

# Synthesis and structure of an ether-bridged double ladder compound: potential in host–guest chemistry

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## Abstract

The synthesis of the first example of an organotin double ladder (**6**) containing a functional group within the spacer is reported. In the solid state, compound **6** shows an interlaminar cavity whose size and shape suggest the possibility of host–guest chemistry. <sup>119</sup>Sn-NMR and ESMS show that compound **6** undergoes extensive dissociation in solution. ESMS of compound **6** to which have been added Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> or Cu<sup>2+</sup> show only minimal interaction.

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**Keywords:** Organotin double ladder; Host–guest chemistry; Ether group; Tetraorganodistannoxane; X-ray

## 1. Introduction

Recently, there has been considerable interest in the synthesis of self-assembled organotin–oxo clusters [1]. In preceding work, we and others have utilized spacer-bridged organotin precursors as building blocks for the preparation of a variety of organotin–oxo clusters having double [2] and triple ladder [3] structures that feature layered dimeric tetraorganodistannoxanes with Sn<sub>4</sub>O<sub>2</sub>X<sub>2</sub>Y<sub>2</sub> (X, Y = F, Cl, Br, OH, O<sub>2</sub>CR) structural units (Chart 1). The spacing between these layers is adjustable by the choice of the organic spacers, Z, e.g. –(CH<sub>2</sub>)<sub>n</sub>– (n = 1–12), *p*- or *m*-CH<sub>2</sub>SiMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SiMe<sub>2</sub>CH<sub>2</sub>–, *p*- or *m*-(CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub> and consequently, well-defined cavities can be created [2]. It was hypothesized that if ether or amine groups were incorporated into the organic spacers it might be possible to bind metal cations in these cavities in a similar manner to crown ethers and cryptands [4].

We report now the synthesis and structure of the first ether-functionalised double ladder compound and in-

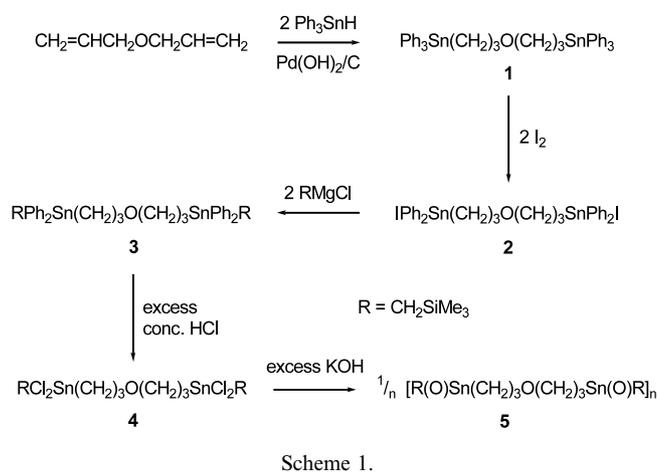
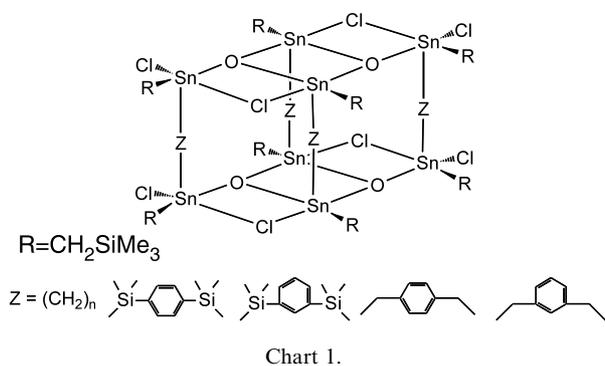
vestigations on its potential for host–guest applications with a number of metal cations using electrospray mass spectrometry (ESMS).

## 2. Discussion

The transition metal-catalyzed double hydrostannylation of allyl ether, (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>O, with Ph<sub>3</sub>SnH provided 1,7-bis(triphenylstannyl)dipropyl ether, [Ph<sub>3</sub>Sn(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>O (**1**). Subsequent reaction of **1** with two equivalents of iodine gave the corresponding 1,7-bis(iododiphenylstannyl)dipropyl ether, [IPh<sub>2</sub>Sn(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>O (**2**). Compound **2** was reacted with two equivalents of trimethylsilylmethylmagnesium chloride, Me<sub>3</sub>SiCH<sub>2</sub>MgCl, to produce 1,7-bis(trimethylsilylmethyldiphenylstannyl)dipropyl ether, [(Me<sub>3</sub>SiCH<sub>2</sub>)Ph<sub>2</sub>Sn(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>O (**3**), which was then converted with conc. hydrochloric acid into 1,7-bis(trimethylsilylmethyldichlorostannyl)dipropyl ether, [(Me<sub>3</sub>SiCH<sub>2</sub>)Cl<sub>2</sub>Sn(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>O (**4**). A portion of **4** was hydrolyzed to the presumed polymeric 1,7-bis(trimethylsilylmethyloxostannyl)dipropyl ether, {[ (Me<sub>3</sub>SiCH<sub>2</sub>) (O)Sn(CH<sub>2</sub>)<sub>3</sub> ]<sub>2</sub>O}<sub>n</sub> (**5**) (Scheme 1).

