

Synthesis and structure of diorganotin dibromides, R_2SnBr_2 ($R = 2,4,6$ -trimethylphenyl or $2,4,6$ -trimethylbenzyl): Hydrolysis of $(2,4,6-Me_3C_6H_2)_2SnBr_2$

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Abstract. The reaction of $SnBr_4$ with *in situ* generated $2,4,6$ -trimethylphenylmagnesium bromide afforded a mixture of $(2,4,6-Me_3C_6H_2)_2SnBr_2$ (**1**) and $(2,4,6-Me_3C_6H_2)_3SnBr$ (**2**) which could be separated from each other by their solubility differences in diethyl ether. On the other hand, the reaction of tin metal with $2,4,6-Me_3C_6H_2CH_2Br$ afforded $(2,4,6-Me_3C_6H_2CH_2)_2SnBr_2$ (**3**). Hydrolysis of the latter using triethylamine as the base afforded $[{(2,4,6-Me_3C_6H_2CH_2)_2Sn}(\mu-O)(Br)(\mu-OH)]_2 \cdot 2CH_2Cl_2$ (**4**) while the use of NaOH as the base afforded $[{(2,4,6-Me_3C_6H_2CH_2)_2Sn}(\mu-O)(OH)(\mu-OH)]_2 \cdot 2CH_2Cl_2$ (**5**). Compounds **4** and **5** are dimeric tetraorganodistannoxanes consisting of a central distannoxane (Sn_2O_2) motif.

Keywords. Organostannoxanes; hydrolysis; diorganotin dibromides.

1. Introduction

Organotin compounds are of interest in catalysis¹ as well as biological activity.² Both these properties depend, crucially on the number and nature of the organic substituents present on tin. Another reason of interest, is that a subclass of this group, viz. organostannoxanes show enormous structural diversity³ and because of this, have received wide spread attention. Even among organotin oxides/hydroxides the nature of the substituent on tin plays a significant role on its eventual structure. For example, among diorganotin oxides, while $(t-BuSnO)_3$ is molecular and contains a six-membered Sn_3O_3 ring,^{4a} many diorganotin oxides $(R_2SnO)_n$ ($R = Me, Et, n-Bu, Ph$) are polymeric.^{4b} On the other hand, $[{(Me_3Si)_2CH}_2Sn(\mu-O)]_2$ is also molecular containing a four-membered ring (chart 1).^{4c} Similarly, other types of products formed in the hydrolysis reactions of organotin halides also seem to depend on the nature of the substituent on tin. We have a long-standing research interest in various aspects of organotin chemistry. Our group has shown that various types of organostannoxane structural types are accessible from the reactions of organotin oxides or organotin oxide-hydroxides with carboxylic acids,⁵ phosphinic acids,⁶ phosphonic acids⁷ or sulfonic

acids.⁸ We have also been successful in demonstrating the efficacy of using organostannoxane platforms to support functional appendages.⁹ Recently we have been probing macrocyclic-coordination polymers of organotin compounds as well as studying the systematic hydrolysis of organotin halides.¹⁰ In view of this research programme, we have an interest in preparing diverse organotin halides and studying their hydrolysis chemistry. In this paper, we report the preparation of new diorganotin dihalides R_2SnBr_2 ($R = 2,4,6$ -trimethylphenyl (**1**) and $2,4,6$ -trimethylbenzyl (**3**)) by (i) the treatment of tin (IV) halides with *in situ* generated Grignard reagents and by (ii) a direct reaction between an aralkyl halide and moist tin. Previously such direct reactions¹¹ were known for the synthesis of industrially important compounds $(n-Bu)_2SnBr_2$ and $(n-octyl)_2SnBr_2$.^{11b} We have also studied the hydrolysis of **3** using two types of bases.

2. Experimental

2.1 Reagents and general procedures

Solvents and other general reagents used in this work were purified according to standard procedures. Mesitylene, magnesium turnings and bromomesitylene were purchased from Sigma Aldrich Ltd. Paraformaldehyde and hydrobromic acid were

