

# Synthesis and Crystal Structures of Three Ladder Distannoxane Dimers $[(\text{PhCH}_2)_2(\text{Cl})\text{SnOSn}(\text{X})(\text{CH}_2\text{Ph})_2]_2$ ( $\text{X} = \text{Cl}, \text{OMe}, \text{OEt}$ )

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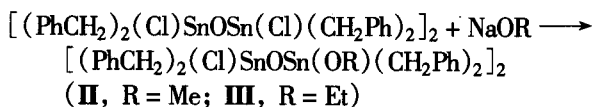
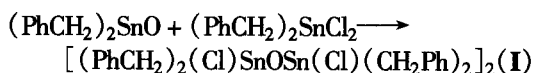
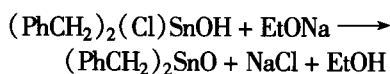
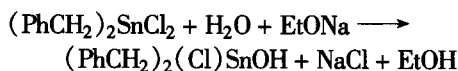
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Three distannoxane dimers  $[(\text{PhCH}_2)_2(\text{Cl})\text{SnOSn}(\text{X})(\text{CH}_2\text{Ph})_2]_2$  ( $\text{X} = \text{Cl}, \text{OMe}, \text{OEt}$ ) were prepared by the hydrolytic reaction of  $(\text{PhCH}_2)_2\text{SnCl}_2$  with sodium alkoxides. The compounds are assigned tetranuclear distannoxane structures in solid state, which contain the so-called ladder arrangement with a central planar  $\text{Sn}_2\text{O}_2$  four-membered ring. The *endo*- and *exo*-cyclic Sn atoms are both five-coordinate, and have distorted trigonal bipyramidal geometries. A variety of hydrolyses of  $(\text{PhCH}_2)_2\text{SnCl}_2$  were performed and these dimers were characterized by IR,  $^1\text{H}$  NMR spectroscopy and X-ray diffraction analysis.

**Keywords** tetraorganodistannoxane, synthesis, hydrolysis, crystal structure, dibenzoyldichlorotin

## Introduction

Tetraorganodistannoxanes of the types  $[\text{R}_2(\text{X})\text{SnOSn}(\text{X})\text{R}_2]_2$  and  $[\text{R}_2(\text{OH})\text{SnOSn}(\text{X})\text{R}_2]_2$  ( $\text{R} = \text{alkyl}, \text{Ph}; \text{X} = \text{halide}, \text{OR}, \text{OAc}, \text{NCS}$ ) are a kind of interesting organotin oxo clusters and have received considerable attention in view of their application as catalysts in industry and as biocides.<sup>1,2</sup> A characteristic feature of this kind of complexes in the solid state is their dimerization that results in the so-called ladder or staircase arrangement which contains a central planar  $\text{Sn}_2\text{O}_2$  four-membered ring.<sup>3</sup> They are usually prepared by the controlled hydrolysis of diorganotin dihalides<sup>4,5</sup> or from reaction of equimolar amount of diorganotin oxide with diorganotin dihalides.<sup>6-10</sup> In order to investigate this type of ladder structure as well as the hydrolysis course further, we performed hydrolysis of  $(\text{PhCH}_2)_2\text{SnCl}_2$  under basic condition giving the compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{SnOSn}(\text{Cl})(\text{CH}_2\text{Ph})_2]_2$  (**I**). The compound **I** continued to have substitution reaction with sodium alkoxides in benzene affording the compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{SnOSn}(\text{OMe})(\text{CH}_2\text{Ph})_2]_2$  (**II**) or  $[(\text{PhCH}_2)_2(\text{Cl})\text{SnOSn}(\text{OEt})(\text{CH}_2\text{Ph})_2]_2$  (**III**). The compounds **I**, **II** and **III** were characterized by IR,  $^1\text{H}$  NMR spectroscopy and X-ray diffraction analysis. The reaction sequences are as follows:



## Experimental

### Instruments

The melting points were obtained with Kofler micro melting point apparatus and uncorrected. The IR spectra were recorded on a Nicolet-460 spectrophotometer and samples were prepared as KBr discs. The  $^1\text{H}$  NMR spectra were obtained on a Jeo-FX-90Q NMR spectrometer in  $\text{CDCl}_3$ , chemical shifts are given relative to  $\text{Me}_4\text{Si}$ . Elemental analyses were performed with a PE-2400 II apparatus. The crystal data were collected by a Bruker Smart-1000 CCD diffractometer.

