

# New synthetic approach and structural characterization of the chloroalkylstannanes $(\text{Cl-CH}_2)_n \text{SnCl}_{4-n}$ ( $n = 2, 4$ ) and the hydrolysis product $[(\text{ClCH}_2)_2\text{Sn}(\text{Cl})-\text{O}-\text{Sn}(\text{Cl})(\text{CH}_2\text{Cl})_2]_2$

Michael Veith \*, Dominique Agustin, Volker Huch

*Institut für Anorganische Chemie, Universität des Saarlandes, Postfach 15 11 50, D-66041 Saarbrücken, Germany*

Received 11 June 2001; accepted 5 July 2001

## Abstract

The chloroalkylstannanes  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{Cl})_2$  (**1**) and  $\text{Sn}(\text{CH}_2\text{Cl})_4$  (**3**) have been prepared in high yields by the treatment of tin tetrachloride with diazomethane under the elimination dinitrogen. The established synthetic process was modified in such a way, that the yields were considerably upgraded and the isolation of the products simplified: instead of using  $\text{CH}_2\text{N}_2$  in solution,  $\text{CH}_2\text{N}_2$  was transported by a nitrogen gas flow in a special apparatus. The compounds **1** and **3** were crystallized and their crystal and molecular structures were obtained (for **1** this was a redetermination) by X-ray diffraction [**1**: orthorhombic; space group:  $Pm\bar{m}n$ ;  $a = 7.760(2)$ ,  $b = 10.190(2)$ ,  $c = 4.840(1)$  Å;  $V = 382.7$  Å<sup>3</sup>;  $Z = 2$ . **3**: monoclinic; space group:  $C2/c$ ;  $a = 9.849(2)$ ,  $b = 9.872(2)$ ,  $c = 10.611(2)$  Å,  $\beta = 96.30(3)^\circ$ ;  $V = 988.3$  Å<sup>3</sup>;  $Z = 4$ ]. Both molecular compounds are connected in the solid state by either intermolecular  $\text{Sn}\cdots\text{Cl}$  interactions (**1**) or weak  $\text{H}\cdots\text{Cl}$  bridges (**3**). In the crystal structure of **1** the molecules adopt almost perfect  $C_{2v}$  symmetry (the twofold axis bisecting the  $\text{Cl-Sn-Cl}$  angle) and stack together in such a way, that all chlorine atoms are oriented in one direction. The two tin bonded chlorine atoms form an  $\text{SnCl}_2$  scissor which chelates the neighboring molecule via the two  $\text{Sn}\cdots\text{Cl}$  contacts (3.76 Å) upgrading the coordination number at tin from 4 to 6. This feature can best be seen from the increase of the  $\text{C-Sn-C}$  bond angle to  $135.4^\circ$  (instead of tetrahedral) and from the simultaneous decrease of  $\text{Cl-Sn-Cl}$  to  $98.9^\circ$ . In the crystal of **3** the central tin atom is almost tetrahedrally coordinated by four carbon atoms, but there are still weak intermolecular interactions caused by  $\text{H}\cdots\text{Cl}$  bridges (3.01 Å). Treatment of compound **1** with moisture converts it to the chlorostannoxane  $(\text{ClCH}_2)_2\text{ClSn-O-SnCl}(\text{CH}_2\text{Cl})_2$  (**2**) which turns out to crystallize as a distinct centrosymmetric dimer. Compound **2** crystallizes in the monoclinic space group  $P2_1/n$  ( $a = 8.842(2)$ ,  $b = 18.704(4)$ ,  $c = 8.693(2)$  Å,  $\beta = 109.48(3)^\circ$ ,  $V = 1352.3$  Å<sup>3</sup>,  $Z = 2$ ) and the dimeric molecule deviates from the typical ladder like structure of chlorostannoxanes with the three adjacent four-membered cycles ( $\text{SnClOSn}$ ,  $\text{Sn}_2\text{O}_2$ ,  $\text{SnClOSn}$ ) by further  $\text{Sn}\cdots\text{Cl}$  interaction (3.450 Å). Through this interaction all tin, tin bonded chlorines and oxygen atoms become assembled within a common plane which is wrapped up by eight  $\text{CH}_2\text{Cl}$ -groups above and below this plane (overall point symmetry almost  $C_{2h}$ ). The ten atoms (4Sn, 4Cl, 2O) can also be described as two oxygen centered interpenetrating  $\text{Cl}_2\text{Sn}_3\text{O}$  distorted hexagons. The tin atoms are either in trigonal bipyramidal or octahedral distorted coordination spheres, while the oxygen atoms are trigonal planarly coordinated by three tin atoms. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Tin; Diazomethane;  $\alpha$ -Halogenoalkylstannanes; Distannoxanes; Crystal structures

## 1. Introduction

Poly(chloroalkyl)stannanes have been synthesized for the first time by Jakubowitch, Makarov, and Grivilov from tin tetrachloride using diazolkanes, a reaction which is considered to proceed via the  $\text{Sn-Cl}$  insertion followed by the elimination of nitrogen [1–3]. In their experiment, they obtained a mixture of several insertion

products which have been partly isolated and characterized only by refraction indices and elemental analyses. Further investigations were sparse and only in the 1970s a structure determination of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{Cl})_2$  was reported from film data without the precision of modern techniques [4]. In the paper, the crystals under investigation were reported as unstable. As these molecules and particularly the tetrasubstituted ones can be used for a stepwise rational synthesis of tin centered branched air-stable molecules, we have reinvestigated