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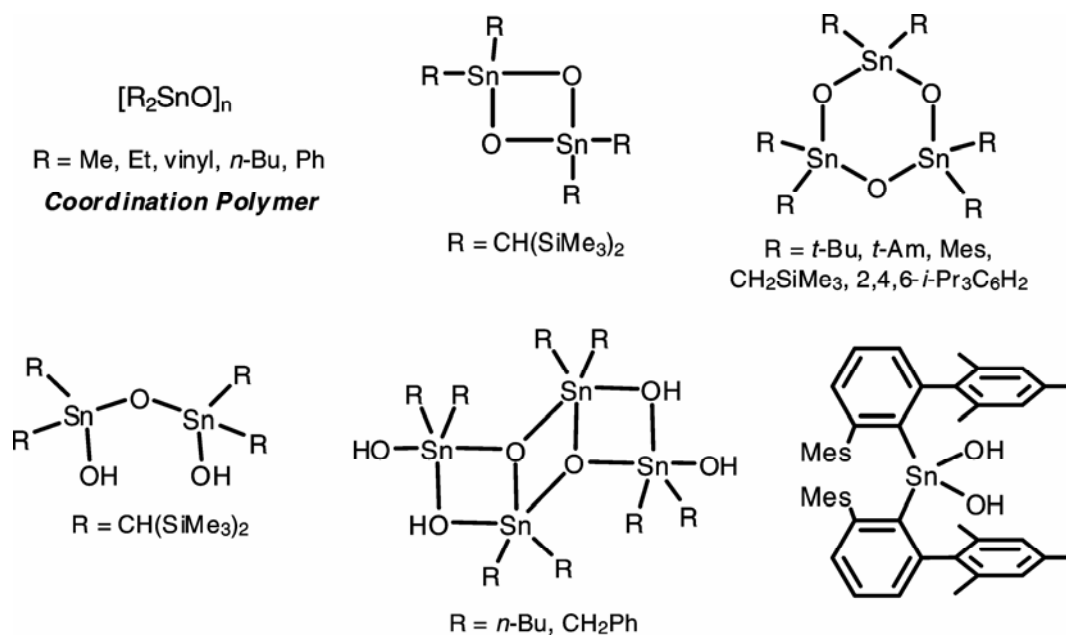


Chart 1. Various types of diorganotin oxides, -hydroxides and -oxide-hydroxides.

purchased from s.d. fine Chemicals, Mumbai. 2,4,6-Trimethylbenzyl bromide was synthesized according to a well-known literature procedure.¹² Melting points were measured using a JSGW melting point apparatus in glass capillaries and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. IR spectra of the samples were recorded as KBr pellets in the range of 4000–400 cm⁻¹ on a Bruker FT-IR Vector 22 model. ¹H and ¹³C{¹H} NMR spectra were obtained using a JEOL-JNM LAMBDA model 400 spectrometer or a JEOL JNM DELTA 500 model spectrometer using CDCl₃ as the solvent. ¹¹⁹Sn{¹H} NMR spectra were recorded on a JEOL-JNM DELTA model 500 operating at 187 MHz.

2.2 Syntheses

2,2a (2,4,6-Me₃C₆H₂)₂SnBr₂ (1) and (2,4,6-Me₃C₆H₂)₃SnBr (2): 2,4,6-Trimethylphenylmagnesium bromide was prepared from the reaction of bromomesitylene (14.70 g, 74.00 mmol) with magnesium turnings (1.80 g, 74.00 mmol) in 150 mL of dry THF. A small amount of iodine was added to initiate the reaction. The reaction mixture was then refluxed for 1 h and cooled. The Grignard reagent, so formed, was slowly added by a cannula to stannic bromide (16.18 g, 37.00 mmol) in 100 mL of THF.

The reaction mixture was stirred for 4 h and then further refluxed for 2 h. After cooling to room temperature, the solvent was stripped off the reaction mixture. The solid obtained was extracted with diethyl ether/dichloromethane. The organic extract was washed with water to remove any inorganic impurities, dried with anhydrous sodium sulfate, filtered and kept for crystallization. Needle-shaped crystals and a precipitate were obtained by slow evaporation of the organic solution. This mixture was treated with 10 mL of diethyl ether. A residue remained undissolved which was identified as **1**. Solvent from the diethyl ether extract was removed *in vacuo* to afford **2** as a colourless solid.

Characterization of 1: Yield: 10.00 g, 52%. m.p. 161–162°C. Anal. Calcd. for C₁₈H₂₂SnBr₂ (**1**): C, 41.83; H, 4.29. Found: C, 41.76; H, 4.26. ¹H NMR (500 MHz, CDCl₃, ppm): 2.30 (*s*, 6H, *p*-CH₃), 2.59 (*s*, 12H, *o*-CH₃), 6.92 (*s*, 4H, aromatic). ¹³C{¹H} NMR (129 MHz, CDCl₃, ppm): 21.25, 24.98, 129.74, 139.14, 141.24, 143.28. ¹¹⁹Sn{¹H} NMR (187 MHz, CDCl₃, ppm): -144.66 (*s*).

Characterization of 2: Yield: 1.00 g, 5%. m.p. 176–177°C. Anal. Calcd. for C₂₇H₃₃SnBr (**2**): C, 58.31; H, 5.98. Found: C, 58.20; H, 5.91. ¹H NMR (500 MHz, CDCl₃, ppm): 2.32 (*s*, 9H, *p*-CH₃), 2.44 (*s*, 18H, *o*-CH₃), 6.92 (*s*, 6H, aromatic). ¹³C{¹H} NMR (129 MHz, CDCl₃, ppm): 21.23, 25.86, 129.15, 139.64, 141.22, 144.27. ¹¹⁹Sn{¹H} NMR (187 MHz, CDCl₃, ppm): -119.30 (*s*).

