostannasiloxane $[Cl_2Sn\{O(SiPh_2O)_2\}_2]$-$\mu$-$(Li(THF)_2)_2]$ (**1**) containing six-membered stannasiloxane rings. A similar reaction between the corresponding sodium compound $[\{Ph_2SiONa\}_2O]$ and $SnCl_4$ surprisingly gave the stannasiloxane $[THF_2Sn\{(OSiPh_2)_3O\}_2]$ (**2**), which crystallised as the mono-toluene solvate) containing eight-membered stannasiloxane rings. Compounds **1** and **2** were obtained in reactions in which the relative molar ratio of the lithium or sodium reagents to $SnCl_4$ was varied from 1 : 1 to 3 : 1. Compounds **1** and **2** were characterised by ^1H and ^{29}Si NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction studies.

Keywords: Silicon; Tin; Metallasiloxanes; Crystal structure; Stannasiloxane; Lithium

1. Introduction

There is considerable current interest in the chemistry of metallasiloxanes derived from silanolates with R_3SiO [1], R_2SiO_2 [2] or $RSiO_3$ [3] functionalities. A substantial portion of the work in this area is necessarily concerned with detailed structural analysis. Interest is also stimulated by the homogeneous catalytic activity (and its mechanistic implications for heterogeneous SiO_2-supported systems) [2e,3f,h–k], as well as by features of the chemistry related to ring-opening polymerisation processes [2h] and by uses as precursors for metal oxides and silicates [1d,f].

We have for some time been studying the reactions of the disiloxanediolates $[(Ph_2SiOM)_2O]$, M = H, Li, or Na, with metal compounds, and our interest has been sustained by frequent observations of unexpected products and latterly of homogeneous catalytic activity for some transition metal derivatives [4,5]. Our investigations of the reaction between the dilithium compound $[\{Ph_2SiOLi\}_2O]$ and metal tetrahalides of Ti, Zr and Hf resulted in either tris-chelated products containing six-membered metallasiloxane rings incorporating bridging alkali metal cations in the case of zirconium and hafnium [5,6] and a product having an eight-membered metallasiloxane ring for titanium [5]. We now report on reactions between $SnCl_4$ and the dilithium or disodium salts of $[\{Ph_2SiO\}_2O]^{2-}$, which surprisingly led to products with greatly different structures.

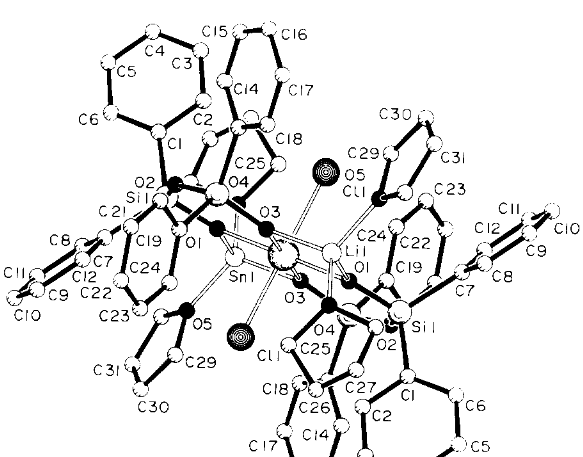

Fig. 1. Molecular structure of compound 1.

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2. Results and discussion

2.1. Synthesis

Treatment of ice-cold toluene solutions of stannic chloride with 1, 2 or 3 equiv. of the dilithium or disodium salts of $[\{Ph_2SiO\}_2O]^{2-}$ in tetrahydrofuran/toluene mixtures gave the compounds $[(THF)_2Li]_2$-μ-$[Cl_2Sn\{O(SiPh_2O)_2\}_2]$ (**1**) and $[THF_2Sn\{(OSiPh_2)_3O\}_2]$ (**2**), the latter isolated as the toluene solvate. Crystals suitable for the X-ray studies were obtained from toluene solutions. The molecular structures are shown in Figs. 1 and 2.