### Syntheses of compounds **I**, **II** and **III**

All reactions were carried out under nitrogen atmosphere using standard Schlenk technique.  $(\text{PhCH}_2)_2\text{SnCl}_2$  (372 mg, 1 mmol) was added to a solution of sodium ethoxide (68 mg, 1 mmol) in ethanol (20 mL, 95%), then the mixture was stirred at 40 °C for 10 h. After cooling to room temperature, the mixture was filtered. The filtrate was gradually evaporated until the solid product was obtained. The solid was then recrystallized from ether-dichloromethane. Colourless crystal compound **I** was formed. Yield 89%, m.p. 174—176 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 90 MHz)  $\delta$ : 7.15—7.46 (m, 40H,

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Ph), 2.43—2.80 (m, 16H, CH<sub>2</sub>Ph); IR (KBr)<sup>11</sup>  $\nu$ : 3021 (w, Ph—H), 2923 (m, C—H), 1631, 1597, 1491, 1451 (m, Ph), 561 (m, Sn—C), 627 (s, Sn—O—Sn), 337 (m, Sn—Cl) cm<sup>-1</sup>. Anal. calcd for C<sub>56</sub>H<sub>56</sub>Cl<sub>4</sub>O<sub>2</sub>Sn<sub>4</sub>: C 48.82, H 4.10; found C 48.71, H 4.07.

A solution of compound **I** (0.5 mmol) and NaOMe (or NaOEt) (1 mmol) in dry benzene (20 mL), was stirred at 60 °C for 8 h. The precipitates were removed by filtration and the filtrate was concentrated under reduced pressure, **II** and **III** were obtained, respectively. The products **II** or **III** were recrystallized from ether-dichloromethane. For **II**: yield 81%, m.p. 138—140 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$ : 7.17—7.56 (m, 40H, Ph), 3.55 (s, 6H, OCH<sub>3</sub>), 2.43—2.81 (m, 16H, CH<sub>2</sub>Ph); IR (KBr)<sup>11</sup>  $\nu$ : 3027 (w, Ph—H), 2920 (m, C—H), 1629, 1587, 1498, 1461 (m, Ph), 563 (m, Sn—C), 629 (s, Sn—O—Sn), 491 (s, Sn—O—Me), 340 (m, Sn—Cl) cm<sup>-1</sup>. Anal. calcd for C<sub>58</sub>H<sub>62</sub>Cl<sub>2</sub>O<sub>4</sub>Sn<sub>4</sub>: C 50.89, H 4.57; found C 50.77, H 4.60. For **III**: yield 85%, m.p. 118—120 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$ : 7.15—7.58 (m, 40H, Ph), 3.75 (q, 4H, OCH<sub>2</sub>), 2.45—2.81 (m, 16H, CH<sub>2</sub>Ph), 1.25

(t,  $J = 5$  Hz, 6H, CH<sub>3</sub>); IR (KBr)<sup>11</sup>  $\nu$ : 3036 (w, Ph—H), 2924 (m, C—H), 1629, 1589, 1488, 1455 (m, Ph), 558 (m, Sn—C), 632 (s, Sn—O—Sn), 489 (s, Sn—O—Et), 343 (m, Sn—Cl) cm<sup>-1</sup>. Anal. calcd for C<sub>60</sub>H<sub>66</sub>Cl<sub>2</sub>O<sub>4</sub>Sn<sub>4</sub>: C 51.59, H 4.76; found C 51.37, H 4.65.

### Crystal structure

All X-ray crystallographic studies were done by using a Bruker Smart 1000 diffractometer fitted with graphite monochromated Mo K $\alpha$  radiation. The  $\omega/2\theta$  scan technique was employed. Corrections were applied for Lorentz and polarization effects but not for absorption, satisfying the  $I \geq 2\sigma(I)$ . Criterion of observability was used for the solution and refinement. The structure was solved by using direct methods and refined by a full-matrix least squares procedure based on  $F^2$  using the SHELXL-97 program system. All non-H atoms were included in the model at their calculated positions.

The crystal data and refinement details are given in Table 1. Fractional atomic coordinates and their isotropic equivalent displacement coefficients are listed in Table 2. The selected bond distances and angles are listed in Table 3.