2.2b $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{SnBr}_2$ (**3**): Moist tin (7.12 g, 6.00×10^{-2} mmol) was placed in a 250 mL round-bottomed flask containing 60 mL of toluene. The reaction mixture was initially stirred at room temperature for 10 min. and then refluxed for 15 min. At this time, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{CH}_2\text{Br}$ (12.79 g, 6.00×10^{-2} mmol) was added all at once and the reflux was continued for 3 h. After allowing the reaction to come to room temperature the reaction flask was kept in an ice bath while maintaining the temperature at 0°C . A pale yellow solid separated from the mixture, which was filtered and then washed with diethyl ether (20 mL) followed by extraction with dichloromethane (40 mL). Removal of solvent from the dichloromethane extract gave a solid which was identified as **3**. This was then recrystallized by the slow diffusion method using chloroform/hexane mixture.

Characterization of 3: Yield: 6.0 g, 37%. m.p. $145\text{--}146^\circ\text{C}$. Anal. Calcd. for $\text{C}_{20}\text{H}_{26}\text{SnBr}_2$ (**3**): C, 44.08; H, 4.81. Found: C, 43.86; H, 4.79. ^1H NMR (500 MHz, CDCl_3 , ppm): 2.02 (s, 12H, *o*- CH_3), 2.18 (s, 6H, *p*- CH_3), 3.17 (s, 4H, $-\text{CH}_2-$), 6.71 (s, 4H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (129 MHz, CDCl_3 , ppm): 21.07, 31.04, 129.25, 129.86, 135.30, 135.77. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (187 MHz, CDCl_3 , ppm): 12.90 (s).

2.2c $[\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\mu\text{-O})(\text{Br})(\mu\text{-OH})]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**4**): Compound **3** (0.50 g, 0.92 mmol) was suspended in 50 mL of ethanol/water mixture (99 : 1). To this was added 0.40 mL of triethylamine, drop-wise. This reaction mixture was stirred for 24 h and filtered. A precipitate was obtained. This was identified as **4**. This was recrystallized by slow evaporation using dichloromethane as the solvent.

Characterization of 4: Yield: 0.33 g, 74%. m.p. $154\text{--}155^\circ\text{C}$. Anal. Calcd. for $\text{C}_{82}\text{H}_{110}\text{Br}_2\text{Cl}_4\text{O}_4\text{Sn}_4$ (**4**): C, 50.87; H, 5.73. Found: C, 50.45; H, 5.60. ^1H NMR (400 MHz, CDCl_3 , ppm): 1.62–2.32 (m, 88H, $-\text{CH}_3$ and $-\text{CH}_2$), 6.40–6.75 (m, 16H, aromatic). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (187 MHz, CDCl_3 , ppm): -222.65 (s), -228.09 (s).

2.2d $[\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\mu\text{-O})(\text{OH})(\mu\text{-OH})]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**5**): Compound **3** (1.0 g, 1.84 mmol) was taken in 20 mL of toluene. To this was added, drop-wise, 10 mL of 2.3 M solution of NaOH at 100°C . After this, the reaction mixture was refluxed for 3 h. The reaction mixture was allowed to come to room temperature and the organic layer was separated, dried (anhydrous Na_2SO_4) and stripped off the solvent to afford a colourless solid. This was washed

with diethyl ether and air-dried. This was purified by recrystallization with dichloromethane.

Characterization of 5: Yield: 0.70 g, 84%. m.p. $130\text{--}131^\circ\text{C}$. Anal. Calcd. for $\text{C}_{82}\text{H}_{112}\text{Cl}_4\text{O}_6\text{Sn}_4$ (**5**): C, 54.40; H, 6.24. Found: C, 54.12; H, 6.13. ^1H NMR (400 MHz, CDCl_3 , ppm): 1.79–2.90 (m, 88H), 6.63 (s, 8H, aromatic), 6.71 (s, 8H, aromatic). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (187 MHz, CDCl_3 , ppm): -202.98 (s), -226.27 (s).

2.3 X-ray crystal structure determination

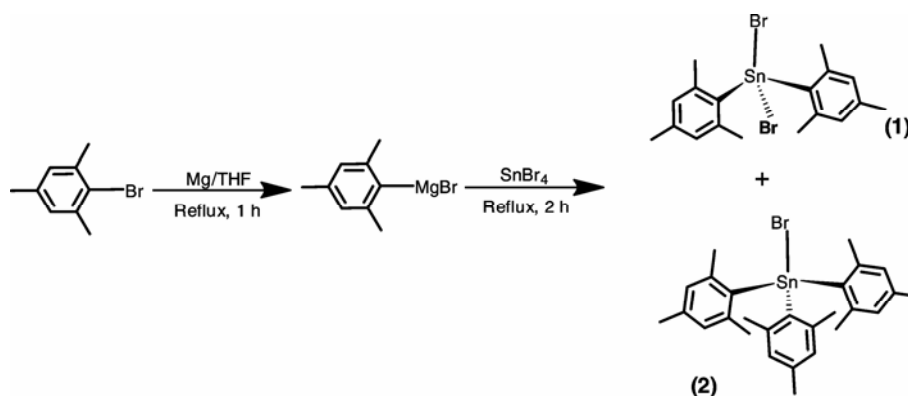
Crystal data and the cell parameters for compounds **1**, **3–5** are given in table 1. Single crystals suitable for X-ray crystallographic analyses were obtained by a slow evaporation of their solutions: $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (**1**), CHCl_3 (**3**) and CH_2Cl_2 (**4** and **5**). The crystal data for compounds **1**, **3–5** were collected on a Bruker SMART CCD diffractometer using a $\text{MoK}\alpha$ sealed tube. The program SMART^{13a} was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT^{13a} for integration of the intensity of reflections and scaling, SADABS^{13b} for absorption correction and SHELXTL^{13c,13d} for space group and structure determination and least-squares refinements on F^2 . All structures were solved by direct methods using the programs SHELXS-97^{13e} and refined by full-matrix least squares methods against F^2 with SHELXL-97.^{13e} Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. Hydrogen atoms for the hydroxyl group were identified by Fourier maps. Figures given in the text were generated using *Diamond 2.1e* software.^{13f}