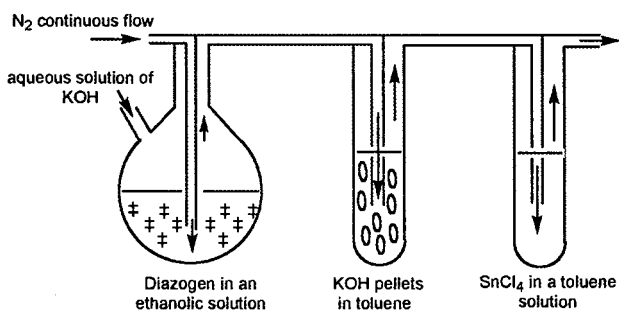
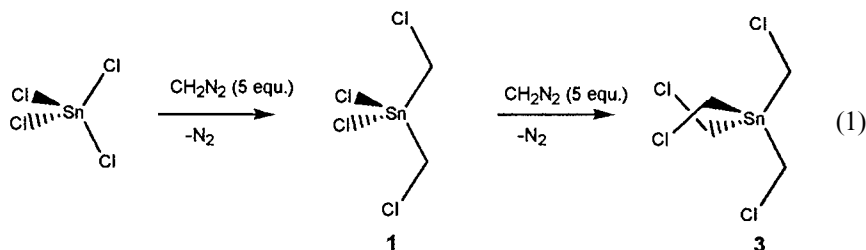
\* Corresponding author. Fax: +49-681-3023995.

the methylene derivatives of this class of compounds and have extensively characterized their spectroscopic and structural properties using multinuclear NMR and X-ray diffraction.

## 2. Results and discussion

The double insertion product of methylene to  $\text{SnCl}_4$  (**1**) and the quadruple insertion product **3** were obtained from  $\text{SnCl}_4$  and diazomethane following a procedure first described by Lombardi [5], but with a new glassware modified for sensitive molecules. In order to avoid any explosion due to gaseous diazomethane [6], no ground glass was used in our apparatus. Their proposal to use diazomethane, not in solution but in the gas phase, was adapted to our reaction. In Scheme 1 the apparatus used is sketched: in a continuous  $\text{N}_2$

gas flow the diazomethane is first obtained in an ethanolic solution from the *p*-toluenesulfonylmethylnitrosamide by treatment with an aqueous solution of KOH in a classical way [6] and transported via the gas phase to a second flask. In this second flask, KOH pellets in toluene are used to trap all the side products and water. After bubbling through the second trap the  $\text{CH}_2\text{N}_2/\text{N}_2$  mixture finally reaches the solution of tin tetrachloride in toluene as the last step and insertions into the Sn–Cl bonds under  $\text{N}_2$  evolution take place. Sequential double insertions of the  $\text{CH}_2$  group into the Sn–Cl bonds can be observed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy of the reaction mixture (Eq. (1)), but no traces of mono- and/or trisubstituted derivatives were detectable under our experimental conditions. Only the disubstituted and tetrasubstituted derivatives  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{Cl})_2$  (**1**) and  $\text{Sn}(\text{CH}_2\text{Cl})_4$  (**3**) could be obtained by crystallization from the solution.



Scheme 1.

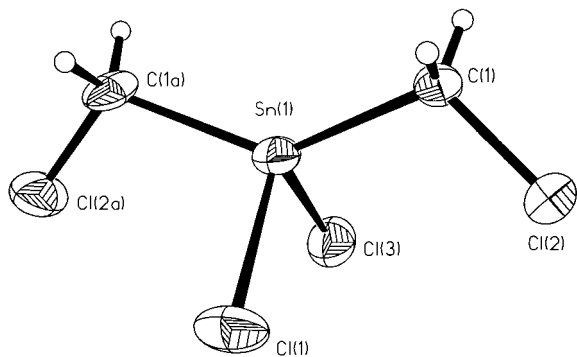


Fig. 1. The molecular structure of  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{Cl})_2$  (**1**) with thermal ellipsoids (50%) of the atoms.

The disubstituted compound **1** forms first and appears, after moderate formation of **3**, to hamper further insertions of  $\text{CH}_2$  moieties as all attempts to obtain the product **3** directly were not successful or gave poor yields. It is preferable to isolate compound **1** first and to repeat the insertion reaction on a pure solution of **1** with an excess of diazomethane in order to get **3** in satisfying yields (80%).

The partly inserted product **1** can be isolated by sublimation of the solid residue from the reaction mixture after the evaporation of the solvent as moisture sensitive, colorless crystals with a yield of 75%. Compound **1** is soluble in coordinating and noncoordinating organic solvents (diethyl ether, benzene, toluene), exhibits one signal at 2.69 ppm in the  $^1\text{H}$ - and 32.35 ppm in  $^{13}\text{C}$ -NMR spectra, respectively. The signals are accompanied by  $^{117/119}\text{Sn}$  satellites from one tin atom as expected and the  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectrum again shows only one broad signal at  $-28.6$  ppm. The compound can be crystallized easily from toluene solutions from which colorless crystals are obtained belonging to the orthorhombic crystal system with the point group  $Pmmn$  as found before (see also Table 5) [4]. The crystals are stable for weeks under exclusion of air and water (see below) contradicting the earlier report [3].