The reactions of the dilithium reagent gave compound **1**, incorporating two of the disiloxanediolate ligands in two six-membered stannasiloxane rings with a relative *trans* orientation in an octahedral complex; the fifth and sixth sites are occupied by chloride ligands. Compound **1** was the only tin product isolated from reactions with 1, 2 or 3 equiv. of the dilithium reagent. The reactions of the disodium reagent gave the 6-coordinated tetrahydrofuran-solvated di-chelated compound (**2**), with eight-membered stannasiloxane rings. Compound **2** was the only tin product isolated from reactions with 1, 2 or 3 equiv. of the disodium reagent. It is noteworthy that a product in which the siloxane chain was similarly expanded was previously isolated from reactions between $TiCl_4$ and the dilithium compound $[\{Ph_2SiOLi\}_2O]$, whereas reactions with zirconium and hafnium tetrachloride proceeded without such chain expansion [5,6]. In the present case, the chain expansion is observed in the product of the reaction between $SnCl_4$ and $[\{Ph_2SiONa\}_2O]$ but not $[\{Ph_2SiOLi\}_2O]$. We also reported previously reactions between the disodium compound and $CrCl_2$ [7] or the dilithium compound and $CoCl_2$ [8], $CuCl_2$ [9] which proceed without chain expansion. It is also important to note that there is no evidence to suggest that more than one structural type is formed in either reaction. At present we are unable to account for the observed chain-expanded reaction products, but it appears that the chain-expansion process may be influenced by the nature of the metals in both reagents. We are currently investigating reactions of the disodium reagent with a wider range of metal halides in order to gain further insight into the possible role of the alkali metal in the promotion of chain expansion. It is noteworthy that reactions between $SnBr_4$ and $[\{(Me_3C)_2SiOLi\}_2O]$ give the spirocyclic product $[Sn[O(Me_3C)_2SiO(Me_3C)_2SiO]_2]$, in which there are two six-membered stannasiloxane rings [10], although structural data are not available. The coordinating THF groups in (**2**) can be replaced by pyridine.

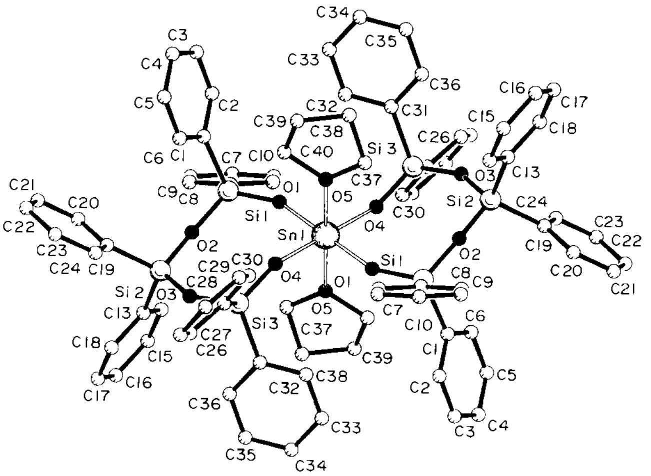

Fig. 2. Molecular structure of compound **2**.

2.2. Molecular structures of compounds 1 and 2

The tin atom in compound **1** has a distorted octahedral geometry whereas the angles about tin in compound **2** are those for a perfect octahedron. The six-membered stannasiloxane rings in **1** are coplanar with each other and also with the four-membered lithiostannoxane rings. The siloxane skeletons of the eight-membered stannasiloxane rings in **2** lie on opposite sides of the equatorial plane of the octahedral core incorporating the tin atom and the chelating oxygens. The rings are related through a centre of symmetry at tin. Compound **2** differs from the previously isolated titanium complex, *cis*-$[Py_2Ti\{(OSiPh_2)_3O\}_2]$ [5] in that the eight-membered stannatrisiloxane rings in the present case are in a *trans* disposition. The average Sn–O(Si) distances in **1** [2.047(4) Å] and **2** [1.972(2) Å] are close to the sum of the covalent radii [2.06 Å] but, as expected, are slightly longer than those reported for $[(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)]$ [1.945(2) Å] [11]. The additional coordination of lithium at the chelating oxygen sites in **1** leads to Sn–O bond distances slightly longer than those in **2**. The average Si–O(Si) and Si–O(Sn) distances in **1** are within the ranges observed in compounds with similar solvated lithium-bridged six-membered metallasiloxane fragments [8,9]. However, the Si–O–Si angle of 141.8(3)° is considerably larger by some 10° than the widest Si–O–Si angle observed in related lithium-bridged spirocyclic metallasiloxanes with six-membered metallasiloxane rings, and is also much bigger than the Si–O–Si angles in $[Ph_2SiO]_3$ [12] or $[PhB(OSiPh_2)_2O]$ [2h]. The angles about the silicons atoms are close to the tetrahedral values, and the Si–O–Sn angles are within the range found for related lithium-bridged metallasiloxanes [8,9]. The Sn–Cl distances in **1** are normal [13].