3. Results and discussion

Mesitylmagnesium bromide was prepared *in situ* by the reaction of bromomesitylene with magnesium turnings in THF. The *in situ* generated 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{MgBr}$ was reacted with stannic bromide under reflux conditions to give a mixture of **1** and **2** (scheme 1). The separation of **1** could be done from **2**, readily, as the latter was soluble in diethyl ether while the former was not. Although previously Molloy *et al*¹⁴ have synthesized a mixture of halogenated products $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{SnCl}_2$, $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{SnClBr}$ and $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{SnBr}_2$ they have not mentioned the separation procedure. Proton NMR of **1** and **2** revealed three types of chemical shifts (see experimental section) consistent with

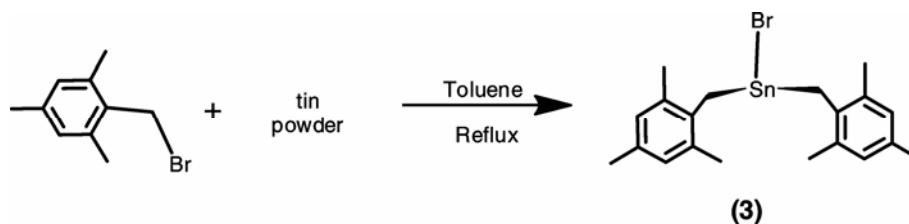
Table 1. X-ray crystallographic data for **1**, **3**–**5**.

	1	3	4	5
Empirical formula	C ₁₈ H ₂₂ Br ₂ Sn	C ₂₀ H ₂₆ Br ₂ Sn	C ₈₂ H ₁₁₀ Br ₂ Cl ₄ O ₄ Sn ₄	C ₈₂ H ₁₁₂ Cl ₄ O ₆ Sn ₄
Formula weight	516.87	544.92	1936.08	1810.28
Temperature (K)	100(2)	100(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71069	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbcn</i>	<i>Pnma</i>	<i>P21/c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	<i>a</i> = 11.2244(8)	<i>a</i> = 9.7522(7)	11.517(5)	<i>a</i> = 15.5928(7)
<i>b</i> (Å)	<i>b</i> = 9.4930(7)	<i>b</i> = 25.2555(17)	14.144(5)	<i>b</i> = 16.4326(8)
<i>c</i> (Å)	<i>c</i> = 17.0419(12)	<i>c</i> = 8.0885(5)	25.747(5)	<i>c</i> = 17.0520(8)
α (°)	α = 90	α = 90	90	95.3680(10)
β (°)	β = 90	β = 90	97.204(5)	105.4340(10)
γ (°)	γ = 90	γ = 90	90	103.7700(10)
<i>V</i> (Å ³)	1815.9(2)	1992.2(2)	4161(2)	4032.8(3)
<i>Z</i> , <i>D</i> _{calc.} (g cm ⁻³)	4, 1.891	4, 1.817	2, 1.545	2, 1.491
μ (mm ⁻¹)	5.800	5.292	2.321	1.406
<i>F</i> (000)	1000	1064	1944	1840
Crystal size (mm)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2
θ Range (°)	2.81 to 27.00°	2.64 to 27.00°	2.15 to 27.00°	1.93 to 27.00
Limiting indices	-11 ≤ <i>h</i> ≤ 14, -11 ≤ <i>k</i> ≤ 12, -21 ≤ <i>l</i> ≤ 21	-12 ≤ <i>h</i> ≤ 12, -31 ≤ <i>k</i> ≤ 32, -7 ≤ <i>l</i> ≤ 10	-14 ≤ <i>h</i> ≤ 14, -17 ≤ <i>k</i> ≤ 18, -32 ≤ <i>l</i> ≤ 26	-19 ≤ <i>h</i> ≤ 15, -14 ≤ <i>k</i> ≤ 20, -21 ≤ <i>l</i> ≤ 21
Reflections collected	10172	11380	25158	24558
Independent reflections	1977 [<i>R</i> (int) = 0.0555]	2218 [<i>R</i> (int) = 0.0373]	9047 [<i>R</i> (int) = 0.0871]	17037 [<i>R</i> (int) = 0.0254]
Data/restraints/parameters	1977/0/99	2218/0/112	9047/0/445	17037/1/899
Goodness-of-fit on <i>F</i> ²	1.096	1.046	1.051	1.134
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0305, <i>wR</i> 2 = 0.0725	<i>R</i> 1 = 0.0266, <i>wR</i> 2 = 0.0602	<i>R</i> 1 = 0.0691, <i>wR</i> 2 = 0.1365	<i>R</i> 1 = 0.0503, <i>wR</i> 2 = 0.1149
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0372, <i>wR</i> 2 = 0.0769	<i>R</i> 1 = 0.0318, <i>wR</i> 2 = 0.0622	<i>R</i> 1 = 0.1142, <i>wR</i> 2 = 0.1548	<i>R</i> 1 = 0.0701, <i>wR</i> 2 = 0.1545