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Compounds **1–5** were obtained in high yields as colorless oils (**1**, **3**, **4**) or solids (**2**, **5**) and were characterized by multinuclear NMR spectroscopy and elemental analysis (experimental section).

The reaction of  $[(\text{Me}_3\text{SiCH}_2)\text{Cl}_2\text{Sn}(\text{CH}_2)_3]_2\text{O}$  (**4**) with  $\{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}(\text{CH}_2)_3]_2\text{O}\}_n$  (**5**), resulted in the formation of the ether-bridged double ladder compound  $\{[(\text{Me}_3\text{SiCH}_2)(\text{Cl})\text{Sn}(\text{CH}_2)_3]_2\text{O}\}_4$  (**6**), which was obtained as a colorless high-melting solid in good yield (Eq. (1)).

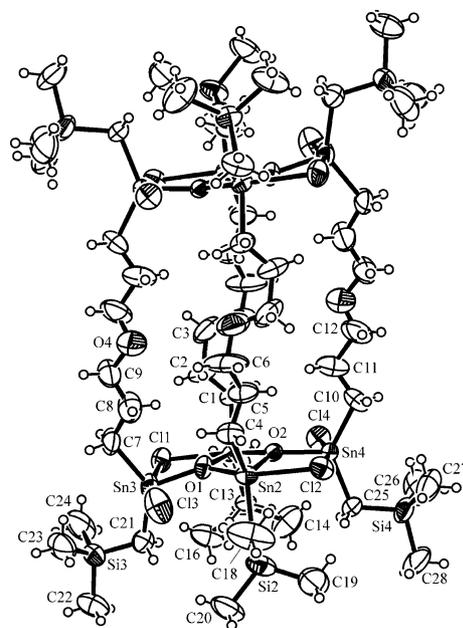
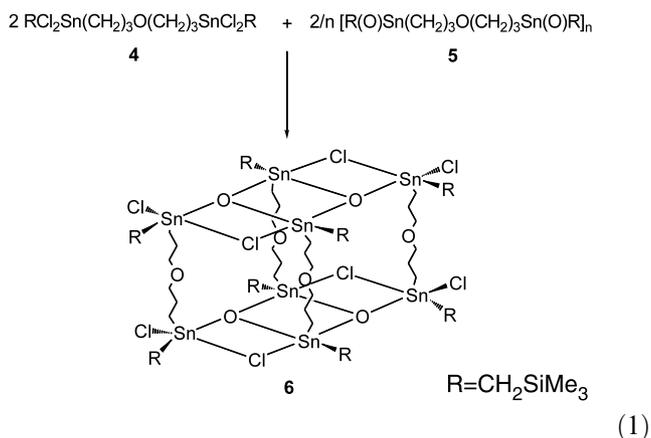


Fig. 1. Molecular structure and crystallographic numbering scheme employed for compound **6**. The Sn2–C4 bond is superimposed upon the Sn1 atom, which in turn obscures the C15 atom, and the C18 atom obscures the C17 atom.

The molecular structure of **6** is shown in Fig. 1 and selected geometric parameters are given in Table 1. The octanuclear molecule features two  $[(\text{R}\text{SnCl})_2\text{O}]_2$  dioxanoxane units defining the faces of a rectangular box. The faces are connected so that centrosymmetrically related Sn atoms (i.e. Sn1 and Sn2<sup>i</sup> & Sn3 and Sn4<sup>i</sup> for symmetry operation  $i = -x, -y, -z$ ) are linked by