The molecule **1** has a crystallographic mirror symmetry, but as can be deduced by the examination of Fig. 1 and Table 1 the distortion from  $mm2$  ( $C_{2v}$ ) is almost

Table 1  
Selected bond lengths (Å) and bond angles (°) for  $\text{Cl}_2\text{Sn}(\text{CH}_2\text{Cl})_2$  (**1**)

Bond lengths	
Sn(1)–C(1)	2.159(11)
Sn(1)–Cl(1)	2.352(3)
Cl(2)–C(1)	1.764(10)
Bond angles	
C(1a)–Sn(1)–C(1)	135.5(5)
C(1)–Sn(1)–Cl(1)	104.27(17)
Cl(1a)–Sn(1)–Cl(1)	98.87(15)
Cl(2)–C(1)–Sn(1)	109.7(5)

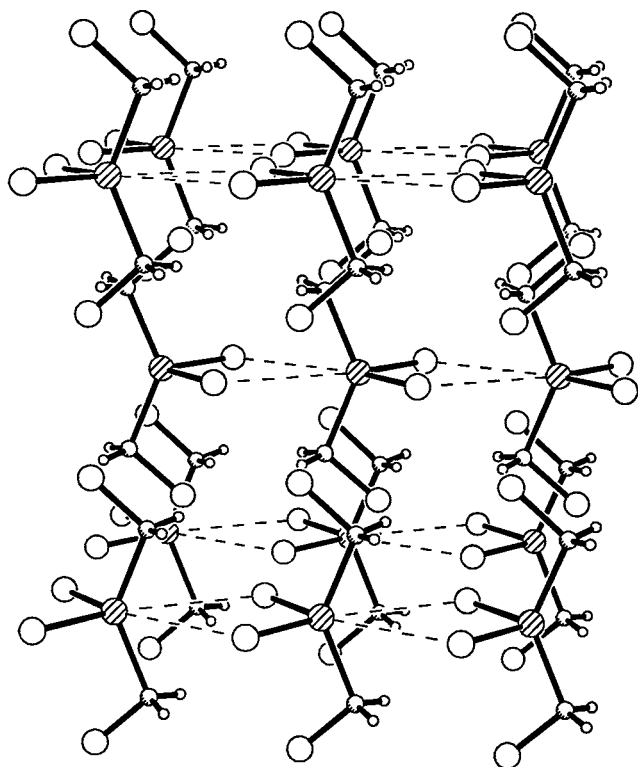


Fig. 2. A section of the three-dimensional arrangements of molecules **1** in the crystal lattice (view along [001]).

negligible (the pseudo-twofold axis is intersecting the  $\text{SnCl}_2$  angle). As for the other compounds with the general formula  $\text{R}_2\text{SnCl}_2$  (e.g.  $(\text{CH}_3)_2\text{SnCl}_2$  [7]) the molecules in the crystal are interacting through  $\text{Sn}\cdots\text{Cl}$  bonds forming a one-dimensional polymer. In the case of **1** the  $\text{SnCl}_2$  unit acts as a bidentate chelate with a second molecule, raising the coordination number at tin from four to six. The intermolecular  $\text{Cl}\cdots\text{Sn}$  interactions (3.768(2) and 3.766(2) Å) are almost equal and can be deduced easily from the increased C–Sn–C angle (135.4°) and the decreased Cl–Sn–Cl angle (98.89°) compared with the ideal tetrahedral value. This less pronounced intermolecular interactions compared with  $(\text{CH}_3)_2\text{SnCl}_2$  (values found here:  $\text{Sn}\cdots\text{Cl}$ , 3.546 Å; C–Sn–C, 123.65°; Cl–Sn–Cl, 93.00°), could be explained

by less steric requirements of methyl compared with  $\text{CH}_2\text{Cl}$ . Besides the  $\text{Sn}\cdots\text{Cl}$  intermolecular bonding there also seem to be intermolecular  $\text{H}\cdots\text{Cl}$  interactions between the molecules ( $\text{H}\cdots\text{Cl}$  distances ranging from 3.0 to 3.2 Å parallel to the (010) plane). These interactions, which arise because of the different charges on the atoms, are responsible for the orientation of all chlorine atoms of the molecule in one direction which is either parallel or antiparallel to [010]. In Fig. 2 a view of the packing is given illustrating this fundamental effect. With respect to the former structure determination, the accuracy in bond lengths and bond angles as well as the packing effects have been substantially improved and modified.

Molecule **3** forms air-stable, colorless needles when crystallized from a benzene solution. In the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of benzene solutions (like for **1**) singlets are observed accompanied by  $^{117/119}\text{Sn}$  satellites at 2.88 and 23.89 ppm, respectively. These values differ very much from **1**, and also the resonance line in the  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR is distinctly shifted to  $\delta = -69.2$  ppm. Allowing  $^1\text{H}$  coupling a nonuplett in the tin NMR spectrum shows up with coupling constants  $^2J(^{119}\text{Sn}-^1\text{H})$  of 19.8 Hz; this feature unambiguously proves the molecule to contain four equal  $\text{CH}_2$  groups.