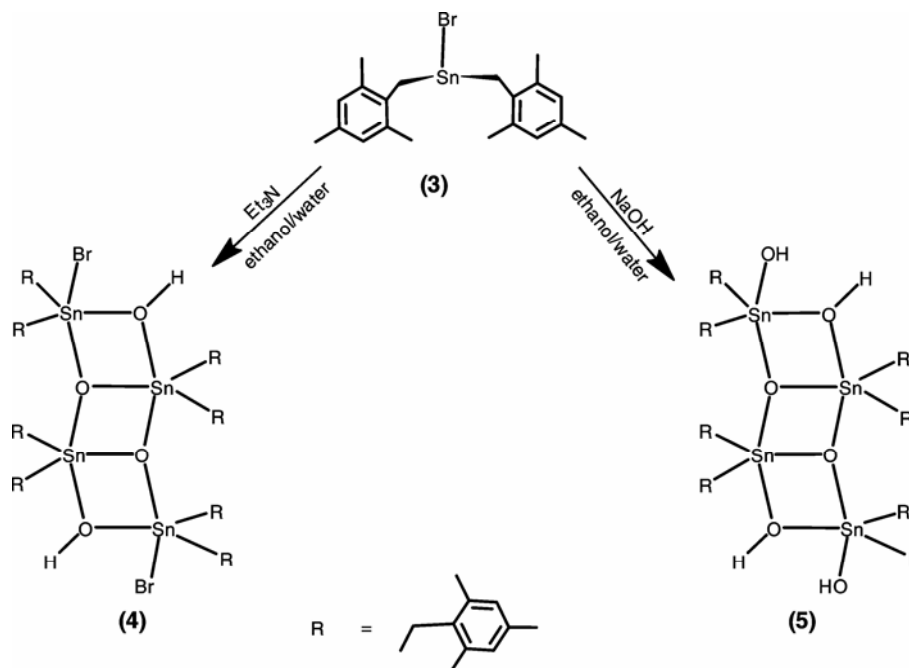
**Scheme 1.** Synthesis of *bis*(2,4,6-trimethylphenyl)tin dibromide and *tris*(2,4,6-trimethylphenyl)tin bromide.

their structures. ¹¹⁹Sn{¹H} NMR spectrum of **1** showed singlet at -144.66 ppm which is upfield shifted in comparison with Ph₂SnBr₂ (-72.90 ppm).¹⁵ On the other hand, ¹¹⁹Sn{¹H} NMR spectrum of **2** showed a peak at -119.30 ppm.

3 was obtained by a direct reaction between 2,4,6-trimethylbenzyl bromide and tin powder under reflux conditions using toluene as the solvent (scheme 2). The proton NMR spectrum of **3** reveals all the distinct chemical shifts which occur at 2.02



Scheme 2. Synthesis of *bis*(2,4,6-trimethylbenzyl)tin dibromide.



Scheme 3. Synthesis of tetraorganodistannoxane ladders.

(*o*-CH₃), 2.18 (*p*-CH₃), 3.17 (CH₂) and 6.71 (Ar) ppm. The -CH₂- chemical shift is up field shifted in comparison to that observed for the starting precursor 2,4,6-Me₃C₆H₂CH₂Br (4.57 ppm).¹² The ¹¹⁹Sn{¹H} NMR of **3** shows a singlet at +12.90 ppm.

In view of the recent interest in the synthesis of organotin oxides, hydroxides and oxide-hydroxides,¹⁶ we have hydrolysed **3** by using two different bases (scheme 3). Hydrolysis of **3** with an excess of Et₃N afforded [$\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\mu\text{-O})(\text{Br})(\mu\text{-OH})\}]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**4**) while the use of NaOH afforded [$\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\mu\text{-O})(\text{OH})(\mu\text{-OH})\}]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**5**) in good yields. ¹¹⁹Sn{¹H} NMR spectrum of **4** shows two equally intense signals at -222.70 ppm and -228.10 ppm. On the other hand, **5** showed chemical shifts at -203.00 (*s*) and -226.30 ppm.