It is of interesting that the marked distortions from regular octahedral geometry at titanium observed in *cis*-$[Py_2Ti\{(OSiPh_2)_3O\}_2]$ [5] are not present in the case of **2** in which stannatrisiloxane rings are in a relative

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**

Li(1)–O(5)#1 [a]	1.929(13)
Li(1)–O(3)	1.980(13)
Li(1)–O(1)#2	1.998(12)
Li(1)–O(4)	1.967(13)
Li(1)–Sn(1)	3.013(11)
Sn(1)–O(1)	2.041(4)
Sn(1)–O(3)	2.053(4)
Sn(1)–Cl(1)	2.408(2)
Sn(1)–Li(1)#2	3.013(11)
Si(1)–O(1)	1.616(4)
Si(1)–O(2)	1.624(4)
Si(1)–C(1)	1.882(4)
Si(1)–C(7)	1.885(4)
Si(2)–O(3)	1.622(4)
Si(2)–O(2)	1.625(4)
Si(2)–C(19)	1.876(4)
Si(2)–C(13)	1.883(4)
O(5)#1–Li(1)–O(3)	117.2(7)
O(5)#1–Li(1)–O(1)#2	114.3(6)
O(3)–Li(1)–O(1)#2	84.9(5)
O(5)#1–Li(1)–O(4)	104.8(6)
O(3)–Li(1)–O(4)	119.6(6)
O(1)#2–Li(1)–O(4)	115.7(6)
O(5)#1–Li(1)–Sn(1)	124.8(5)
O(3)–Li(1)–Sn(1)	42.6(2)
O(1)#2–Li(1)–Sn(1)	42.3(2)
O(4)–Li(1)–Sn(1)	130.2(6)
O(1)–Sn(1)–O(1)#2	180.0
O(1)–Sn(1)–O(3)	98.1(2)
O(1)#2–Sn(1)–O(3)	81.9(2)
O(3)–Sn(1)–O(3)#2	180.0
O(1)–Sn(1)–Cl(1)#2	90.13(12)
O(1)#2–Sn(1)–Cl(1)#2	89.87(12)
O(3)–Sn(1)–Cl(1)#2	89.11(13)
O(3)#2–Sn(1)–Cl(1)#2	90.89(13)
O(1)–Sn(1)–Cl(1)	89.87(12)
O(1)#2–Sn(1)–Cl(1)	90.13(12)
O(3)–Sn(1)–Cl(1)	90.89(13)
O(3)#2–Sn(1)–Cl(1)	89.11(13)
Cl(1)#2–Sn(1)–Cl(1)	180.0
O(1)–Sn(1)–Li(1)#2	41.2(3)
O(1)#2–Sn(1)–Li(1)#2	138.8(3)
O(3)–Sn(1)–Li(1)#2	139.2(3)
O(3)#2–Sn(1)–Li(1)#2	40.8(3)
Cl(1)#2–Sn(1)–Li(1)#2	89.4(2)
Cl(1)–Sn(1)–Li(1)#2	90.6(2)
O(1)–Sn(1)–Li(1)	138.8(3)
O(1)#2–Sn(1)–Li(1)	41.2(3)
O(3)–Sn(1)–Li(1)	40.8(3)
O(3)#2–Sn(1)–Li(1)	139.2(3)
Cl(1)#2–Sn(1)–Li(1)	90.6(2)
Cl(1)–Sn(1)–Li(1)	89.4(2)
Li(1)#2–Sn(1)–Li(1)	180.0
O(1)–Si(1)–O(2)	109.1(2)
O(1)–Si(1)–C(1)	110.4(2)
O(2)–Si(1)–C(1)	107.3(2)
O(1)–Si(1)–C(7)	112.1(2)
O(2)–Si(1)–C(7)	107.4(2)
C(1)–Si(1)–C(7)	110.4(2)
O(3)–Si(2)–O(2)	109.7(2)
O(3)–Si(2)–C(19)	112.2(2)
O(2)–Si(2)–C(19)	106.7(2)
O(3)–Si(2)–C(13)	112.0(2)
O(2)–Si(2)–C(13)	108.0(2)
C(19)–Si(2)–C(13)	108.1(2)
Si(1)–O(1)–Li(1)#2	132.4(4)
Si(1)–O(1)–Sn(1)	131.1(2)
Li(1)#2–O(1)–Sn(1)	96.5(4)
Si(1)–O(2)–Si(2)	141.8(3)
Si(2)–O(3)–Li(1)	133.0(4)
Si(2)–O(3)–Sn(1)	130.0(2)
Li(1)–O(3)–Sn(1)	96.6(4)
C(28)–O(4)–C(25)	108.7(9)
C(28)–O(4)–Li(1)	122.8(9)
C(25)–O(4)–Li(1)	119.8(7)