Table 1  
Selected bond lengths (Å) and bond angles (°) for **6**

Bond lengths			
Sn1–Cl1	2.699(2)	Sn1–O1	2.048(5)
Sn1–O2	2.142(4)	Sn1–C1	2.109(8)
Sn1–Cl3	2.098(7)	Sn2–Cl2	2.724(2)
Sn2–O1	2.126(5)	Sn2–O2	2.048(5)
Sn2–C4	2.116(7)	Sn2–C17	2.104(8)
Sn3–Cl1	2.761(3)	Sn3–Cl3	2.456(3)
Sn3–O1	2.019(5)	Sn3–C7	2.113(9)
Sn3–C21	2.113(9)	Sn4–Cl2	2.745(2)
Sn4–Cl4	2.455(2)	Sn4–O2	2.007(4)
Sn4–C10	2.123(8)	Sn4–C25	2.124(7)
Bond angles			
Cl1–Sn1–O2	151.35(13)	Cl2–Sn2–O1	151.10(15)
Cl1–Sn3–Cl3	163.13(9)	Cl2–Sn4–Cl4	164.66(7)
Sn1–Cl1–Sn3	81.91(6)	Sn2–Cl2–Sn4	81.26(5)
Sn1–O1–Sn2	105.4(2)	Sn1–O1–Sn3	123.3(2)
Sn2–O1–Sn3	128.5(3)	Sn1–O2–Sn2	104.8(2)
Sn1–O2–Sn4	128.0(2)	Sn2–O2–Sn4	122.8(2)

the 'ether' spacers. The Sn atoms exist in distorted trigonal bipyramidal geometries defined by a  $C_2ClO_2$  donor set for the endocyclic Sn1 and Sn2 atoms and by a  $C_2Cl_2O$  donor set for the exocyclic Sn3 and Sn4 atoms. The axial positions are occupied by Cl and O atoms for the endocyclic Sn atoms and Cl atoms for the exocyclic Sn centers. The terminal Sn–Cl bond distances formed by the exocyclic Sn atoms are significantly shorter than those involving the Cl1 and Cl2 atoms owing to the latter occupying bridging positions in the molecule. There is evidence for some minor buckling within the distannoxane unit so that the dihedral angles between the planes through Sn1/Sn3/Cl1/O1, Sn1/Sn2/O1/O2, and Sn2/Sn4/Cl2/O2 are  $2.86(17)$ ,  $7.23(12)$  and  $4.47(17)^\circ$ , respectively. Owing to the symmetry in the molecule, the dihedral angle between the two distannoxane faces is  $0^\circ$ . The average separation calculated between the two Sn4 planes is  $10.3 \text{ \AA}$  with values ranging from  $10.14$  to  $10.38 \text{ \AA}$ . From Fig. 1 it is evident that the ether-O atoms are directed towards the middle of the polygon, thereby demonstrating potential as a host for the coordination of metal ions. The O...O separations within the cavity of the molecule are  $2 \times 4.04$  and  $2 \times 4.80 \text{ \AA}$  and therefore indicates that the separations between the diagonally opposite O atoms are non-symmetric at  $4.67$  and  $7.54 \text{ \AA}$ . Assuming an atomic radius of  $0.76 \text{ \AA}$  or a van der Waals radius of  $1.40 \text{ \AA}$  for the ether-O atom, and that the O4 rectangle is robust, the 'hole-size' of the cavity along the shortest diagonal would be approximately  $3.1 \text{ \AA}$  or  $1.9 \text{ \AA}$ , respectively. Along the other diagonal, the 'hole-size' is significantly larger at approximately  $6.0 \text{ \AA}$  or  $4.7 \text{ \AA}$ , respectively. Mitigating factors against host-guest chemistry could be the (i) non-symmetric shape of the cavity, (ii) the large size of the cavity that would not allow for optimal bonding interactions, and (iii) the presence, in very close proximity, above and below the O<sub>4</sub> plane, of methylene groups that can be conceived as providing steric hindrance.

The ether-bridged double ladder compound  $\{[(Me_3SiCH_2)(Cl)Sn(CH_2)_3]_2O\}_4$  (**6**), is readily soluble in most common organic solvents. The  $^{119}Sn$ -NMR spectrum ( $CDCl_3$ ) of an analytically pure, crystalline sample of **6** is complex and shows 19 signals at  $\delta -80.0$  (integral 1.4%),  $-84.0$  (integral 4.5%),  $-93.4$  (integral 14.0%),  $-96.0$  (integral 5.0%),  $-100.1$  (integral 1.0%),  $-103.6$  (integral 8.0%),  $-123.9$  (integral 8.1%),  $-127.6$  (integral 5.8%),  $-132.0$  (integral 2.0%),  $-133.0$  (integral 2.0%),  $-133.8$  (integral 5.0%),  $-136.0$  (integral 17.0%),  $-137.8$  (integral 1.4%),  $-148.7$  (integral 2.8%),  $-150.2$  (integral 11.0%),  $-153.5$  (integral 0.5%),  $-154.5$  (integral 0.5%),  $-155.5$  (integral 0.5%) and  $-175.5$  (integral 0.5%) (Fig. 2). Attempts were made to establish the connectivity of these signals using variable temperature 2D INADEQUATE  $^{119}Sn$ -NMR