Compound **3** has a crystallographic twofold axis as the symmetry element which runs through the central tin atom. This arranges all the chlorine atoms in pairs with respect to the twofold axis creating a screwing direction (Fig. 3). In the crystal **3** is therefore chiral, the enantiomeric molecules being connected to one and another by inversion centers. The tin atom is almost tetrahedrally coordinated by the carbon atoms, with angles ranging from 106.8(3) to 112.1(3)° and Sn–C distances from 2.145(5) to 2.172(5) Å (see also Table 2). Whereas the carbon–chlorine bonds of the  $\text{CH}_2\text{Cl}$  groups at C(2) are oriented in the direction of the  $\text{C}_2$  axis, they are almost perpendicular for the similar

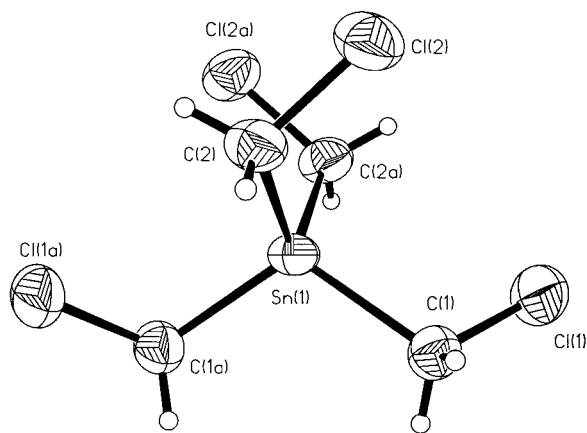


Fig. 3. The molecular structure of  $(\text{ClCH}_2)_4\text{Sn}$  (**3**) with thermal ellipsoids (50%) of the atoms.

Table 2  
Selected bond lengths (Å) and bond angles (°) for Sn(CH<sub>2</sub>Cl)<sub>4</sub> (**3**)

Bond lengths	
Sn(1)–C(2)	2.145(5)
Sn(1)–C(1)	2.172(5)
Cl(1)–C(1)	1.793(5)
Cl(2)–C(2)	1.786(6)
Bond angles	
C(2)–Sn(1)–C(2a)	106.8(3)
C(2)–Sn(1)–C(1a)	108.8(2)
C(2)–Sn(1)–C(1)	110.1(2)
C(1a)–Sn(1)–C(1)	112.1(3)
Cl(1)–C(1)–Sn(1)	109.5(3)
Cl(2)–C(2)–Sn(1)	110.1(2)

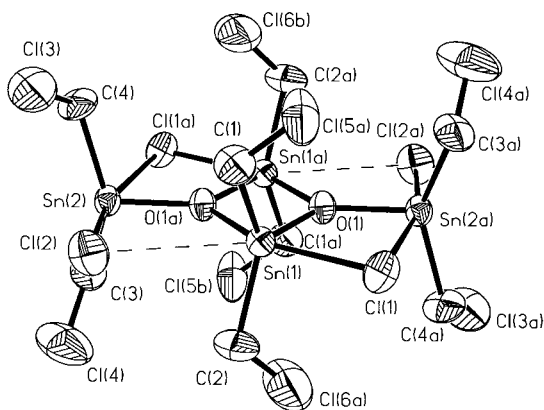
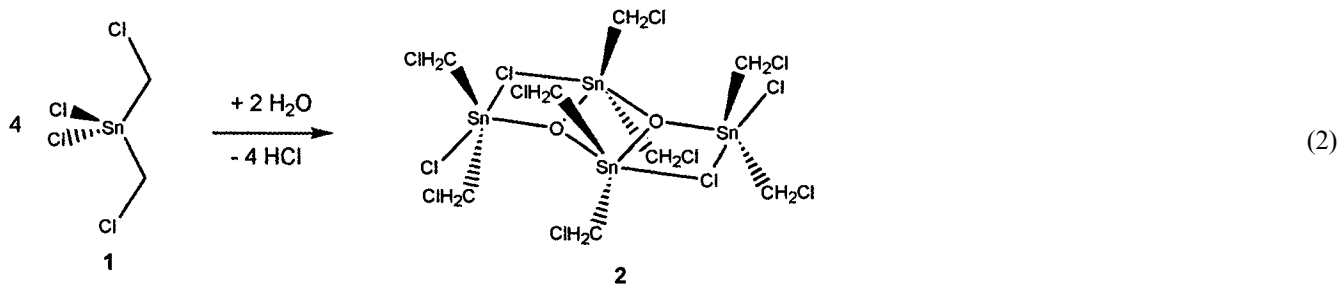


Fig. 4. The molecular structure of [Cl(ClCH<sub>2</sub>)<sub>2</sub>SnOSn(CH<sub>2</sub>Cl)<sub>2</sub>Cl]<sub>2</sub> (**2**) with thermal ellipsoids (50%) of the atoms.

bonds of groups at C(1). The closest intramolecular and intermolecular H···Cl distances between different CH<sub>2</sub>Cl groups are found to be 3.15 Å, indicating that the whole molecular and crystal structure of **3** is dominated by H···Cl attractions.

When compound **1** is in contact with air or moisture, it immediately reacts to the distannoxane (ClCH<sub>2</sub>)<sub>2</sub>ClSn–O–SnCl(CH<sub>2</sub>Cl)<sub>2</sub>, **2**, under elimination of hydrogen chloride. This reaction is also observed with half an equivalent of water added to a toluene solution of **1** (Eq. (2)).



