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Crystal Structures and Spectral Studies of [$Ph_3Sn(O_2AsMe_2)$], [$Bu_2ClSn(O_2AsMe_2)$] and [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)$]$_2$

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Abstract. [$Ph_3Sn(O_2AsMe_2)$] (**1**) and [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)$]$_2$ (**3**) have been synthesized by treatment of Ph_3SnCl and Ph_2SnCl_2 with $Na(O_2AsMe_2)$ in methanol, respectively. [$Bu_2ClSn(O_2AsMe_2)$] (**2**) has been prepared by the reaction of Bu_2SnCl_2 with HO_2AsMe_2 in methanol. X-ray diffraction studies show **1** to crystallize in the monoclinic space group $P2_1/n$ with a = 699.8(1), b = 1961.4(2), c = 1433.6(2) pm, β = 95.17(1)°, and Z = 4. **2** also crystallizes monoclinic in the space group $P2_1/m$, the cell parameters being a = 480.6(1), b = 1992.7(2), c = 808.8(1) pm, β = 103.726(5)°, and Z = 2. Both compounds form infinite chains with alternating $(Me_2AsO_2)^-$ and $(R_3Sn)^+$ or $(R_2ClSn)^+$ units. The dimer **3** consists of 8-membered $(OSnOAs)_2$ rings in which the tin atoms are bridged by methanolate bridges. It crystallizes triclinic in the space group $P\bar{1}$ with a = 822.8(2), b = 910.4(2), c = 929.2(2) pm, α = 77.04(3)°, β = 82.35(3)°, γ = 68.69(3)°, and Z = 1 for the dimer. The vibrational and mass spectra of **1**, **2** and **3** are given and discussed.

Keywords: Tin; Crystal structures; Vibrational spectra; Mass spectra; Dimethylarsinates; Methoxo bridges

1 Introduction

Various methods have been applied to the synthesis of organotin diorganoarsinates. [$Me_2Sn(O_2AsMe_2)_2$] has been prepared by the reaction of Me_2SnCl_2 with $Ag(O_2AsMe_2)$ [1] or with $[Me_4N](O_2AsMe_2)\cdot H_2O$ [2] in 1:2 molar proportions. The oxidation of [$R_nSn(AsR'_2)_{4-n}$] (R, R′ = alkyl, phenyl) by oxygen leads to [$R_nSn(O_2AsR'_2)_{4-n}$] [3−5]. The reaction of Ph_2SnCl_2 with HO_2AsPh_2 in the presence of triethylamine afforded [$Ph_2Sn(O_2AsPh_2)_2$] [4]. Treatment of R_2SnCl_2 (R_2 = Me_2, Et_2) with HO_2AsMe_2 in methanol at ambient temperature produced [$R_2ClSn(O_2AsMe_2)$] [6]. Despite the synthesis of several organotin diorganoarsinates, only the crystal structures of [$R_2ClSn(O_2AsMe_2)$] have been reported.

X-ray diffraction studies of [$Me_2ClSn(O_2AsMe_2)$] and [$Et_2ClSn(O_2AsMe_2)$] show that the $(O_2AsMe_2)^-$ groups behave as bidentate bridge ligands between $(R_2ClSn)^+$ units forming polymeric chain structures [6]. A similar chain structure with $(O_2PMe_2)^-$ bridges was also found in the analogous [$Et_2ClSn(O_2PMe_2)$] [7]. In view of their possible application as biocides and catalysts, numerous related organotin diorganophosphinates $R_nSn(O_2PR'_2)_{4-n}$ were synthesized and structurally characterized by X-ray crystallographic studies [8, 9].

The reaction of Ph_2SnCl_2 with HO_2PPh_2 in methanol gave [$Ph_2Sn(O_2PPh_2)_2$] along with [$PhClSn(O_2PPh_2)OMe$]$_2$. In the latter dimer two tin atoms are connected by two (O_2PPh_2) bridges in a bidentate fashion and by two bridged methoxo groups leading to eight-memberd $(SnOPO)_2$ and four-membered Sn_2O_2 rings [9]. In the light of our earlier experience with synthesis and structural studies of organotin diorganophosphinates [9], we made attempts to prepare crystals of organotin dimethylarsinates suitable for X-ray crystallographic studies.

The present work deals with the synthesis and crystal structures of [$Ph_3Sn(O_2AsMe_2)$] (**1**), [$Bu_2ClSn(O_2AsMe_2)$] (**2**), and [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)$]$_2$ (**3**). The vibrational and mass spectra are given and discussed.