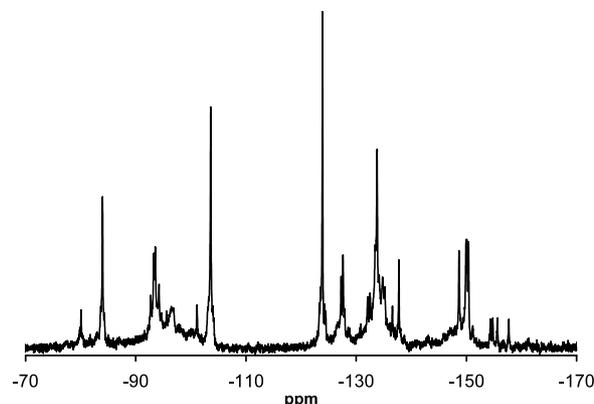
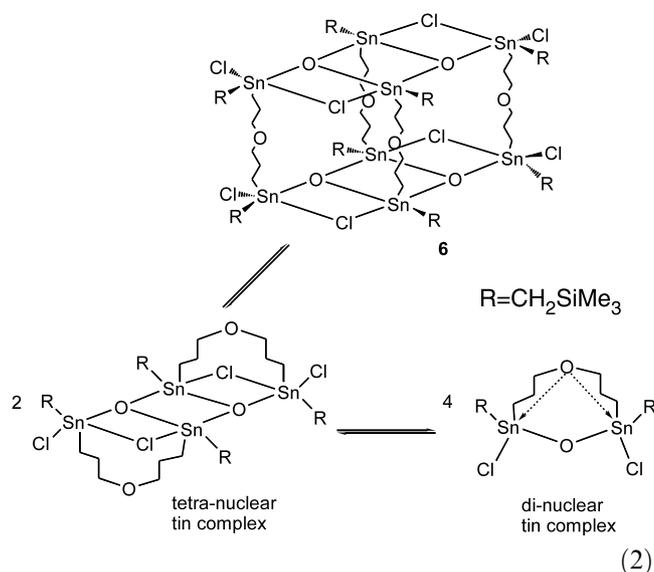


Fig. 2.  $^{119}Sn$ -NMR spectrum (100.7 MHz) of **6** in  $CDCl_3$ .

spectroscopy. Thus, the signals at  $\delta -84.0$  and  $-133.8$  appear to be related and are tentatively assigned to exocyclic and endocyclic tin sites of  $\{[(Me_3SiCH_2)(Cl)Sn(CH_2)_3]_2O\}_4$  (**6**). Additionally, there also appears to be a correlation between the signals at  $\delta -103.6$  and  $-123.9$ , however no assignment of these or the remaining signals was made.

The ESMS spectrum (cone voltage 20 V) of **6** in MeCN reveals positively charged species at  $m/z = 1125.0$  (34%) and  $m/z = 1143.0$  (50%), which were confirmed by their isotropic patterns as belonging to  $[1/2M - 3Cl + 2OH]^+$  and  $[1/2M - 2Cl + OH]^+$ , respectively. In the negative mode, the same sample shows dominate peaks at  $m/z = 634.9$  (20%) and  $m/z = 688.9$  (100%) indicative for  $[1/4M + Cl]^-$  and  $[1/4M - O + 3Cl]^-$ , respectively. The observation of mass clusters at about half or a quarter of the mass expected for the double ladder compound  $\{[(Me_3SiCH_2)(Cl)Sn(CH_2)_3]_2O\}_4$  (**6**) and the number of signals in the  $^{119}Sn$ -NMR spectrum suggests that compound **6** is involved in extensive equilibria with tetra- and di-nuclear organotin complexes in solution (Eq. (2)). Although, the analogous n-methylene-spacer bridged double ladder compounds  $\{[R_2Sn(Cl)]_2(CH_2)_n\}_4$  ( $n = 5-8, 10, 12$ ) are also known to be in equilibrium with their respective dimers in solution [2], the dissociation of **6** into di-nuclear complexes was somewhat unexpected and is tentatively attributed to intramolecular stabilization by the ether group, which would maintain a pentacoordinate tin environment as depicted in Eq. (2). This hypothesis is supported by the recently reported solution and solid-state structures of diorganotin dichlorides  $R_2SnCl_2$  and  $PhR_2SnCl_2$  having intramolecularly coordinating (3-(2-methoxyethoxy)propyl substituents ( $R = CH_2CH_2CH_2OCH_2CH_2OCH_3$ ) [5].



The feasibility of  $\{[(\text{Me}_3\text{SiCH}_2)(\text{Cl})\text{Sn}(\text{CH}_2)_3]_2\text{O}\}_4$  (**6**) forming host–guest complexes with the metal cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  was investigated using ESMS spectrometry.