4. X-ray crystal structures of **1**, **3**, **4** and **5**

The molecular structures of **1** and **3** are given in figures 1 and 2 respectively. The bond parameters of

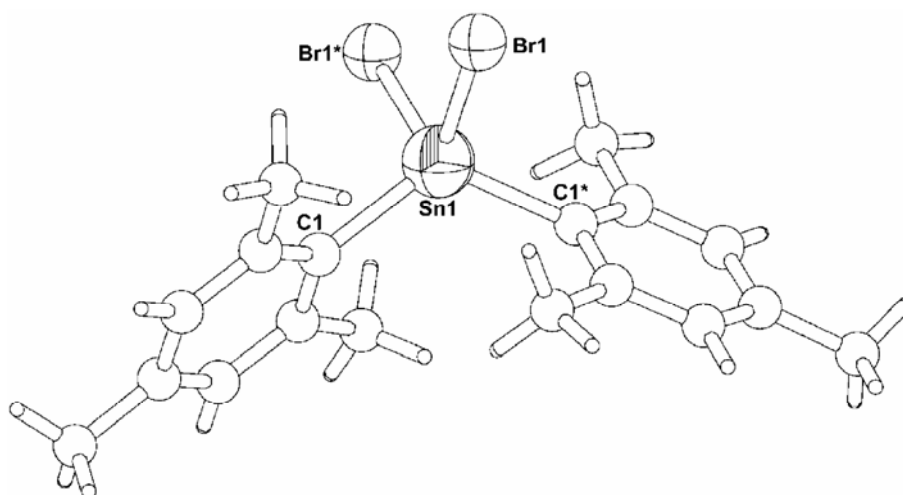
these compounds are given in table 2. Both **1** and **3** crystallized in the orthorhombic crystal system. The geometry around the tin center in both these compounds can be described as distorted tetrahedral. The Sn-C bond distances for **1** and **3** are 2.140(3) and 2.171(3) Å, respectively. The Sn-Br distances are 2.5029(4) Å for **1** and 2.5234(5) and 2.5349(5) Å for **3**. The primary difference in the structures of **1** and **3** is the orientation of the phenyl groups around the tin centers (figures 1 and 2). Interestingly, intramolecular Br... π interactions (3.977 Å) are observed in compound **3**, but such an interaction is absent in compound **1**.

The molecular structures of compounds **4** and **5** are given in figures 3 and 4 respectively. The metric parameters for these compounds are given in tables 2 and 3. The symmetrically related dimeric tetraorganodistannoxane **5** crystallized in a triclinic system whereas **4** crystallized in a monoclinic crystal system. Both of these compounds possess structures consisting of two independent tin atoms which are

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **3** and **4**.

1			
Sn(1)–Br(1)#1	2.5029(4)	Sn(1)–C(1)#1	2.140(3)
C(1)–Sn(1)–C(1)#1	118.74(17)	C(1)–Sn(1)–Br(1)#1	102.41(8)
C(1)–Sn(1)–Br(1)	115.89(9)	Br(1)–Sn(1)–Br(1)#1	100.512(19)
3			
Sn(1)–C(1)#2	2.171(3)	Sn(1)–Br(2)	2.5349(5)
Sn(1)–Br(1)	2.5234(5)	C(1)#2–Sn(1)–Br(2)	104.09(7)
C(1)–Sn(1)–C(1)#2	132.94(15)	Br(1)–Sn(1)–Br(2)	100.770(16)
C(1)–Sn(1)–Br(1)	105.39(8)		
4			
Sn(1)–O(1)	2.060(5)	Sn(2)–C(31)	2.141(7)
Sn(1)–O(1)#3	2.151(5)	Sn(2)–C(21)	2.171(7)
Sn(1)–O(2)	2.151(5)	Sn(2)–O(2)	2.234(5)
Sn(1)–C(11)	2.162(7)	Sn(2)–Br(1)	2.6040(13)
Sn(1)–C(1)	2.173(7)	O(2)–H(2)	0.81(2)
Sn(2)–O(1)	2.038(5)	O(1)–Sn(2)–C(31)	104.1(2)
O(1)–Sn(1)–O(1)#3	73.0(2)	O(1)–Sn(2)–C(21)	125.3(3)
O(1)–Sn(1)–O(2)	73.18(19)	C(31)–Sn(2)–C(21)	128.0(3)
O(1)#3–Sn(1)–O(2)	146.03(19)	O(1)–Sn(2)–O(2)	71.84(19)
O(1)–Sn(1)–C(11)	117.9(3)	C(31)–Sn(2)–O(2)	91.2(2)
O(1)#3–Sn(1)–C(11)	97.9(3)	C(21)–Sn(2)–O(2)	89.9(2)
O(2)–Sn(1)–C(11)	100.3(2)	O(1)–Sn(2)–Br(1)	88.82(14)
O(1)–Sn(1)–C(1)	121.3(3)	C(31)–Sn(2)–Br(1)	101.5(2)
O(1)#3–Sn(1)–C(1)	98.5(2)	C(21)–Sn(2)–Br(1)	95.1(2)
O(2)–Sn(1)–C(1)	96.4(2)	O(2)–Sn(2)–Br(1)	159.09(14)
C(11)–Sn(1)–C(1)	120.8(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 3/2$; #2 $x, -y + 1/2, z$; #3 $-x, -y + 1, -z + 2$