[a] Symmetry transformations used to generate equivalent atoms: #1: $x, y, z-1$; #2: $-x+1, -y+1, -z$.

trans disposition. This difference in geometrical configuration is accompanied by markly different ring parameters between **2** and *cis*-$[Py_2Ti\{(OSiPh_2)_3O\}_2]$, which illustrates the flexibility of the siloxane skeleton within these eight-membered rings. While the titanatrisiloxane rings in the latter are relatively planar, the tin atom lies well outside the siloxane skeleton planes of the stannatrisiloxane rings in **2**. The (Si)OSnO(Si) bite angles in **2** are some 5° smaller than the (Si)OTiO(Si) angles in *cis*-$[Py_2Ti\{(OSiPh_2)_3O\}_2]$. The SiOSi angles in *cis*-$[Py_2Ti\{(OSiPh_2)_3O\}_2]$ [146.4(3)° and 156.0(3)°] are smaller than those in **2** [149.09(12)° and 164.14(14)°] and the latter are closer to those in $[Ph_2SiO]_4$ [152.3(2)°, 167.4(2)°] [14]. The average M–O–Si angles and Si–O(M) distances are, however, similar in both compounds, viz. 154.3°, 1.595 Å (Sn) and 154.8°, 1.607 Å (Ti). The two distinct silicon environments in these eight-membered metallasiloxane ring compounds show up in the ^{29}Si NMR spectra, with those in the titanium compound apparently slightly more shielded [δ −41.8 (Si(OSi); −43.7 (Si(OTi) ppm] than those in the tin compound [δ −34.7 (Si(OSi); −40.6 (Si(OSn) ppm].

3. Experimental details

All manipulations were carried out in an under purified nitrogen. The ^{1}H and ^{29}Si NMR spectra were recorded on Bruker (80 MHz) and (600 MHz) spectrometers, respectively, for samples in $[^2H_8]$toluene (chemical shifts, δ, in ppm, relative to $SiMe_4$ in $[^2H_8]$toluene).

Procedures for the 2:1 reactions between $[(Ph_2SiOM)_2O]$ M = Li, Na, and $SnCl_4$ are described below.