Solutions of **6** in MeCN ( $c = 0.1$  mM) and solutions of the metal chlorides in  $\text{H}_2\text{O}$  ( $c = 0.1$  mM) were mixed and ESMS spectra measured in the positive mode at various cone voltages. (i)  $\text{Na}^+$ : Low intensity peaks were observed at  $m/z = 2418.8$  (rel. intensity 1%),  $m/z = 2476.8$  (2%) and  $m/z = 2534.7$  (rel. intensity 2%), which were assigned to the complexes  $[\text{M} + \text{Na}]^+$ ,  $[\text{M} + \text{Na} + \text{NaCl}]^+$  and  $[\text{M} + \text{Na} + 2\text{NaCl}]^+$ , respectively. (ii)  $\text{Li}^+$ : At 200 V, the ESMS spectrum showed peaks at  $m/z = 605.0$  (rel. intensity 16%),  $m/z = 646.0$  (rel. intensity 15%) and  $m/z = 1204.9$  (rel. intensity 10%), which were assigned to the complexes  $[1/4\text{M} + \text{Li}]^+$ , for  $[1/4\text{M} + \text{Li} + \text{MeCN}]^+$  and  $[1/2\text{M} + \text{Li}]^+$ , respectively. No evidence for complex formation between **6** and the divalent metal cations  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  was observed.

It appears that compound **6** has only a limited potential to form host–guest complexes with metal cations. This limitation could arise from the geometric constraints associated with the interlamellar cavity. It is more likely, however, that the entropy gained from dissociation of the double ladder into dimers and monomers outweighs the thermodynamic contribution gained by host–guest adduct formation as discussed above and/or the kinetic lability of the cluster in solution.

### 3. Experimental

All solvents were dried and purified by standard procedures. NMR spectra were recorded in  $\text{CDCl}_3$  solution using a Varian 300 Unity Plus ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and a JEOL-GX 270 spectrometer ( $^{119}\text{Sn}$ ) and were refer-

enced to  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{SnMe}_4$  ( $^{119}\text{Sn}$ ). Uncorrected melting points were determined on a Reichert hot stage. Microanalysis was performed by CMAS, Belmont, Australia. The ESMS 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  $\mu\text{l}$  loop. A Harvard 22 syringe pump delivered the solutions to the vaporisation nozzle of the electrospray ion source at a flow rate of 10  $\mu\text{l min}^{-1}$ . Nitrogen was used as both a drying gas and for nebulisation with flow rates of approximately 200 and 20  $\text{ml min}^{-1}$ , respectively. Pressure in the mass analyser region was usually about  $4 \times 10^{-5}$  mbar. Typically ten signal-averaged spectra were collected. The isotope pattern of the experimentally obtained mass clusters was consistent with expected mass clusters based on the natural abundance of the elements involved.

#### 3.1. Synthesis of $[\text{Ph}_3\text{Sn}(\text{CH}_2)_3]_2\text{O}$ (**1**)

A solution of  $\text{Ph}_3\text{SnH}$  (58.2 g, 166 mmol) in toluene (80 ml) was added slowly over a 3 h period to a solution of allyl ether (6.51 g, 66.3 mmol) in toluene (40 ml) and  $\text{Pd}(\text{OH})_2/\text{C}$  (20 mg) at  $80^\circ\text{C}$ . The reaction mixture was stirred at  $80^\circ\text{C}$  for 3 d and the solvent removed in vacuo to afford a slightly yellow residue. To the residue, chloroform (80 ml),  $\text{H}_2\text{O}_2$  (40 ml) and a solution of KF (5.00 g) in water (40 ml) were added and stirred at room temperature (r.t.) for 6 h, after which the solvent was removed in vacuo. The residue was extracted with diethyl ether ( $3 \times 80$  ml), dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was removed in vacuo to yield a greenish residue. The volatile by-products were removed using a Kugelrohr apparatus ( $230^\circ\text{C}$ , 0.01 mmHg). Further purification of the crude product was achieved by column chromatography (silica gel 60, 70–230 mesh) using hexane as the eluent. The solvent was removed in vacuo to give **1** as a colorless oil (46.5 g, 70%).