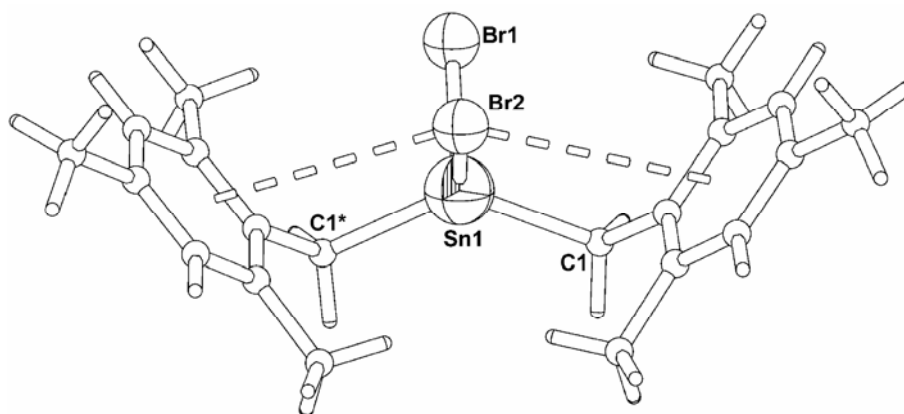
**Figure 1.** Molecular structure of **1**.

bridged by oxide and hydroxide ligands. These belong to the well-known family of ladder structures, which consist of a central distannoxane (Sn_2O_2) motif.¹⁷ All the tin atoms in both of these com-

pounds are present in a distorted trigonal bipyramidal geometry. The equatorial sites are occupied by two carbon atoms and one oxygen atom. The axial positions in the case of the central tin centers, are

Table 3. Selected bond lengths (Å) and angles (°) for **5**.

5							
Sn(1)–O(1)	2.023(5)	Sn(2)–O(4)	2.142(4)	Sn(3)–C(51)	2.162(6)		
Sn(1)–O(3)	2.029(4)	Sn(2)–C(31)	2.163(6)	Sn(4)–O(6)	2.017(5)		
Sn(1)–C(1)	2.150(7)	Sn(2)–C(21)	2.167(6)	Sn(4)–O(4)	2.041(4)		
Sn(1)–C(11)	2.162(6)	Sn(3)–O(4)	2.072(4)	Sn(4)–C(71)	2.160(6)		
Sn(1)–O(2)	2.333(5)	Sn(3)–O(5)	2.102(5)	Sn(4)–C(61)	2.173(6)		
Sn(2)–O(3)	2.060(4)	Sn(3)–O(3)	2.148(4)	Sn(4)–O(5)	2.320(5)		
Sn(2)–O(2)	2.128(4)	Sn(3)–C(41)	2.161(6)	O(5)–H(20)	0.82(2)		
O(1)–H(1)	0.8200	O(2)–H(23)	0.81(12)	O(6)–H(6A)	0.8200		
O(1)–Sn(1)–C(1)	100.4(2)	O(4)–Sn(3)–O(5)	74.66(17)	O(3)–Sn(1)–C(1)	110.2(2)	O(4)–Sn(3)–O(3)	73.56(16)
O(1)–Sn(1)–O(3)	90.32(18)	O(5)–Sn(3)–O(3)	145.76(17)	O(1)–Sn(1)–C(11)	99.3(2)	O(4)–Sn(3)–C(41)	134.1(2)
O(3)–Sn(1)–C(11)	121.8(2)	O(5)–Sn(3)–C(41)	95.9(2)	O(1)–Sn(1)–O(2)	160.83(18)	O(3)–Sn(3)–C(41)	97.1(2)
C(1)–Sn(1)–C(11)	123.7(3)	O(4)–Sn(3)–C(41)	103.5(2)	O(3)–Sn(1)–O(2)	71.28(16)	O(5)–Sn(3)–C(51)	100.9(2)
O(1)–Sn(1)–O(2)	160.83(18)	O(3)–Sn(3)–C(51)	98.6(2)	O(3)–Sn(1)–O(2)	71.28(16)	O(6)–Sn(4)–O(4)	90.95(19)
O(3)–Sn(1)–O(2)	71.28(16)	C(41)–Sn(3)–C(51)	122.4(3)	C(1)–Sn(1)–O(2)	91.2(2)	O(6)–Sn(4)–C(71)	99.7(2)
C(1)–Sn(1)–O(2)	91.2(2)	O(6)–Sn(4)–C(71)	123.0(2)	C(11)–Sn(1)–O(2)	86.5(2)	O(4)–Sn(4)–C(61)	100.3(3)
C(11)–Sn(1)–O(2)	86.5(2)	O(4)–Sn(4)–C(61)	109.3(2)	O(3)–Sn(2)–O(2)	75.12(17)	C(71)–Sn(4)–C(61)	123.1(3)
O(3)–Sn(2)–O(4)	73.93(16)	O(6)–Sn(4)–O(5)	160.26(19)	O(3)–Sn(2)–O(4)	146.48(17)	O(4)–Sn(4)–O(5)	70.63(17)
O(2)–Sn(2)–O(4)	146.48(17)	O(4)–Sn(4)–O(5)	70.63(17)	O(3)–Sn(2)–C(31)	105.1(2)	C(71)–Sn(4)–O(5)	85.2(2)
O(2)–Sn(2)–C(31)	98.4(2)	C(61)–Sn(4)–O(5)	92.7(2)	O(4)–Sn(2)–C(31)	101.7(2)		
O(4)–Sn(2)–C(31)	101.7(2)			O(3)–Sn(2)–C(21)	134.1(2)		
O(3)–Sn(2)–C(21)	134.1(2)			O(2)–Sn(2)–C(21)	95.3(2)		
O(2)–Sn(2)–C(21)	95.3(2)			O(4)–Sn(2)–C(21)	97.0(2)		
O(4)–Sn(2)–C(21)	97.0(2)			C(31)–Sn(2)–C(21)	120.8(3)		
C(31)–Sn(2)–C(21)	120.8(3)						