The reaction can be followed by <sup>1</sup>H-NMR. Near the original signal at 2.69 ppm two new signals at 2.72 and

2.86 ppm appear, which correspond to compound **2**. In the <sup>13</sup>C-NMR and <sup>119</sup>Sn-NMR two singlets are observed (at 27.46 and 32.13 ppm in <sup>13</sup>C and at –17.5 ppm and –21.5 ppm in <sup>119</sup>Sn) indicative of dimeric molecules in solution, which are also present in the solid state. The dimeric structure of **2** can be unambiguously shown by an X-ray diffraction study of the colorless single crystals (Fig. 4).

The compound **2** is situated on the crystallographic inversion center in the crystal but deviates only slightly from the higher point symmetry *C*<sub>2h</sub> (*2/m*). Because of this pseudo-symmetry all tin, oxygen and chlorine atoms are arranged in a plane forming five annealed four-membered cycles which are coordinated above and below the plane by eight CH<sub>2</sub>Cl groups. The central Sn<sub>2</sub>O<sub>2</sub> ring is planar for symmetry reasons while the rings Cl(1)–Sn(2)–O(1)–Sn(1) and Cl(2)–Sn(2)–O(1)–Sn(1) differ slightly from planarity (dihedral angles Cl(1)–Sn(2)–O(1)–Sn(1) 0.21(1)° and Cl(2)–Sn(2)–O(1)–Sn(1) 0.39(1)°). The chlorine atom Cl(1) takes part in an almost symmetrical Sn···Cl···Sn bridge (Cl(1)–Sn(2) differing only by 0.18 Å from Cl(1)–Sn(1)) while the corresponding chlorine atom Cl(2) is situated in a highly unsymmetrical bridge (difference between Sn(2)–Cl(2) and Cl(2)–Sn(1) is almost 0.97 Å) (for detailed bond lengths and angles compare Table 3). From the Cl(2)–Sn(2)–O(1) angle, which is 89.4(1)° it can be deduced—assuming a trigonal bipyramidal coordination sphere at Sn(2) with the chlorine substituents in axial positions—that the Cl(2)–Sn(1) interaction must be very weak, as the Cl(2)–Sn(2)–O(1) angle is almost ideal and not deformed. As a matter of fact the Sn(1)–Cl(2) distance of 3.450(1) Å is just near the sum of the van der Waals radii of Sn and Cl which is calculated to be 3.90 Å [8]. The corresponding O(1)–Sn(2)–Cl(1) angle on the other hand is found to be 73.8(1)°; the deviation from 90° indicating a strong bridging of Cl(1).

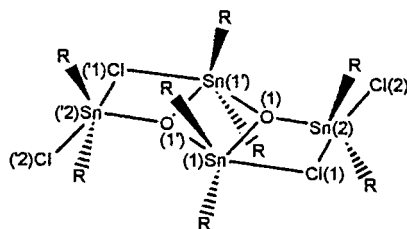
The tin atom Sn(1) can be either described in a trigonal bipyramidal coordination sphere with Cl(1) and O(1a) as axial ligands and O(1), C(1) and C(2) occupying the equatorial sites or in a very distorted octahedral coordination sphere with Cl(2a) as an addi-

tional ligand. Definitely the experimentally characterized coordination sphere is in between these two ideal-

Table 3  
Selected bond lengths (Å) and bond angles (°) for [(ClCH<sub>2</sub>)<sub>2</sub>ClSnOSnCl(CH<sub>2</sub>Cl)<sub>2</sub>]<sub>2</sub> (**2**)

<i>Bond lengths</i>			
Sn(1)–O(1)	2.050(7)	Cl(1)–Sn(2a)	2.824(3)
Sn(1)–O(1a)	2.140(6)	Cl(3)–C(4)	1.789(13)
Sn(1)–C(2)	2.152(12)	Cl(4)–C(3)	1.737(14)
Sn(1)–C(1)	2.160(12)	Cl(5a)–C(1)	1.628(14)
Sn(1)–Cl(1)	2.638(3)	Cl(5b)–C(1)	1.564(18)
Sn(2)–O(1a)	2.026(6)	Cl(6a)–C(2)	1.600(17)
Sn(2)–C(3)	2.142(11)	Cl(6b)–C(2)	1.635(18)
Sn(2)–C(4)	2.152(11)	O(1)–Sn(2a)	2.026(6)
Sn(2)–Cl(2)	2.423(3)	O(1)–Sn(1a)	2.140(6)
Sn(2)–Cl(1a)	2.824(3)		
<i>Bond angles</i>			
O(1)–Sn(1)–O(1a)	74.8(3)	O(1a)–Sn(2)–Cl(1a)	73.9(2)
O(1)–Sn(1)–C(2)	114.6(4)	C(3)–Sn(2)–Cl(1a)	83.8(4)
O(1a)–Sn(1)–C(2)	99.1(4)	C(4)–Sn(2)–Cl(1a)	82.6(3)
O(1)–Sn(1)–C(1)	111.8(4)	Cl(2)–Sn(2)–Cl(1a)	163.24(10)
O(1a)–Sn(1)–C(1)	97.3(4)	Sn(1)–Cl(1)–Sn(2a)	82.94(8)
C(2)–Sn(1)–C(1)	133.3(5)	Sn(2a)–O(1)–Sn(1)	125.3(3)
O(1)–Sn(1)–Cl(1)	77.91(18)	Sn(2a)–O(1)–Sn(1a)	129.5(3)
O(1a)–Sn(1)–Cl(1)	152.72(18)	Sn(1)–O(1)–Sn(1a)	105.2(3)
C(2)–Sn(1)–Cl(1)	91.0(4)	Cl(5b)–C(1)–Cl(5a)	55.7(14)
C(1)–Sn(1)–Cl(1)	93.9(3)	Cl(5b)–C(1)–Sn(1)	110.5(9)
O(1a)–Sn(2)–C(3)	105.8(4)	Cl(5a)–C(1)–Sn(1)	117.8(7)
O(1a)–Sn(2)–C(4)	106.7(4)	Cl(6a)–C(2)–Cl(6b)	44.4(11)
C(3)–Sn(2)–C(4)	139.4(6)	Cl(6a)–C(2)–Sn(1)	116.8(8)
O(1a)–Sn(2)–Cl(2)	89.4(2)	Cl(6b)–C(2)–Sn(1)	113.0(8)
C(3)–Sn(2)–Cl(2)	102.3(4)	Cl(4)–C(3)–Sn(2)	115.1(7)
C(4)–Sn(2)–Cl(2)	101.7(4)	Cl(3)–C(4)–Sn(2)	112.7(6)