Table 1 Crystal data and refinement details for compounds **I**, **II** and **III**

Data and details	Compound <b>I</b>	Compound <b>II</b>	Compound <b>III</b>
Chemical formula	C <sub>56</sub> H <sub>56</sub> Cl <sub>4</sub> O <sub>2</sub> Sn <sub>4</sub>	C <sub>58</sub> H <sub>62</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>4</sub>	C <sub>60</sub> H <sub>66</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>4</sub>
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P-1$	$P-1$
$a$ (nm)	1.0400(2)	1.0638(2)	1.1010(5)
$b$ (nm)	1.8469(4)	1.0875(2)	1.1300(5)
$c$ (nm)	1.4868(3)	1.3599(3)	1.2786(6)
$\alpha$ (°)	90	81.80(3)	97.481(7)
$\beta$ (°)	107.126(3)	73.87(3)	110.524(6)
$\gamma$ (°)	90	70.40(3)	102.014(7)
$V$ (nm <sup>3</sup> )	2.7290(10)	1.4216(5)	1.4208(11)
$D_c$ (g/cm <sup>3</sup> )	1.676	1.599	1.632
Formula weight	1377.57	1368.74	1396.78
$\lambda$ (nm)	0.071073	0.071073	0.071073
$Z$	2	1	1
$F(000)$	1352	676	692
Crystal size (nm)	0.25 × 0.15 × 0.10	0.25 × 0.20 × 0.15	0.30 × 0.15 × 0.08
$\theta$ range (°)	1.81 to 23.31	1.56 to 23.33	1.74 to 25.02
Index range	-11 ≤ $h$ ≤ 10, -20 ≤ $k$ ≤ 20, -16 ≤ $l$ ≤ 16	-8 ≤ $h$ ≤ 11, -12 ≤ $k$ ≤ 12, -14 ≤ $l$ ≤ 15	-13 ≤ $h$ ≤ 13, -12 ≤ $k$ ≤ 13, -14 ≤ $l$ ≤ 15
$\mu$ (mm <sup>-1</sup> )	2.044	1.873	1.876
$T$ (K)	298(2)	298(2)	298(2)
Reflections collected/unique	12153/3896 [ $R_{int} = 0.0362$ ]	6559/4092 [ $R_{int} = 0.0234$ ]	7266/4958 [ $R_{int} = 0.0229$ ]
Refinement	Full-matrix	Full-matrix	Full-matrix
Method	Least-squares on $F^2$	Least-squares on $F^2$	Least-squares on $F^2$
Parameters	410	431	428
Goodness-of-fit on $F^2$	0.965	0.950	0.917
Final $R$ indices [ $I > 2.0\sigma(I)$ ]	$R_1 = 0.0318$ , $wR_2 = 0.0570$	$R_1 = 0.0323$ , $wR_2 = 0.0519$	$R_1 = 0.0392$ , $wR_2 = 0.0614$
$R$ indices (all data)	$R_1 = 0.0603$ , $wR_2 = 0.0664$	$R_1 = 0.0561$ , $wR_2 = 0.0593$	$R_1 = 0.0761$ , $wR_2 = 0.0715$
Largest diff. peak and hole	702 and -841	759 and -483	841 and -419
Max. and min. transmission	0.8127 and 0.6289	0.7764 and 0.6517	0.8644 and 0.6030

$R = \sum ||F_0| - |F_c|| / \sum |F_0|$ ;  $W_R = \{ \sum [W(F_0^2 - F_c^2)^2] / \sum [W(F_0^2)^2] \}^{1/2}$ . **I**:  $w = 1 / [\sigma^2(F_0^2) + (0.0273P)^2 + 0.0000P]$ , **II**:  $w = 1 / [\sigma^2(F_0^2) + (0.0184P)^2 + 0.0000P]$ , **III**:  $w = 1 / [\sigma^2(F_0^2) + (0.0224P)^2 + 0.0000P]$ ; where  $P = (F_0^2 + 2F_c^2) / 3$ .

**Table 2** Selected interatomic distances (nm) and interbond angles ( $^{\circ}$ ) for compounds I, II and III

Bond distances (nm)					
I		II		III	
Sn(1)—O(1)	0.2043(3)	Sn(1)—O(2)	0.2033(3)	Sn(1)—O(2)	0.2035(4)
Sn(1)—O(1A)	0.2145(3)	Sn(1)—O(2A)	0.2139(3)	Sn(1)—O(2A)	0.2154(3)
Sn(1A)—O(1)	0.2145(3)	Sn(1A)—O(2)	0.2139(3)	Sn(1A)—O(2)	0.2154(3)
Sn(1)—Cl(1)	0.2573(2)	Sn(1)—O(1)	0.2159(3)	Sn(1)—O(1)	0.2158(4)
Sn(2)—Cl(1)	0.27241(19)	Sn(2)—O(1)	0.2183(3)	Sn(2)—O(1)	0.2192(4)
Sn(2)—O(1)	0.2019(3)	Sn(2)—O(2)	0.2020(3)	Sn(2)—O(2)	0.2019(3)
Sn(1)—C(1)	0.2140(6)	Sn(1)—C(1)	0.2134(6)	Sn(1)—C(3)	0.2155(7)
Sn(1)—C(8)	0.2146(6)	Sn(1)—C(8)	0.2134(6)	Sn(1)—C(10)	0.2134(6)
Sn(2)—Cl(2)	0.24139(15)	Sn(2)—Cl(1)	0.24780(19)	Sn(2)—Cl(1)	0.2493(2)
Sn(2)—C(15)	0.2142(6)	Sn(2)—C(15)	0.2153(7)	Sn(2)—C(17)	0.2149(7)
Sn(2)—C(22)	0.2144(7)	Sn(2)—C(22)	0.2139(9)	Sn(2)—C(24)	0.2140(7)