3.1. Preparation of compound 1

Tin(IV) chloride (2.41 cm^3 of a 1.0 mol dm^{-3} solution in toluene; 2.41 mmol) was added dropwise to a stirred solution of dilithium tetraphenyldisiloxanediolate (4.82 mmol) in THF (20 cm^3) at 0°C. The mixture was stirred overnight, then the solvent was removed in vacuo and toluene (30 cm^3) added to the white residue. The mixture was filtered leaving an off-white precipitate (identified as LiCl; red flame and positive Lassaigne test) and giving a clear colourless filtrate. This was concentrated to (20 cm^3) and then kept at room temperature to deposit colourless crystals (2.26 g, 71.2%, m.p. 173–175°C) of **1**. (Anal. Found: C, 58.48; H, 5.51%. $C_{64}H_{72}Cl_2O_{10}Si_2Li_2Sn$ Calc.: C, 58.36; H, 5.51%.) IR (Nujol) (cm^{-1}): 1617 (w); 1590 (w); 1429 (m); 1305 (w); 1261 (m); 1190 (m); 1115 (s); 1093 (m); 1045 (s); 1027 (s); 1001 (m); 998 (s); 925 (vs); 800 (m); 745 (m); 716 (s); 701 (m); 535 (m); 514 (s); 491 (m); 462 (w); 434 (m); 394 (w); 345 (w); 300 (w); 274 (w); 221 (m). ^{1}H NMR δ: 1.12 (m, 8H, THF); 3.13 (m, 8H, THF); 7.18 (m, 12H, Ph); 7.70 (m, 8H, Ph) ppm. ^{29}Si NMR (C_7D_8) δ: −34.58 (s) ppm.

Table 2
Selected bond lengths (Å) and angles (°) for compound **2**

Sn(1)-O(1)#1 [a]	1.972(2)
Sn(1)-O(4)	1.972(2)
Sn(1)-O(1)	1.972(2)
Sn(1)-O(4)#1	1.972(2)
Sn(1)-O(5)#1	2.170(2)
Sn(1)-O(5)	2.170(2)
Si(1)-O(1)	1.597(2)
Si(1)-O(2)	1.625(2)
Si(1)-C(1)	1.884(2)
Si(1)-C(7)	1.8840(14)
Si(2)-O(2)	1.606(2)
Si(2)-O(3)	1.613(2)
Si(2)-C(19)	1.873(2)
Si(2)-C(13)	1.875(2)
Si(3)-O(4)	1.593(2)
Si(3)-O(3)	1.635(2)
Si(3)-C(25)	1.878(2)
Si(3)-C(31)	1.8864(14)
O(1)#1-Sn(1)-O(4)	89.58(7)
O(1)#1-Sn(1)-O(1)	180.0
O(4)-Sn(1)-O(1)	90.42(7)
O(1)#1-Sn(1)-O(4)#1	90.42(7)
O(4)-Sn(1)-O(4)#1	180.0
O(1)-Sn(1)-O(4)#1	89.58(7)
O(1)#1-Sn(1)-O(5)#1	90.18(7)
O(4)-Sn(1)-O(5)#1	87.81(7)
O(1)-Sn(1)-O(5)#1	89.82(7)
O(4)#1-Sn(1)-O(5)#1	92.19(7)
O(1)#1-Sn(1)-O(5)	89.82(7)
O(4)-Sn(1)-O(5)	92.19(7)
O(1)-Sn(1)-O(5)	90.18(7)
O(4)#1-Sn(1)-O(5)	87.81(7)
O(5)#1-Sn(1)-O(5)	180.0
O(1)-Si(1)-O(2)	113.06(10)
O(1)-Si(1)-C(1)	112.02(9)
O(2)-Si(1)-C(1)	106.88(9)
O(1)-Si(1)-C(7)	108.80(9)
O(2)-Si(1)-C(7)	106.57(9)
C(1)-Si(1)-C(7)	109.32(8)
O(2)-Si(2)-O(3)	110.61(10)
O(2)-Si(2)-C(19)	111.05(10)
O(3)-Si(2)-C(19)	108.22(10)
O(2)-Si(2)-C(13)	106.51(10)
O(3)-Si(2)-C(13)	110.50(11)
C(19)-Si(2)-C(13)	109.97(10)
O(4)-Si(3)-O(3)	112.73(10)
O(4)-Si(3)-C(25)	109.41(9)
O(3)-Si(3)-C(25)	106.44(10)
O(4)-Si(3)-C(31)	112.80(9)
O(3)-Si(3)-C(31)	105.80(10)
C(25)-Si(3)-C(31)	109.40(9)
Si(1)-O(1)-Sn(1)	154.35(11)
Si(2)-O(2)-Si(1)	164.14(14)
Si(2)-O(3)-Si(3)	149.09(12)
Si(3)-O(4)-Sn(1)	153.27(12)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z$.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**