2 Results and Discussion

Crystals of [$Ph_3Sn(O_2AsMe_2)$] (**1**) have been isolated from the reaction of Ph_3SnCl with an equimolar amount of $Na(O_2AsMe_2)$ in methanol at ambient temperature. The reaction of Bu_2SnCl_2 with HO_2AsMe_2 under similar conditions afforded [$Bu_2ClSn(O_2AsMe_2)$] (**2**) along with HCl. Crystalline [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)$]$_2$ (**3**) was formed by treatment of Ph_2SnCl_2 with $Na(O_2AsMe_2)$ (1:1) in methanol according to the following equation.

$$2\,Ph_2SnCl_2 + 2\,Na(O_2AsMe_2) + 2\,HOMe \rightarrow [PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2\ (\mathbf{3}) + 2\,HPh + 2\,NaCl$$

The cleavage of an Sn-Ph bond in this reaction was also observed in the synthesis of the analogous [$PhClSn(O_2PPh_2)(\mu\text{-}OMe)$]$_2$ from Ph_2SnCl_2 and HO_2PPh_2 in methanol [9]. In this connection, it is worth noting that the reaction of Ph_3PbCl with HO_2PR_2 (R_2 = Me_2, Ph_2) causes break of Pb-Ph and Pb-Cl bonds to give

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Table 1 IR and Raman Spectra (1200−400 cm^{-1} IR; 1200−100 cm^{-1} Raman) of **1**, **2** and **3**

$[Ph_3Sn(O_2AsMe_2)]$ (**1**)		$[Bu_2ClSn(O_2AsMe_2)]$ (**2**)		$[PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**3**)		
IR	Raman	IR	Raman	IR	Raman	Assignment
	1195 vw	1194 w	1195 vw			$\delta(CH)Ph$ in-plane
	1186 vw			1183 vw	1185 w	
	1155 vw	1157 m	1158 m	1148 vw	1156 w	
1088 w	1082 vw	1078 m	1083 vw			
1068 w-m	1070 vw			1073 w	1076 w	
			1049 m		1065 w	
1024 w	1027 m				1027 m	$\delta(CH)Ph$ in-plane
		1018 w				$\nu(C\text{-}C)Bu$
				1012 s		$\nu(O\text{-}CH_3)$
		1005 vw				$\nu(C\text{-}C)Bu$
997 w	1001 vs				1001 vs	Ph ring breathing
	987 vw				990 vw	
					976 vw	
		916 m	917 vw			$\rho(CH_3)$
				907 w		
			886 vw	890 w		
			875 vw			
877 s	886 m	869 vs	865 m-s	843 m	838 w	$\nu_{as}(AsO_2)$
	855 vw					
836 vs	838 vw	798 vs	797 s	815 vs	823 vw	$\nu_s(AsO_2)$
					800 vw	
		744 vw	750 vw			$\rho(CH_2)$
732 s	742 vw			735 m-s		$\delta(CH)$-Ph out-of-plane
700 s	702 vw			698 m		
		686 s				
	663 w				662 vs	$\delta(C\text{-}C)$ out-of-plane
658 vw	655 vs	650 m	652 w	651 w	653 s	$\nu_{as}(AsC_2)$
634 w	637 w					
	620 m				620 m-s	(C-C-C) Ph bend
	604 w	608 w	611 vs	611 vw	615 vs	$\nu_s(AsC_2)$
		602 m	603 s			$\nu_s(SnC_2)$
				493 vw		$\nu(Sn\text{-}O\text{-}Sn)$
	468 vw			462 s	464 m	
453 m		453 s	454 w	452 s		$\nu_s(Sn\text{-}OAs)$
441 w	444 vw				439 vw	
	405 w		396 vw		398 vw	
			366 m-s		372 vw	
			324 vw		351 w	
					296 m	$\nu(SnCl)$
	286 vw					$\nu_{as}(SnPh_3)$
	271 vw				268 m	
			246 m		257 m	
	233 vw				237 vw	
			228 vs			$\nu(SnCl)$
					220 w	$\nu(SnPh)$ in-phase
	211 s					$\nu_s(SnPh_3)$
	196 vw				188 s	
	179 w		169 w			
			156 w			

$[Ph_2Pb(O_2PR_2)_2]$ [10]. Moreover, $[Ph_3Sn(O_2AsMe_2)]$ (**1**) was obtained as a colorless insoluble powder by the oxidation of $[Ph_3SnAsMe_2]$ with oxygen [5]. $[Bu_2ClSn(O_2AsMe_2)]$ was prepared as white precipitate from $[Me_4N][O_2AsMe_2]\cdot H_2O$ and Bu_2SnCl_2 (1:1) in ethanol [2].