Bond angles ( $^{\circ}$ )					
I		II		III	
O(1)—Sn(1)—O(1A)	73.16(14)	O(2)—Sn(1)—O(2A)	73.93(13)	O(2)—Sn(1)—O(2A)	72.09(15)
Sn(1A)—O(1)—Sn(1)	106.84(14)	Sn(1A)—O(2)—Sn(1)	106.07(13)	Sn(1A)—O(2)—Sn(1)	107.91(15)
Cl(1)—Sn(1)—O(1)	80.37(10)	O(1)—Sn(1)—O(2)	72.39(13)	O(1)—Sn(1)—O(2)	72.53(14)
Sn(1)—O(1)—Sn(2)	119.57(16)	Sn(1)—O(2)—Sn(2)	113.14(15)	Sn(1)—O(2)—Sn(2)	113.04(15)
O(1)—Sn(2)—Cl(1)	77.08(10)	O(2)—Sn(2)—O(1)	72.11(12)	O(2)—Sn(2)—O(1)	72.11(14)
Sn(2)—Cl(1)—Sn(1)	82.96(6)	Sn(2)—O(1)—Sn(1)	102.34(15)	Sn(2)—O(1)—Sn(1)	102.05(14)
Cl(1)—Sn(1)—O(1A)	153.51(9)	O(1)—Sn(1)—O(2A)	146.31(12)	O(1)—Sn(1)—O(2A)	144.48(15)
Sn(1A)—O(1)—Sn(2)	133.53(16)	Sn(1A)—O(2)—Sn(2)	140.75(16)	Sn(1A)—O(2)—Sn(2)	138.39(19)
C(1)—Sn(1)—C(8)	127.2(3)	C(1)—Sn(1)—C(8)	125.4(3)	C(3)—Sn(1)—C(10)	124.9(3)
O(1)—Sn(2)—Cl(2)	90.47(10)	O(2)—Sn(2)—Cl(1)	86.89(10)	O(2)—Sn(2)—Cl(1)	88.68(11)
O(1)—Sn(2)—C(15)	113.0(2)	O(2)—Sn(2)—C(15)	114.9(2)	O(2)—Sn(2)—C(17)	113.3(2)
O(1)—Sn(2)—C(22)	112.3(3)	O(2)—Sn(2)—C(22)	116.3(4)	O(2)—Sn(2)—C(24)	120.1(2)
Cl(1)—Sn(2)—C(15)	86.2(2)	O(1)—Sn(2)—C(15)	93.8(2)	O(1)—Sn(2)—C(17)	96.4(3)
Cl(1)—Sn(2)—C(22)	83.6(2)	O(1)—Sn(2)—C(22)	95.0(4)	O(1)—Sn(2)—C(24)	92.4(3)
Cl(1)—Sn(2)—Cl(2)	167.51(6)	O(1)—Sn(2)—Cl(1)	159.00(9)	O(1)—Sn(2)—Cl(1)	160.42(10)
C(15)—Sn(2)—C(22)	129.7(4)	C(15)—Sn(2)—C(22)	128.2(4)	C(17)—Sn(2)—C(24)	126.0(3)
C(15)—Sn(2)—Cl(2)	99.8(2)	C(15)—Sn(2)—Cl(1)	95.4(2)	C(17)—Sn(2)—Cl(1)	94.7(3)
C(22)—Sn(2)—Cl(2)	100.5(2)	C(22)—Sn(2)—Cl(1)	94.0(4)	C(24)—Sn(2)—Cl(1)	94.1(3)