Atom	x	y	z	U_{eq} [a]
Li(1)	3702(6)	4121(6)	349(12)	56(3)
Sn(1)	5000	5000	0	34(1)
Cl(1)	4842(1)	4513(1)	−2161(2)	55(1)
Si(1)	4577(1)	6565(1)	−1317(2)	40(1)
Si(2)	3253(1)	5662(1)	−986(2)	42(1)
O(1)	5168(2)	5952(2)	−713(4)	41(1)
O(2)	3720(2)	6310(2)	−1375(4)	45(1)
O(3)	3843(2)	5061(2)	−293(4)	40(1)
O(4)	3285(4)	4009(4)	1883(7)	91(2)
O(5)	3149(3)	3465(3)	9073(6)	89(2)
C(1)	4607(3)	6766(2)	−3052(4)	54(2)
C(2)	4575(4)	6203(2)	−3886(5)	71(2)
C(3)	4557(4)	6308(3)	−5200(5)	95(3)
C(4)	4571(4)	6976(4)	−5681(4)	96(3)
C(5)	4602(4)	7539(3)	−4847(6)	95(3)
C(6)	4621(3)	7434(2)	−3533(5)	70(2)
C(7)	4764(3)	7370(2)	−274(5)	51(2)
C(8)	5399(3)	7774(3)	−247(6)	85(3)
C(9)	5543(3)	8363(3)	536(7)	115(4)
C(10)	5052(4)	8548(3)	1292(6)	113(4)
C(11)	4418(4)	8144(3)	1265(5)	92(3)
C(12)	4274(3)	7555(3)	482(5)	73(2)
C(13)	2558(3)	5347(3)	−2533(4)	56(2)
C(14)	2589(3)	5598(3)	−3755(5)	72(2)
C(15)	2067(4)	5370(4)	−4889(4)	95(3)
C(16)	1514(3)	4891(4)	−4801(6)	105(4)
C(17)	1483(3)	4640(3)	−3579(7)	106(4)
C(18)	2005(3)	4868(3)	−2444(5)	97(3)
C(19)	2696(2)	6011(3)	141(5)	52(2)
C(20)	1930(3)	6171(3)	−339(5)	84(3)
C(21)	1531(2)	6455(4)	495(8)	112(4)
C(22)	1898(4)	6578(4)	1808(7)	123(5)
C(23)	2665(4)	6417(4)	2288(5)	96(3)
C(24)	3063(2)	6134(3)	1454(5)	73(2)
C(25)	3442(10)	4529(8)	2920(16)	148(6)
C(26)	3350(12)	4078(14)	4140(16)	187(9)
C(27)	3035(21)	3513(14)	3686(22)	288(17)
C(28)	3212(11)	3345(8)	2459(16)	176(7)
C(29)	3343(6)	3407(6)	7810(10)	98(3)
C(30)	2786(10)	2894(10)	7046(15)	171(7)
C(31)	2329(10)	2666(10)	7858(16)	178(8)
C(32)	2519(7)	3021(6)	9103(13)	122(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3.2. Preparation of compound 2