$^1\text{H}$ -NMR:  $\delta$  0.85 (t, 4H), 1.23 (m, 4H), 3.25 (t, 4H), 7.25–7.64 (m, 30H; Ph).  $^{13}\text{C}\{^1\text{H}\}$ -NMR:  $\delta$  7.77 ( $^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 382/401$  Hz), 26.97 ( $^2J(^{13}\text{C}-^{117/119}\text{Sn}) = 21$  Hz), 74.02 ( $\text{CH}_2$ ,  $^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 64$  Hz), 128.92, 129.27, 137.50 ( $^2J(^{13}\text{C}_o-^{117/119}\text{Sn}) = 35$  Hz), 139.58 ( $^1J(^{13}\text{C}_i-^{117/119}\text{Sn}) = 467/490$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR:  $\delta$  -98.4 ( $^1J(^{119}\text{Sn}-^{13}\text{C}) = 487$  Hz). Anal. Calc. for  $\text{C}_{42}\text{H}_{42}\text{OSn}_2$  (800.27): C, 63.2; H, 5.3; Found: C, 63.6; H, 5.1%.

#### 3.2. Synthesis of $[\text{IPh}_2\text{Sn}(\text{CH}_2)_3]_2\text{O}$ (**2**)

A solution of iodine (9.96 g, 39.2 mmol) in dichloromethane (1.0 l) was added to a solution of **1** (15.7 g, 19.6 mmol) in dichloromethane (100 ml) at  $0^\circ\text{C}$  over 10 h. Removal of the solvent and by-product in vacuo and

crystallization from chloroform–hexane afforded **2** as a white crystalline solid (16.8 g, 95%). m.p. 98–100 °C.

$^1\text{H-NMR}$ :  $\delta$  1.58 (t, 4H), 1.82 (m, 4H), 3.26 (t, 4H), 7.26–7.63 (m, 20H; Ph).  $^{13}\text{C}\{^1\text{H}\}$ -NMR:  $\delta$  14.41 ( $^1J(^{13}\text{C}_{-117/119}\text{Sn}) = 420/439$  Hz), 25.80 ( $^2J(^{13}\text{C}_m-^{117/119}\text{Sn}) = 27$  Hz), 72.10 ( $^3J(^{13}\text{C}_p-^{117/119}\text{Sn}) = 63$  Hz), 128.54, 129.56 ( $^2J(^{13}\text{C}_m-^{117/119}\text{Sn}) = 13$  Hz), 135.73 ( $^2J(^{13}\text{C}_o-^{117/119}\text{Sn}) = 47$  Hz), 137.14 ( $^1J(^{13}\text{C}_i-^{117/119}\text{Sn}) = 531/554$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR:  $\delta$  -85.8. Anal. Calc. for  $\text{C}_{30}\text{H}_{32}\text{I}_2\text{OSn}_2$  (899.86): C, 40.0; H, 3.6; Found: C, 40.1; H, 3.5%.

### 3.3. Synthesis of $[(\text{Me}_3\text{SiCH}_2)\text{Ph}_2\text{Sn}(\text{CH}_2)_3]_2\text{O}$ (**3**)

A solution of **2** (10.4 g, 11.6 mmol) in THF (100 ml) was added to a solution of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  [prepared from magnesium (2.47 g, 102 mmol) and  $\text{Me}_3\text{SiCH}_2\text{Cl}$  (3.12 g, 25.4 mmol) in THF (150 ml)] and the mixture stirred at reflux for 2 d. The reaction was quenched by the addition of saturated ammonium chloride at 25 °C. The organic layer was separated, and the aqueous layer was extracted with diethyl ether ( $3 \times 100$  ml). The combined organic extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel 60, 70–230 mesh) using hexane. Removal of the solvent in vacuo yielded **3** as a colorless oil (7.57 g, 80%).

$^1\text{H-NMR}$ :  $\delta$  0.18 (s, 18H,  $\text{SiMe}_3$ ), 0.89 (s, 4H,  $\text{SiCH}_2$ ), 1.29 (s, 4H), 1.85 (s, 4H,  $\text{SnCH}_2$ ), 3.30 (s, 4H), 7.27 (m, 20H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR:  $\delta$  -9.97 (s,  $^1J(^{13}\text{C}_{-117/119}\text{Sn}) = 245/257$  Hz;  $\text{SiCH}_2$ ), -2.92 (s,  $^3J(^{13}\text{C}_{-117/119}\text{Sn}) = 16$  Hz,  $^1J(^{13}\text{C}_{-29}\text{Si}) = 51$  Hz;  $\text{Me}_3\text{Si}$ ), 3.22 ( $^1J(^{13}\text{C}_{-117/119}\text{Sn}) = 363/380$  Hz), 22.11 ( $^2J(^{13}\text{C}_{-117/119}\text{Sn}) = 19$  Hz), 69.32 ( $^3J(^{13}\text{C}_{-117/119}\text{Sn}) = 72$  Hz), 123.71, 123.97, 132.15 ( $^2J(^{13}\text{C}_o-^{117/119}\text{Sn}) = 39$  Hz), 136.22 ( $^1J(^{13}\text{C}_i-^{117/119}\text{Sn}) = 440/461$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR:  $\delta$  -56.5 ( $^1J(^{119}\text{Sn}-^{13}\text{C}) = 463$  Hz). Anal. Calc. for  $\text{C}_{38}\text{H}_{54}\text{OSi}_2\text{Sn}_2$  (820.49): C, 55.6; H, 6.6; Found: C, 55.4; H, 6.7%.