**Table 3** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^5 \text{ nm}^2$ ) for three dimers

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Compound I				
Sn(1)	8409(1)	221(1)	4402(1)	48(1)
Sn(2)	10479(1)	1749(1)	5077(1)	50(1)
O(1)	10243(3)	663(2)	5070(2)	53(1)
Cl(1)	7831(2)	1572(1)	4112(1)	94(1)
Cl(2)	12833(1)	1620(1)	5929(1)	72(1)
C(1)	7967(7)	29(4)	2923(4)	61(2)
C(2)	6591(6)	312(3)	2398(4)	54(2)
C(3)	6448(8)	952(4)	1923(5)	73(2)
C(4)	5171(11)	1193(5)	1443(6)	92(3)
C(5)	4073(9)	819(6)	1435(6)	95(3)
C(6)	4224(8)	191(5)	1918(6)	92(3)
C(7)	5460(7)	-65(4)	2396(5)	70(2)

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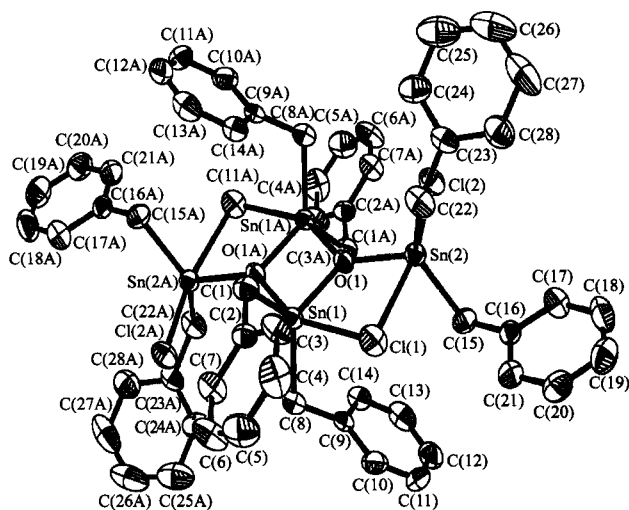
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Compound I				
C(8)	7081(8)	79(4)	5253(6)	68(2)
C(9)	7246(6)	616(3)	6029(4)	51(2)
C(10)	6360(8)	1188(4)	5981(7)	71(2)
C(11)	6516(10)	1650(5)	6715(8)	85(3)
C(12)	7549(11)	1576(5)	7504(8)	84(3)
C(13)	8439(10)	1034(6)	7580(6)	85(3)
C(14)	8311(7)	552(4)	6844(5)	64(2)
C(15)	9783(8)	2279(4)	6128(5)	60(2)
C(16)	9412(6)	3037(3)	5896(4)	53(2)
C(17)	10334(10)	3592(5)	6180(6)	78(2)
C(18)	9966(13)	4300(5)	5961(7)	97(3)
C(19)	8729(12)	4479(5)	5452(7)	92(3)
C(20)	7804(10)	3952(5)	5132(6)	86(2)
C(21)	8142(7)	3236(4)	5364(5)	71(2)
C(22)	10617(8)	2150(6)	3756(5)	77(2)
C(23)	11957(6)	2415(4)	3732(4)	62(2)
C(24)	12885(8)	1984(6)	3509(5)	85(2)
C(25)	14118(11)	2248(9)	3468(7)	122(4)
C(26)	14382(13)	2968(10)	3668(8)	138(6)
C(27)	13507(14)	3400(9)	3875(8)	125(5)
C(28)	12298(9)	3125(5)	3929(5)	89(2)
Compound II				
Sn(1)	6552(1)	3937(1)	9571(1)	45(1)
Sn(2)	5741(1)	6111(1)	7626(1)	54(1)
Cl(1)	3503(2)	7878(2)	7894(1)	87(1)
O(1)	7377(4)	4393(3)	7973(2)	55(1)
O(2)	5128(3)	5525(3)	9109(2)	45(1)
C(1)	8146(7)	4196(7)	10108(6)	63(2)
C(2)	7900(6)	5547(6)	10377(5)	56(2)
C(3)	7330(8)	5935(8)	11358(6)	85(2)
C(4)	7095(11)	7211(10)	11599(9)	121(3)
C(5)	7430(12)	8089(10)	10838(11)	124(4)
C(6)	7979(12)	7724(10)	9881(10)	120(4)
C(7)	8212(9)	6480(9)	9649(6)	89(2)
C(8)	6345(7)	2100(6)	9398(6)	61(2)
C(9)	7626(6)	1235(5)	8754(4)	49(1)
C(10)	8868(7)	853(6)	9013(5)	65(2)
C(11)	10042(8)	75(7)	8393(6)	74(2)
C(12)	9995(9)	-345(7)	7508(6)	79(2)
C(13)	8797(9)	21(7)	7234(6)	78(2)
C(14)	7633(8)	809(6)	7833(5)	67(2)
C(15)	6979(8)	7394(8)	7356(6)	71(2)
C(16)	6912(7)	8313(7)	6450(5)	67(2)
C(17)	5929(9)	9516(8)	6511(6)	82(2)
C(18)	5936(12)	10410(10)	5668(11)	110(3)
C(19)	6883(15)	10088(14)	4774(10)	133(5)
C(20)	7845(14)	8906(13)	4689(7)	120(4)