Tin(IV) chloride (2.41 cm^3 of a 1.0 mol dm^{-3} solution in toluene; 2.41 mmol) was added to a solution of disodium tetraphenyldisiloxanediolate (4.82 mmol) in 1:1 toluene/THF (40 cm^3). The mixture was stirred overnight, then the solvent was removed in vacuo and toluene (30 cm^3) added to the white residue. The mixture was filtered to leave a white residue (identified as NaCl; positive Lassaigne test) and give a clear, colourless filtrate. This was concentrated to approximately 15 cm^3. Colourless crystals of **2** (2.27 g, 63.4%, m.p. 134–135°C) were deposited at room temperature. A sample dried under vacuum for several hours was submitted for elemental analysis. (Anal. Found: C, 63.84; H, 5.11%, $C_{87}H_{84}O_{10}Si_6Sn \cdot$ toluene Calc.: C, 66.27; H, 5.37%, $C_{80}H_{76}O_{10}Si_6Sn$ Calc. C, 64.72; H, 5.16%.) IR (Nujol) (cm^{-1}) 1590 (m); 1428 (s); 1304 (m); 1261 (m); 1119 (vs); 1098 (s); 1062 (s); 1032 (s); 1013 (vs); 998 (s); 917 (m); 862 (m); 801 (m); 740 (m); 716 (s); 699 (s); 680 (m); 626 (w); 533 (m); 522 (s); 509 (m); 487 (m); 476 (m); 460 (m); 437 (w); 403 (m); 393 (m); 382 (m); 309 (m); 296 (w); 256 (m); 217 (m). ^{1}H NMR (C_6D_6) δ: 1.22 (m, 4H, THF); 3.65 (m, 4H, THF); 7.23 (m, 18H, Ph); 7.71 (m, 12H, Ph) ppm. ^{29}Si NMR (C_{7_8}) δ: -34.74 (s); -40.58 (s) ppm.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for compound **2**

Atom	x	y	z	U_{eq} [a]
Sn(1)	0	0	0	26(1)
Si(1)	985(1)	2437(1)	1660(1)	30(1)
Si(2)	987(1)	1230(1)	3150(1)	35(1)
Si(3)	−419(1)	−900(1)	1880(1)	32(1)
O(1)	607(2)	1511(1)	743(1)	37(1)
O(2)	1184(2)	1908(2)	2438(1)	42(1)
O(3)	225(2)	27(2)	2736(1)	45(1)
O(4)	−599(2)	−400(1)	1103(1)	37(1)
O(5)	1896(2)	−586(2)	−86(1)	40(1)
C(1)	−278(2)	3482(1)	2161(1)	38(1)
C(2)	−202(2)	4431(2)	1897(1)	53(1)
C(3)	−1170(2)	5174(1)	2214(2)	73(1)
C(4)	−2215(2)	4967(2)	2795(2)	77(1)
C(5)	−2292(2)	4018(2)	3059(2)	69(1)
C(6)	−1323(2)	3275(2)	2743(1)	51(1)
C(7)	2572(1)	3194(1)	1419(1)	38(1)
C(8)	3191(2)	3923(2)	2139(1)	60(1)
C(9)	4359(2)	4494(2)	1975(2)	77(1)
C(10)	4908(2)	4336(2)	1092(2)	76(1)
C(11)	4288(2)	3607(2)	372(1)	67(1)
C(12)	3120(2)	3036(2)	535(1)	49(1)
C(13)	2642(2)	1049(2)	3384(1)	43(1)
C(14)	3741(2)	1374(2)	2905(1)	57(1)
C(15)	4956(2)	1247(2)	3103(2)	78(1)
C(16)	5073(2)	796(3)	3779(2)	87(1)
C(17)	3974(2)	471(3)	4258(2)	90(1)
C(18)	2759(2)	598(2)	4060(2)	65(1)
C(19)	39(2)	2022(2)	4226(1)	43(1)
C(20)	471(2)	3118(2)	4673(2)	73(1)
C(21)	−189(3)	3723(2)	5485(2)	88(1)
C(22)	−1281(3)	3231(2)	5850(1)	96(2)
C(23)	−1713(3)	2135(2)	5403(2)	114(2)
C(24)	−1053(2)	1530(2)	4591(2)	78(1)
C(25)	−2039(2)	−1384(2)	2343(1)	41(1)
C(26)	−2127(2)	−1767(2)	3081(1)	60(1)
C(27)	−3312(3)	−2176(2)	3404(1)	78(1)
C(28)	−4409(5)	−2201(2)	2989(2)	86(1)
C(29)	−4321(2)	−1817(2)	2251(2)	88(1)
C(30)	−3136(2)	−1409(2)	1928(1)	62(1)
C(31)	665(2)	−2099(1)	1474(1)	38(1)
C(32)	572(2)	−2896(2)	626(1)	49(1)
C(33)	1342(2)	−3798(1)	337(1)	61(1)
C(34)	2206(2)	−3904(2)	896(2)	61(1)
C(35)	2299(2)	−3108(2)	1743(2)	62(1)
C(36)	1529(2)	−2205(2)	2033(1)	53(1)
C(37)	2789(3)	−226(3)	595(2)	43(1)
C(38)	3735(3)	−1126(3)	294(2)	53(1)
C(39)	3789(3)	−1502(3)	−723(3)	61(1)
C(40)	2448(3)	−1431(3)	−890(2)	57(1)
C(41)	3862(7)	4974(7)	4646(4)	119(2)
C(42)	4252(7)	4092(6)	4795(5)	119(2)
C(43)	5348(7)	4072(5)	5148(4)	111(2)
C(44)	3609(18)	2900(8)	4610(14)	290(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