### 3.4. Synthesis of $[(\text{Me}_3\text{SiCH}_2)\text{Cl}_2\text{Sn}(\text{CH}_2)_3]_2\text{O}$ (**4**)

To a solution of **3** (6.00 g, 7.31 mmol) in chloroform (100 ml) was added excess concentrated HCl (200 ml, 32%). The reaction mixture was stirred and maintained at 70 °C for 1 d. The organic layer was separated and the aqueous layer extracted with chloroform ( $3 \times 100$  ml). The combined organic extracts were dried ( $\text{CaCl}_2$ ) and the solvent removed in vacuo to afford **4** as a brown oil (3.35 g, 70%) of sufficient purity for further use.

$^1\text{H-NMR}$ :  $\delta$  0.15 (s, 18H,  $\text{Me}_3\text{Si}$ ), 0.83 (s, 4H,  $\text{SiCH}_2$ ), 1.69 (t, 4H), 2.08–2.10 (m, 4H), 3.57 (t, 4H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR:  $\delta$  1.02 (s,  $^3J(^{13}\text{C}_{-117/119}\text{Sn}) = 28$  Hz,  $^1J(^{13}\text{C}_{-29}\text{Si}) = 52$  Hz;  $\text{Me}_3\text{Si}$ ), 12.39 (s,  $^1J(^{13}\text{C}_{-117/119}\text{Sn}) = 327/342$  Hz;  $\text{SiCH}_2$ ), 23.36 ( $^1J(^{13}\text{C}_{-117/119}\text{Sn}) = 503/526$  Hz), 24.03

( $^2J(^{13}\text{C}_{-117/119}\text{Sn}) = 36$  Hz), 71.06 ( $^3J(^{13}\text{C}_{-117/119}\text{Sn}) = 73$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR:  $\delta$  79.1. Anal. Calc. for  $\text{C}_{14}\text{H}_{34}\text{Cl}_2\text{OSi}_2\text{Sn}_2$  (653.83): C, 25.7; H, 5.2; Found: C, 25.7; H, 5.6%.

### 3.5. Synthesis of $\{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}(\text{CH}_2)_3]_2\text{O}\}_n$ (**5**)

A solution of KOH (0.24 g, 4.28 mmol) in water (50 ml) was added to a solution of **4** (0.70 g, 1.07 mmol) in toluene (50 ml) and the mixture stirred at 100 °C for 1 d. The white precipitate that formed was collected by filtration. The collected precipitate was then stirred with water (400 ml), filtered and further dried by heating at 80 °C (0.01 mm Hg) for 2 d to give **5** as a white solid (0.50 g, 86%). m.p. > 300 °C (decomp.).

Anal. Calc. for  $\text{C}_{14}\text{H}_{34}\text{O}_3\text{Si}_2\text{Sn}_2$  (544.01): C, 30.9; H, 6.3; Found: C, 30.5; H, 6.2%.

### 3.6. Synthesis of $\{\{[(\text{Me}_3\text{SiCH}_2)(\text{Cl})\text{Sn}(\text{CH}_2)_3]_2\text{O}\}_4$ (**6**)

A solution of **4** (90.0 mg, 0.13 mmol) in toluene (2 ml) was added to a suspension of **5** (70.0 mg, 0.13 mmol) in toluene (2 ml) and stirred at 100 °C for 24 h. Removal of the solvent in vacuo and crystallization from chloroform–hexane (30:70) afforded **6** as a colorless crystals (170 mg, 92%). m.p. 268–270 °C.

$^1\text{H-NMR}$ :  $\delta$  0.13 (s, 36H,  $\text{Me}_3\text{Si}$ ), 0.72–1.28 (m, 16H,  $\text{SiCH}_2$ ), 1.59–1.89 (m, 16H), 2.13–2.29 (m, 16H), 3.47–3.62 (m, 16H).  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR: refer to text and Fig. 2. Anal. Calc. for  $\text{C}_{56}\text{H}_{136}\text{Cl}_8\text{O}_8\text{Si}_8\text{Sn}_8$  (2395.68): C, 28.1; H, 5.7; Found: C, 28.2; H, 5.5%.