Table 4  
Some relevant data of dimeric [R<sub>2</sub>ClSnOSnClR<sub>2</sub>]<sub>2</sub> stannoxanes



(3)

R	Me[9a]	Me[9b]	Me[9c]	<sup>t</sup> Pr[9d]	Bu[9e]	Ph[9f]	CH <sub>2</sub> Cl
<i>Distances (Å)</i>							
Sn(1)–O(1)	2.053(8)	2.105(7)	2.038(4)	2.042(10)	2.068(9)	2.050(3)	2.050(7)
Sn(2)–O(1)	2.030(9)	2.013(7)	2.030(4)	2.037(10)	2.017(10)	2.040(3)	2.026(6)
Sn(1)–Cl(1)	2.720(6)	2.692(3)	2.702(2)	2.675(6)	2.666(5)	2.688(1)	2.639(3)
Sn(2)–Cl(1)	2.788(5)	2.790(4)	2.789(2)	2.804(5)	2.831(6)	2.697(1)	2.824(3)
Sn(2)–Cl(2)	2.435(4)	2.442(4)	2.445(2)	2.462(6)	2.426(6)	2.430(1)	2.425(3)
Sn(1)–O(1')	2.114(9)	2.079(8)	2.118(4)	2.164(10)	2.152(10)	2.107(3)	2.140(6)
Sn(1)–Cl(2')	3.408(5)	3.392(4)	3.409(2)	3.473(6)	3.513(6)	3.355(2)	3.450(2)
<i>Torsion angles (°)</i>							
Cl(1)–Sn(2)–O(1)–Sn(1)	4.99(3)	6.86(3)	6.37(1)	0.69(3)	0.41	1.06(1)	0.21(1)
Cl(2)–Sn(2)–O(1)–Sn(1')	0.18(3)	4.26(3)	1.71(1)	2.17(3)	0.53	4.53(1)	0.39(1)

Table 5  
Crystal data and structure refinement parameters for **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>2</sub> H <sub>4</sub> Cl <sub>4</sub> Sn	C <sub>8</sub> H <sub>16</sub> Cl <sub>12</sub> O <sub>2</sub> Sn <sub>4</sub>	C <sub>4</sub> H <sub>8</sub> Cl <sub>4</sub> Sn
Formula weight	288.54	1044.37	316.59
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pmmm</i>	<i>P2(1)/c</i>	<i>C2/c</i>
Unit cell dimensions			
<i>a</i> (Å)	7.760(2)	8.848(2)	9.489(2)
<i>b</i> (Å)	10.190(2)	18.704(4)	9.875(2)
<i>c</i> (Å)	4.8400(10)	8.693(2)	10.611(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	109.48(3)	96.30(3)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	382.72(15)	1356.3(5)	988.3(3)
<i>Z</i>	2	2	4
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	2.504	2.557	2.128
Absorption coefficient (mm <sup>-1</sup> )	4.623	4.828	3.591
<i>F</i> (000)	268	968	600
$\theta$ Range for data collection (°)	3.30–22.44	2.18–24.08	2.99–23.80
Index ranges	0 ≤ <i>h</i> ≤ 8 0 ≤ <i>k</i> ≤ 10 0 ≤ <i>l</i> ≤ 5	−9 ≤ <i>h</i> ≤ 9 −21 ≤ <i>k</i> ≤ 21 −9 ≤ <i>l</i> ≤ 9	−10 ≤ <i>h</i> ≤ 10 −11 ≤ <i>k</i> ≤ 11 −12 ≤ <i>l</i> ≤ 11
Reflections collected	287	8371	2683
Independent reflections	287 [ <i>R</i> <sub>int</sub> = 0.0000]	2024 [ <i>R</i> <sub>int</sub> = 0.0894]	649 [ <i>R</i> <sub>int</sub> = 0.0670]
Completeness to $\theta$ (%)	99.3	94.5	85.8
Absorption correction	Empirical	Numerical	Numerical
Data/restraints/parameters	287/0/23	2024/0/136	649/0/42
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.217	0.975	1.180
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0477, <i>wR</i> <sub>2</sub> = 0.1099	<i>R</i> <sub>1</sub> = 0.0488, <i>wR</i> <sub>2</sub> = 0.1394	<i>R</i> <sub>1</sub> = 0.0301, <i>wR</i> <sub>2</sub> = 0.1269
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0484, <i>wR</i> <sub>2</sub> = 0.1107	<i>R</i> <sub>1</sub> = 0.0596, <i>wR</i> <sub>2</sub> = 0.1484	<i>R</i> <sub>1</sub> = 0.0303, <i>wR</i> <sub>2</sub> = 0.1281
Largest difference peak and hole (e Å <sup>-3</sup> )	1.458 and −1.529	1.951 and −1.052	0.493 and −0.375

ized models as may be deduced from the Cl(1)–Sn(1)–C(1) angle of 132.5(1)° or the Cl(1)–Sn(1)–O(1a) angle of 152.6°.