Vibrational Spectra

The observed IR and Raman frequencies of **1**, **2** and **3** (Table 1) are assigned by comparison with the vibrational spectra of $[R_2ClSn(O_2AsMe_2)]$ [6], with the Raman spectrum of $[PhClSn(O_2PPh_2)(\mu\text{-}OMe)]_2$ [9] and with vibrational spectra of related compounds [2, 5, 7, 11]. The IR and Raman spectra of **1**, **2** and **3** show ν_{as} (AsO_2) and $\nu_s(AsO_2)$ bands between 790-900 cm^{-1} which indicate bidentately bonded $(O_2AsMe_2)^-$ [2, 6]. The medium band at 602 cm^{-1} (IR) and the strong band at 603 cm^{-1} (Raman) in the spectra of **2** are assigned to $\nu_s(SnC_2)$. The appearance of this frequency in both IR and Raman spectra is consistent with the nonlinear SnC_2 arrangement. The absence of these bands in the spectra of **1** and **3** supports this assignment. A corresponding $\nu_s(SnC_2)$ mode appears as strong band at 603 cm^{-1} only in the Raman spectrum of $[Bu_2Sn(O_2PPh_2)_2]$ in which tin atoms are hexa-coordinated with the butyl groups in trans positions [9, 12]. The $\nu_{as}(SnC_2)$ vibration of **2** is not observed and may be obscure by the $\nu_{as}(AsC_2)$ bands. The Raman spectra of **1** and **3** exhibit the characteristic bands due to phenyl ring breathing at 1001 cm^{-1} and the typical (C-C-C) bending-in-plane vibrations at 620 cm^{-1}.

Table 2 Characteristic ions formed in the 70 eV mass spectra of **1**, **2** and **3** (m/e (%))

	[$Ph_3Sn(O_2AsMe_2)$] (**1**) **R = Ph**	[$Bu_2ClSn(O_2AsMe_2)$] (**2**) **R = Bu**	[$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**3**) **R = Ph**
$RCl_2Sn_2(O_2AsMe_2)_2(OMe)_2^+$			721 (3)
$R_3Sn_2O_5As_2Me_4^+$		699 (6)	
$RCl_2Sn_2(O_2AsMe_2)_2^+$			659 (2)
$Cl_2Sn_2(O_2AsMe_2)_2OMe^+$			613 (3)
$RSn_2O_5As_2Me_4^+$		585 (3)	
$Cl_2Sn_2(O_2AsMe_2)O_2AsMe^+$			567 (3)
$RCl_2HSn_2O_2AsMe_2$		503 (2)	
$RSn(O_2AsMe)_2^+$		451 (1)	471 (4)
$Sn(O_2AsMe_2)_2OMe^+$			425 (2)
$R_2SnO_2AsMe_2^+$	411 (100)		
$R_2ClSnO_2AsMe^+$		391 (5)	
$RClSn(O_2AsMe_2)^+$		349 (7)	369 (2)
R_3Sn^+	351 (2)	291 (3)	351 (4)
R_2ClSn^+		269 (27)	309 (76)
RCl_2Sn^+		247 (43)	267 (12)
$Sn(O_2AsMe_2)^+$	257 (26)	257 (13)	257 (3)
$RClSn^+$		212 (48)	232 (19)
RMe_2Sn^+	227 (10)		
RSn^+	197 (10)	177 (5)	197 (17)
$SnCl_2^+$		190 (7)	
$SnCl^+$		155 (48)	
R_2^+	154 (6)		154 (100)
$HO_2AsMe_2^+$		138 (4)	
$O_2AsMe_2^+$			137 (6)
$MeSn^+$	135 (1)		
SnH^+		121 (14)	
Sn^+	120 (5)		120 (10)
AsO_2^+, $HOAsMe^+$			107 (54)
AsO^+, $HAsMe^+$	91 (8)	91 (4)	91 (10)
R^+	77 (11)	57 (100)	77 (65)