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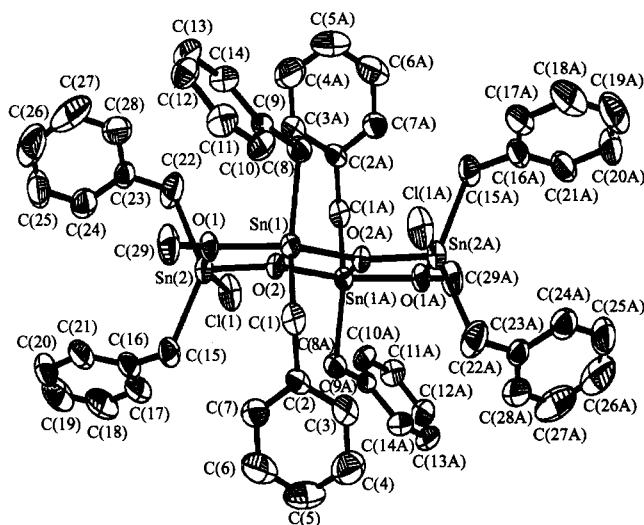
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
<b>Compound II</b>				
C(21)	7861(9)	8015(9)	5514(7)	88(2)
C(22)	5303(11)	5199(16)	6521(8)	103(3)
C(23)	6459(7)	4697(8)	5630(5)	63(2)
C(24)	6878(9)	5539(9)	4860(7)	85(2)
C(25)	7932(13)	5083(15)	4030(8)	124(4)
C(26)	8556(13)	3820(20)	3941(11)	149(6)
C(27)	8184(16)	2943(16)	4670(14)	152(6)
C(28)	7161(12)	3390(9)	5500(8)	102(3)
C(29)	8753(9)	3877(9)	7378(6)	92(2)
<b>Compound III</b>				
Sn(1)	6058(1)	10274(1)	4311(1)	50(1)
Sn(2)	3278(1)	7958(1)	2625(1)	55(1)
Cl(1)	1332(2)	7298(2)	3186(1)	82(1)
O(1)	5175(4)	9056(4)	2632(3)	60(1)
O(2)	4205(4)	9248(3)	4110(3)	52(1)
C(1)	5748(8)	8650(8)	1838(7)	108(3)
C(2)	6398(13)	9439(9)	1461(10)	222(7)
C(3)	7837(8)	9641(7)	4977(7)	66(2)
C(4)	7624(6)	8289(6)	4828(5)	56(2)
C(5)	6960(7)	7633(8)	5403(6)	74(2)
C(6)	6780(10)	6396(10)	5293(10)	104(4)
C(7)	7217(13)	5784(12)	4586(11)	130(6)
C(8)	7908(12)	6347(12)	4011(8)	119(4)
C(9)	8067(9)	7599(10)	4137(6)	86(3)
C(10)	6036(8)	12019(6)	3848(6)	54(2)
C(11)	6906(6)	12486(5)	3248(5)	47(1)
C(12)	6383(8)	12743(6)	2181(6)	58(2)
C(13)	7192(9)	13215(7)	1655(6)	68(2)
C(14)	8541(9)	13484(8)	2162(7)	77(2)
C(15)	9099(9)	13222(8)	3220(7)	89(3)
C(16)	8281(8)	12753(7)	3739(6)	73(2)
C(17)	3845(11)	6255(7)	2727(6)	77(2)
C(18)	3316(7)	5365(5)	1584(5)	55(2)
C(19)	4184(8)	4898(7)	1210(7)	69(2)
C(20)	3695(11)	4092(8)	164(8)	87(3)
C(21)	2376(11)	3746(7)	- 542(7)	84(2)
C(22)	1506(9)	4194(7)	- 188(7)	82(2)
C(23)	1991(9)	5011(7)	870(7)	78(2)
C(24)	2105(9)	8437(8)	1095(6)	67(2)
C(25)	1737(7)	9612(6)	1312(5)	57(2)
C(26)	2567(7)	10712(7)	1333(5)	62(2)
C(27)	2271(9)	11820(7)	1521(6)	75(2)
C(28)	1114(10)	11832(9)	1703(6)	82(3)
C(29)	291(9)	10764(9)	1695(7)	82(2)
C(30)	595(8)	9653(8)	1515(6)	74(2)

## Results and discussion

The molecular structures of compounds **I**, **II** and **III** are illustrated in Figs. 1—3.