It is interesting to compare the stannoxane **2** with the other structures of compounds with the general formula [ClR<sub>2</sub>Sn–O–SnR<sub>2</sub>Cl]<sub>2</sub> [9]. In Table 4 a compilation of relevant data are given showing two effects: there is a tendency to planarity in all these ladder-like structures and the distances correlate with the electrophilicity of the tin atoms which is most pronounced in compound **2** showing the shortest O–Sn distances (as sum of the three independent distances). On the same line compound **2** has the shortest Sn–Cl bonds. Thus, it can be deduced that chlorine situated at the  $\beta$ -position with respect to tin has a strong  $-I$  effect and makes the tin atom highly nucleophilic.

### 3. Experimental

#### 3.1. General procedures

All manipulations were carried out under an inert

atmosphere of nitrogen or argon using Stock techniques. Dry, oxygen-free solvents were employed throughout. Toluene and benzene were distilled from sodium benzophenone before use. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker AC-F 200 spectrometer operating at 200 MHz (chemical shifts are reported in ppm relative to internal Me<sub>4</sub>Si). <sup>119</sup>Sn-NMR spectra were recorded on a Bruker AC-P 200 MHz (chemical shifts are reported in ppm relative to external Me<sub>4</sub>Sn). Elemental analyses (C, H, N) were performed on a LECO-900 apparatus.

#### 3.2. Synthesis of Cl<sub>2</sub>Sn(CH<sub>2</sub>Cl)<sub>2</sub> (**1**)

To a suspension of 56.5 g (170 mmol) of *p*-toluenesulphonylmethylnitrosamide in 150 ml EtOH a solution of 12 g (210 mmol) KOH in 10 ml of water was added slowly at 25 °C with continuous stirring. The diazomethane formed is pushed through the system (see Scheme 1) with a continuous nitrogen flux and reacts with an ice-cold solution of 7.4 g (28.4 mmol) of SnCl<sub>4</sub> in 100 ml toluene. **Caution: gaseous CH<sub>2</sub>N<sub>2</sub> can explode according to the literature [6]**

Immediately, the  $\text{SnCl}_4$  solution becomes orange (due to the presence of diazomethane) and the bubbling is stronger as with the normal nitrogen flux. The solution was totally clear after all the diazomethane had reacted. The solution was stirred for 10 h and after removing the solvent by vacuum, the crude product was distilled. Compound **1** was isolated, after crystallization in benzene, as white needles (7 g, 85.4%). **1**: m.p. (dec.): 89 °C.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.69$  (m, 4H,  $\text{CH}_2$ ,  $^2J(^1\text{H}-^{119}\text{Sn}) = 18$  Hz).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 32.35$  ( $\text{CH}_2$ ).  $^{119}\text{Sn-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -28.6$ . Anal. Found: C, 8.34; H, 1.49. Calc. for  $\text{C}_2\text{H}_4\text{SnCl}_4$ : C, 8.32; H, 1.40%.

### 3.3. Reaction of **1** with $\text{H}_2\text{O}$ (synthesis of $[\text{Cl}(\text{ClCH}_2)_2\text{SnO}(\text{Sn}(\text{CH}_2\text{Cl})_2\text{Cl})_2]$ (**2**))

Water (9 mg, 0.5 mmol) in benzene (10 ml) was added dropwise to a 10 ml benzene solution of **1** (0.28 g, 0.97 mmol). The reaction is left for 2 days and small transparent crystals of **2** appeared on slow evaporation of the solvent (0.20 g, 80%). **2**: m.p. (dec.): 102–103 °C.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.73$  (m, 8H,  $\text{CH}_2$ ,  $^2J(^1\text{H}-^{119}\text{Sn}) = 19.0$  Hz), 2.86 (m, 8H,  $\text{CH}_2$ ,  $^2J(^1\text{H}-^{119}\text{Sn}) = 19.0$  Hz).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 27.46$  ( $\text{CH}_2$ ,  $^1J(^{13}\text{C}-^{119}\text{Sn}) = 488$  Hz,  $^1J(^{13}\text{C}-^{117}\text{Sn}) = 464$  Hz, 32.13 ( $\text{CH}_2$ ,  $^1J(^{13}\text{C}-^{119}\text{Sn}) = 633$  Hz,  $^1J(^{13}\text{C}-^{117}\text{Sn}) = 605$  Hz).  $^{119}\text{Sn-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -17.3, -21.5$ . Anal. Found: C, 9.31; H, 1.50. Calc. for  $\text{C}_4\text{H}_8\text{SnOCl}_6$ : C, 9.20; H, 1.54%.