## 4. Crystallography

Slow evaporation of a chloroform–hexane (30:70) solution of **6** gave crystals suitable for X-ray analysis. Data were collected for a colorless crystal of **6**,  $0.12 \times 0.21 \times 0.34$ , at 183 K employing graphite monochromatized Mo-K $_{\alpha}$  radiation,  $\lambda = 0.71069$  Å, on a Bruker AXS SMART CCD diffractometer.

Crystal data for **6**:  $\text{C}_{56}\text{H}_{136}\text{Cl}_8\text{O}_8\text{Si}_8\text{Sn}_8$ ,  $M = 2395.49$ , monoclinic, space group  $C2/c$ ,  $a = 38.014(1)$ ,  $b = 12.438(3)$ ,  $c = 21.972(5)$  Å,  $\beta = 105.805(9)^\circ$ ,  $V = 9996(4)$  Å $^3$ ,  $D_x = 1.592$  g cm $^{-3}$ ,  $m = 2.312$  mm $^{-1}$ ,  $F(000) = 4736$ , 14484 unique data, 11203 data with  $I \geq 2.0\sigma(I)$ ,  $R = 0.079$ ,  $R_w$  (all data) = 0.207,  $\rho = 2.34$  e Å $^{-3}$  (near Sn).

The structure was solved by heavy-atom methods [6] and refined by a full-matrix least-squares procedure based on  $F^2$  [6b]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the model in the riding model approximation and a weighting scheme of the form  $w = 1/[\sigma^2(F_o)^2 + (0.0848P)^2 +$

48.442P] where  $P = (F_o^2 + 2F_c^2)/3$  was applied. Most Sn atoms had a significant residual electron density peak ( $< 2.4 \text{ e } \text{\AA}^{-3}$ ) in close proximity, indicating some disorder operating in the structure. However, it was not possible to model this. Fig. 1 showing 50% displacement ellipsoids was drawn with ORTEP [6c]. Calculations were performed using TEXSAN [6d].

## 5. Supplementary material

Crystallographic data for **6** have been deposited at the Cambridge Crystallographic Data Centre with deposition number 211304. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www.http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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## References

- [1] V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* 235 (2002) 1 (and references cited therein).
- [2] (a) D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, *Organometallics* 13 (1994) 4121;  
(b) M. Mehring, M. Schürmann, I. Paulus, D. Horn, K. Jurkschat, A. Orita, J. Otera, D. Dakternieks, A. Duthie, *J. Organomet. Chem.* 574 (1999) 176;
- (c) M. Schulte, M. Schürmann, D. Dakternieks, K. Jurkschat, *J. Chem. Soc. Chem. Comm.* (1999) 1291;
- (d) M. Schulte, M. Mehring, I. Paulus, M. Schürmann, K. Jurkschat, D. Dakternieks, A. Duthie, A. Orita, J. Otera, IXth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (ICCOG-GTL-9), vol. 150–151, Gordon and Breach Science Publishers, Melbourne, Australia, 1999, p. 201;
- (e) M. Mehring, I. Paulus, B. Zobel, M. Schürmann, K. Jurkschat, A. Duthie, D. Dakternieks, *Eur. J. Inorg. Chem.* (2001) 153;
- (f) D. Dakternieks, A. Duthie, K. Jurkschat, M. Schürmann, E.R.T. Tiekink, *Main Group Met. Chem.* 25 (2002) 73;
- (g) D. Dakternieks, A. Duthie, B. Zobel, K. Jurkschat, M. Schürmann, E.R.T. Tiekink, *Organometallics* 21 (2002) 647.
- [3] M. Mehring, M. Schürmann, H. Reuter, D. Dakternieks, K. Jurkschat, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1112.
- [4] (a) J.-M. Lehn, *Science* 227 (1985) 849;  
(b) H.J. Schneider, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1417;  
(c) F.P. Schmidtchen, M. Berger, *Chem. Rev.* 97 (1997) 1609;  
(d) P.D. Beer, P.A. Gale, *Angew. Chem. Int. Ed. Engl.* 40 (2001) 486.
- [5] (a) J. Susperregui, M. Bayle, J.M. Léger, G. Déléris, M. Biesemans, R. Willem, M. Kemmer, M. Gielen, *J. Organomet. Chem.* 545–546 (1997) 559;  
(b) M. Kemmer, M. Biesemans, M. Gielen, E.R.T. Tiekink, R. Willem, *J. Organomet. Chem.* 634 (2001) 55.
- [6] (a) P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, J.M.M. Smits, C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992;  
(b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997;  
(c) C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976;  
(d) TEXSAN, Single Crystal Structure Analysis Software, Version 1.04, Molecular Structure Corporation, The Woodlands, TX, 1997.