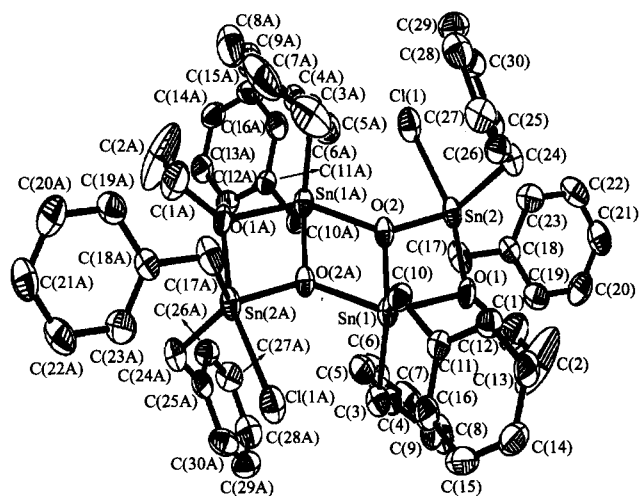
**Fig. 1** Molecular structure of the compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{Cl})(\text{CH}_2\text{Ph})_2]_2$  (**I**).



**Fig. 2** Molecular structure of the compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{OMe})(\text{CH}_2\text{Ph})_2]_2$  (**II**).

### Synthesis aspect

In view of the results of our present study and those of earlier works,<sup>5,8,12,13</sup> the mechanistic sequence of base-catalyzed hydrolysis of  $(\text{PhCH}_2)_2\text{SnCl}_2$  was the same as that reported in the literature for  $\text{Ph}_2\text{SnCl}_2$ .<sup>4,5</sup> First  $(\text{PhCH}_2)_2\text{SnCl}_2$  was hydrolyzed with sodium ethoxide catalysis to form intermediate  $(\text{PhCH}_2)_2\text{SnO}$ , then  $(\text{PhCH}_2)_2\text{SnO}$  reacted with excess  $(\text{PhCH}_2)_2\text{SnCl}_2$  to produce compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{Cl})(\text{CH}_2\text{Ph})_2]_2$  (**I**). The two chlorine atoms of compound **I** were substituted by NaOMe or NaOEt in benzene to give the compounds **II** or **III**.



**Fig. 3** Molecular structure of the compound  $[(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{OEt})(\text{CH}_2\text{Ph})_2]_2$  (**III**).

### Crystal structures

The dichlorodistannoxanes  $(\text{PhCH}_2)_2\text{ClSnOSn}(\text{Cl})\text{-}(\text{CH}_2\text{Ph})_2$ , the chloromethoxydistannoxane  $(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{OMe})(\text{CH}_2\text{Ph})_2$ , and the chloroethoxydistannoxane  $(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{OEt})(\text{CH}_2\text{Ph})_2$  all have dimeric formulations  $[(\text{PhCH}_2)_2(\text{Cl})\text{-SnOSn}(\text{X})(\text{CH}_2\text{Ph})_2]_2$  ( $\text{X} = \text{Cl}, \text{OMe}, \text{OEt}$ ). They adopt the most common structural type found for compounds of the general formula  $[\text{R}_2(\text{Cl})\text{-SnOSn}(\text{Cl})\text{R}_2]_2$  and exist as ladder structure that contains two *endo*- and two *exo*-cyclic Sn atoms. In compounds **I**, **II** and **III**, the benzyl groups are the same for both the *endo*- and the *exo*-Sn atoms, so they can be viewed as centrosymmetric dimers with centrosymmetric units held in a two-dimensional polymeric lattice by chloro- or oxo-bridges. The central part of the dimeric unit consists of a four membered  $\text{Sn}_2\text{O}_2$  ring, which is essentially planar. Of the center  $\text{Sn}_2\text{O}_2$ , the bridge-oxo atom functions as tridentate and the internal angles ( $73.16^\circ$  and  $106.84^\circ$  for **I**;  $73.93^\circ$  and  $106.07^\circ$  for **II**;  $72.09^\circ$  and  $107.9^\circ$  for **III**) are consistent with those in other distannoxane systems, such as  $74.9^\circ$ ,  $105.1^\circ$  of  $[\text{ClMe}_2\text{-SnOSnMe}_2\text{Cl}]_2$ ,<sup>8</sup>  $74.2^\circ$ ,  $106.0^\circ$  of  $[\text{ClPh}_2\text{SnOSnPh}_2\text{OH}]_2$ <sup>5</sup> and  $76.2^\circ$ ,  $105.5^\circ$  of  $[\text{ClPh}_2\text{SnOSnPh}_2\text{Cl}]_2$ .<sup>5</sup>