### 3.4. Synthesis of $\text{Sn}(\text{CH}_2\text{Cl})_4$ (**3**)

(a) Similar to the one described for **1** (see above), the reaction of 2.36 g (8.18 mmol) of **1** and 20g (93.3mmol) of *p*-toluenesulphonylmethylnitrosamide in 150 ml EtOH and 5 g (88.4 mmol) of KOH in 20 ml water afforded **3** as colorless crystals after crystallization in benzene (2.10 g, 74%). (b) In a direct synthesis with 11.13 g (42.7 mmol)  $\text{SnCl}_4$  in 150 ml toluene, 100 g (466 mmol) *p*-toluenesulphonylmethylnitrosamide in 400 ml EtOH and 40 g (707 mmol) KOH in 40 ml water. Only 5.4 g (40%) of **3** were separated by crystallization.

**3**: m.p. (dec.): 58 °C.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.88$  (m, 8H,  $\text{CH}_2$ ,  $^2J(^1\text{H}-^{119}\text{Sn}) = 19.8$  Hz).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 23.89$  ( $\text{CH}_2$ ,  $^1J(^{13}\text{C}-^{119}\text{Sn}) = 410$  Hz,  $^1J(^{13}\text{C}-^{117}\text{Sn}) = 390$  Hz,  $^1J(^1\text{H}-^{13}\text{C}) = 151$  Hz).  $^{119}\text{Sn-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -69.2$  (n,  $^2J(^1\text{H}-^{119}\text{Sn}) = 19.8$  Hz,  $^1J(^{13}\text{C}-^{119}\text{Sn}) = 410$  Hz). Anal. Found: C, 15.21; H, 2.60. Calc. for  $\text{C}_4\text{H}_8\text{SnCl}_4$ : C, 15.17; H, 2.55%.

### 3.5. X-ray crystal data

X-ray reflections intensities for **1–3** were collected at 293 K at  $\lambda = 0.71073$  Å using capillary-coated crystals on a STOE AED2 diffractometer. The structures were solved by direct methods (SHELXS-97 [10] and SHELXL-

97 [11]). The parameters were refined using the least-squares method on  $F^2$ .

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Crystallographic Data Centre, CCDC no. 166371–166373 for compounds **1**, **2** and **3**. Copies of this 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>).

## Acknowledgements

We thank the Fonds der Chemischen Industrie and the DFG (Deutsche Forschungsgemeinschaft) for the financial support within the 'Europäische Graduiertenkolleg' with the title: 'Physikalische Methoden (insbesondere massenspektroskopische) in der strukturellen Erforschung Neuer Materialien'.

## References

- [1] For a review about diazoalkanes insertions, see: (a) D. Seyferth, Chem. Rev. (1955) 1155; for Si, Ge, and Sn compounds see also: (b) D. Seyferth, E.G. Rochow, J. Am. Chem. Soc. 77 (1955) 907; (c) D. Seyferth, E.G. Rochow, Inorg. Synth. VI (1960) 37; (d) D. Seyferth, D.J. Hettflejs, Organomet. Chem. 11 (1968) 253; for other synthetic pathways, see also: (e) Seyferth D. Andrews, J. Organomet. Chem. 30 (1971) 151.
- [2] A.G. Davies, Organotin Chemistry, VCH, Weinheim, Germany, 1997.
- [3] (a) A.Ya. Yakubovich, S.P. Makarov, G.I. Gravilov, Zh. Obshch. Khim. 22 (1952) 1788; (b) A.Ya. Yakubovich, S.P. Makarov, G.I. Gravilov, J. Gen. Chem. USSR 22 (1952) 1827–1829; (c) A.Ya. Yakubovich, S.P. Makarov, V.A. Ginsburg, Gravilov, E.N. Merkulova, Dokl. Akad. Nauk. SSSR 72 (1950) 69.
- [4] (a) N.G. Bokii, Yu.T. Struchtov, A.K. Prokof'ev, Zh. Strukt. Khim. 13 (1972) 665; (b) N.G. Bokii, Yu.T. Struchtov, A.K. Prokof'ev, J. Struct. Chem. 13 (1972) 619.
- [5] P. Lombardi, Chem. Ind. 5 (1990) 708.
- [6] (a) Th.J. De Boer, H.J. Backer, Recl. Trav. Chim. Pays-Bas 73 (1954) 229; (b) Th.J. De Boer, H.J. Backer, Org. Synth. Coll. Vol. 4 (1963) 250.
- [7] A.G. Davies, H.J. Milledge, D.C. Puxley, P.J. Smith, J. Chem. Soc. A (1970) 1862.
- [8] J. Huheey, E. Keiter, R. Keiter, Anorganische Chemie, Prinzipien von Struktur und Reaktivität, 2nd ed., de Gruyter, 1995.

- [9] (a) P.G. Harrisson, M.G. Begley, K.C. Molloy, *J. Organomet. Chem.* 186 (1980) 213;  
(b) R. Graziani, U. Casellato, G. Plazzogna, *Acta Crystallogr. C* 39 (1983) 1188;  
(c) D. Dakternieks, R.W. Gable, B.F. Hoskins, *Inorg. Chim. Acta* 85 (1984) L43;  
(d) H. Puff, E. Friedrichs, F. Visel, *Z. Anorg. Allg. Chem.* 477 (1981) 50;  
(e) R. Hamalainen, U.J. Turpeinen, *Organomet. Chem.* 333 (1987) 323;  
(f) J.F. Vollano, R.O. Day, R.R. Holmes, *Organometallics* 3 (1984) 745.
- [10] G.M. Sheldrick, *Acta Crystallogr. A* 46 (1990) 467.
- [11] G.M. Sheldrick, SHELXL-97, Program for Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.