**Figure 2.** Molecular structure of **3**.

occupied by an oxide and a hydroxide group. In the terminal tin centers these sites are occupied by an oxygen atom and a bromide atom in the case of **4**, and two hydroxide groups in the case of **5**. The $Sn_4O_2(OH)_2(X)_2$ ($X = Br$ (**4**) and OH (**5**)) structural motifs are almost planar with maximum deviations

observed for H2 (0.36 Å) in **4** and H23 (0.89 Å) in **5**. Additionally, in **4** an intramolecular interaction between tin and bromine ($Sn1-Br1^* 3.8549(15)$ Å) (figure 3) was observed. This distance is shorter than the sum of the van der Waals radii for tin and bromide (4.1 Å).¹⁸

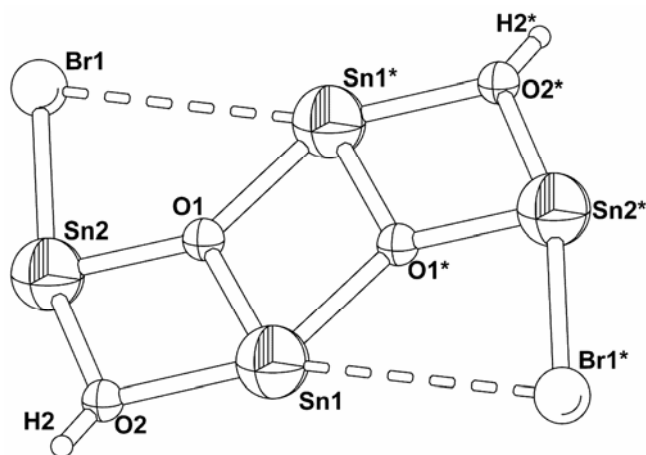


Figure 3. Core structure of **4**. All the aralkyl groups and solvent molecules have been omitted for clarity.

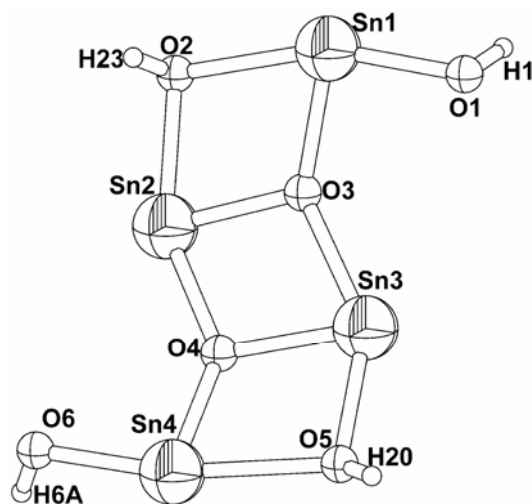


Figure 4. Core structure of **5**. All the aralkyl groups and solvent molecules have been omitted for clarity.

5. Conclusion

In conclusion, we report the synthesis of sterically hindered diorganotin dibromides (2,4,6-Me₃C₆H₂)₂SnBr₂ (**1**), (2,4,6-Me₃C₆H₂)₃SnBr (**2**) and (2,4,6-Me₃C₆H₂CH₂)₂SnBr₂ (**3**). Hydrolysis of (2,4,6-Me₃C₆H₂CH₂)₂SnBr₂ using Et₃N and NaOH afford two distinct products [$\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\text{Br})(\mu\text{-OH})(\mu\text{-O})_2$] and [$\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{CH}_2)_2\text{Sn}\}_2(\text{OH})(\mu\text{-OH})(\mu\text{-O})_2$]. Both of these belong to the well-studied family of dimeric tetraorganodistannoxanes.

Supplementary information

CCDC 759091-759094 (for **1–4**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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