The distances of  $\mu_3\text{-O}$  to Sn atoms are extremely similar in the three compounds: O(1)—Sn(1) 0.2043(3) nm, O(1)—Sn(1A) 0.2145(3) nm and O(1)—Sn(2) 0.2019(3) nm for **I**; O(2)—Sn(1) 0.2033(3) nm, O(2)—Sn(1A) 0.2139(3) nm and O(2)—Sn(2) 0.2020(3) nm for **II**; O(2)—Sn(1) 0.2035(4) nm, O(2)—Sn(1A) 0.2154(3) nm and Sn(2)—O(2) 0.2019(3) nm for **III**, respectively, reflecting the strong coordination of bridge-oxo with tin atoms in the dimer. There are other bridges in these three compounds, linking the crystallographic asymmetric unit and the inversion center, for **I**, which are chloro-bridges (0.2573(2) nm and 0.27241(19) nm); while for **II** and **III**, are oxo-bridges (0.2159(3) nm and 0.2183(3) nm, 0.2158(4) nm and 0.2192(4) nm, respectively).

The ladder structures of **I**, **II** and **III** are different from

the staircase structure of  $[\text{Me}_4\text{Sn}_2(\text{OSiMe}_3)_2\text{O}]_2^7$  (three four-membered rings are not coplanar), as evidenced by the near coplanarity of the atoms comprising the fused ring system.<sup>5</sup> For **I**, the eight atoms Sn(1), Sn(2), O(1), Cl(1), Sn(1A), Sn(2A), O(1A), and Cl(1A) are coplanar to an extent within  $\pm 0.004$  nm; for **II**, the atoms Sn(1), Sn(2), O(1), O(2), Sn(1A), Sn(2A), O(1A) and O(2A) are coplanar (within  $\pm 0.0065$  nm), while for **III**, the corresponding atoms Sn(1), Sn(2), O(1), O(2), Sn(1A), Sn(2A), O(1A) and O(2A) are coplanar (within  $\pm 0.0063$  nm). This near coplanarity is also seen in the dihedral angle between the planes defined by the central and terminal four-atom rings, and all dihedral angles of compounds **I**, **II** and **III** were between  $0.4^\circ$ – $1.5^\circ$ .

The geometries at the *endo*- and *exo*-cyclic tin atoms are essentially similar in each compound, all of which are pentacoordinated and arranged in distorted trigonal bipyramidal. The trigonal plane is defined by two carbon atoms of benzyl groups and O(2). The axial angles Cl(1)-Sn(2)-Cl(2) ( $167.51^\circ$ ) and Cl(1)-Sn(1)-O(1A) ( $153.51^\circ$ ) for compound **I**, O(1)-Sn(1)-O(2A) ( $146.31^\circ$ ), and Cl(1)-Sn(2)-O(1) ( $159.00^\circ$ ) for compound **II**, O(1)-Sn(1)-O(2A) ( $144.48^\circ$ ) and O(1)-Sn(2)-Cl(1) ( $160.42^\circ$ ) for compound **III**, are all smaller than the ideal value ( $180^\circ$ )<sup>3</sup> of trigonal bipyramidal.

## References

- Otera, J.; Yano, T.; Okawara, R. *Organometallics* **1986**, *5*, 1167.
- Yokoo, M.; Ogura, J.; Kanzawa, T. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 57.
- Lu, Y.; Weng, L.-H.; Lan, Z.-L.; Li, J.; Xie, Q.-L. *Chin. Chem. Lett.* **2002**, *13*, 185.
- Chu, C. K.; Murray, J. D. *J. Chem. Soc. (A)* **1971**, 360.
- Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 145.
- Alleston, D. L.; Davies, A. G.; Hancodk, M.; White, R. F. M. *J. Chem. Soc.* **1963**, 5469.
- Okawara, R. *Proc. Chem. Soc. London* **1961**, 383.
- Harrison, P. G.; Begley, M. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *186*, 213.
- Puff, H.; Bung, I.; Friedriehs, E.; Jansen, A. *J. Organomet. Chem.* **1983**, *254*, 23.
- Parulekar, C. S.; Jain, V. K.; Das, T. K.; Gupya, A. R.; Hoskins, B. F.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *372*, 193.
- Yin, H. D.; Wang, C. H.; Wang, Y.; Ma, C. L. *Indian J. Chem.* **2001**, *40A*, 1089.
- Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.
- Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

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