When **2** was recrystallised from a mixture of toluene and pyridine the corresponding pyridine adduct $[Sn\{O(SiPh_2O)_3\}_2 \cdot 2Py]$ was obtained m.p. 121–123°C. (Anal. Found: C, 62.75; H, 4.70; N, 1.98%. $C_{82}H_{70}O_8N_2Si_6Sn$ Calc.: C, 65.72; H, 4.71; N, 1.87%.) ^{1}H NMR (C_6D_6, 298 K) δ: 6.90 (m, 2H, py); 7.80 (m, 1H, py); 8.05 (m, 2H, py); 7.23 (m, 18H, Ph); 7.72 (m, 12H, Ph) ppm.

3.3. X-Ray crystallography

Data were collected, from crystals sealed in glass capillaries under nitrogen on a CAD4 diffractometer operating in the ω–2θ scan mode. The structures were solved by standard heavy-atom techniques and refined by least squares using SHELX-93 [15], with phenyl groups being treated as rigid hexagons {(C–C, 1.395 Å; C–C–C, 120°) and with the inclusion of hydrogen atoms at fixed positions (C–H, 0.96 Å)}. The methyl group of the toluene solvent molecule in **2** showed disorder and refinement was based on 50:50 occupancy of two sites with the ring-methyl C–C distances fixed at 1.53 Å.

Crystal data for compound **1**: $C_{64}H_{72}Cl_2Li_2O_{10}Si_4Sn$, $M = 1317.05$, monoclinic, $a = 18.223(2)$, $b = 19.337(2)$, $c = 10.526(2)$ Å, $\beta = 105.13(1)°$, $U = 3580.5(9)$ Å^3, $Z = 2$, space group $P2_1/n$, $D_c = 1.222$ g cm^{-3}; λ(Mo Kα) = 0.71069 Å, $\mu = 0.548$ mm^{-1}, $F(000) = 1364$. A total of 7885 reflections was measured of which 6287 were independent. The final R indices were $R_1 = 0.0663$, $wR_2 = 0.2206$ for $[I > 2\sigma(I)]$ and $R_1 = 0.0892$, $wR_2 = 0.2257$ (all data) for 333 parameters.

Crystal data for compound **2** mono-toluene solvate: $C_{87}H_{84}O_{10}Si_6Sn$, $M = 1576.77$, triclinic, space group $P\bar{1}$, $a = 10.4850(10)$, $b = 12.6860(10)$, $c = 15.748(2)$ Å,

$\alpha = 109.360(10)$, $\beta = 82.260(10)$, $\gamma = 96.390(10)^\circ$, $U = 1953.3(3)$ Å^3, $Z = 1$, $D_c = 1.340$ mg m^{-3}; λ(Mo Kα) = 0.71069 Å, $\mu = 0.479$ mm^{-1}, $F(000) = 820$. A total of 9709 reflections was measured of which 8950 were independent. The final R indices were $R_1 = 0.0351$, $wR_2 = 0.0948$ for $[I > 2\sigma(I)]$ and $R_1 = 0.0452$, $wR_2 = 0.0969$ (all data) for 439 parameters. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \sqrt{}\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \sqrt{}\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]$.

Selected bond lengths and angles are given in Tables 1 and 2, and fractional atomic coordinates and thermal parameters in Tables 3 and 4. Tables of thermal parameters and hydrogen atom coordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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