The band at 493 cm^{-1} in the Raman spectrum of **3** is attributed to ν_s(Sn-O-Sn). The region of 480-530 cm^{-1} is given for ν(Sn-O-Sn) modes in dimeric compounds containing bridging alkoxy groups [13]. The Sn-Ph vibrations in phenyltin compounds fall within the 200-300 cm^{-1} range [14]. Consequently, the bands at 286 cm^{-1} and at 211 cm^{-1} in the Raman spectrum of **1** are assigned to $\nu_{as}(SnPh_3)$ and $\nu_s(SnPh_3)$, respectively, and the band at 220 cm^{-1} in the Raman spectrum of **3** is ascribed to the ν(Sn-Ph) in-phase vibration. The ν(SnCl) vibrations in the Raman spectra of **2** and **3** are assigned by comparison with ν(SnCl) in the spectra of [$R_2ClSn(O_2AsMe_2)$], [$PhClSn(O_2PPh_2)(\mu\text{-}OMe)]_2$, and with consideration of the Sn-Cl bond length from X-ray data [6, 9]. Accordingly, the band at 228 cm^{-1} and 296 cm^{-1} are attributed to ν(SnCl) in **2** and **3**, respectively.

Mass Spectra

Table 2 gives the principal peaks in the EI mass spectra (70 eV) of the compounds **1**, **2**, and **3**.

The molecular ion of the monomer is absent but the mass spectrum of **1** exhibits the molecular ion minus phenyl radical ($Ph_2SnO_2AsMe_2^+$) as a base peak. Related triphenyltin diorganophosphinates similarly show ($Ph_2SnO_2PR_2^+$) (R = Me, Ph) as base peaks [11]. The molecular ion of **2** minus butyl group and that of **3** minus phenyl group appear also in the spectra of **2** and **3** respectively. However Bu^+ and Ph_2^+ represent the base peaks of **2** and **3**, respectively. The mass spectra of **2** and **3** show chlorine containing fragments RCl_2Sn^+, R_2ClSn^+ and $RClSn^+$ (R = Bu or Ph) with relatively high abundance compared with R_3Sn^+ and RSn^+ suggesting the greater ease with which Sn-C bonds are cleaved compared with Sn-Cl bonds. In harmony herewith molecular ions minus chlorine are not observed in the spectra of **2** and **3**. The peaks at 227 and 135 in the mass spectrum of **1** are assigned to the ions $PhMe_2Sn^+$ and $MeSn^+$, respectively. The appearance of such peaks can be considered as an indication for methyl groups transfer.

The mass spectra of **1**, **2**, **3**, and [$Et_2ClSn(O_2AsMe_2)$] [6] display peaks due to the ion $Sn(O_2AsMe_2)^+$. On the other hand, the mass spectra of many organotin diorganophosphinates such as [$Et_2ClSn(O_2PMe_2)$] [7] and [$Bu_2Sn(O_2PR_2)_2$] (R = Me, Ph) [12] exhibit the analogous $Sn(O_2PR_2)^+$ ions as base peaks. The spectrum of **2** shows $BuCl_2HSn_2O_2AsMe_2^+$ and SnH^+ ions which may be formed by β-hydrogen elimination.

Structural results

Compounds of type [$R_3Sn(O_2ER'_2)$] have been investigated structurally for E = phosphorus [15−19], whereas for arsen only an analogous hydrogen arsenate is reported, composed of $[R_3SnO_2AsOOH]^{2-}$ units [20]. Apparently the array of the O-Sn-O-E chain links depends largely on the volume of the substituents at atom E. With big ligands the chains tend to close to ring systems of various sizes [15−17], which also holds for polymers in which Ph_3Sn groups are linked by transition metalates [21]. They can also evade sterical stress coiling to helices [19], and when the the substituents R′ are methyl groups, too, a helix results [20]. The arsinate **1**, in which longer As-O distances give additional space, forms infinite chains of almost collinear O-Sn-O units, with a bond angle of 178°, linked by O-As-O bridges with angles of 106°, all pointing in the same direction (Fig.1). The phenyl groups at the tin atom do not allow for an alternating orientation of the AsO_2 bridges as found in $[Me_3Sn(O_2PMe_2)]$ for the PO_2 motifs [20]. This chain configuration forces phenyl group 3 (C31 to C36) into a position nearly coplanar with the equatorial plane at the tin atom (the angle of the two planes is 3.5°) − the other phenyl groups are set at 85.9° (C21 to C26) and 66.4° (C21 to C26) to the plane SnC_3. Bond lengths and angles are dependent on structural tension in the chains. In the phosphinates Sn-O bond lengths as well as O-P-O angles decrease slightly from the four-membered rings [15, 16] (224-227 pm, 117°) to the six-membered ring and the open chains [17, 19] (220-221 pm, 115-117°) with decreasing chain stress. In **1** both values are found very low (Tab.3), indicating an essentially unstressed system.

Replacement of one organic substituent R in the formula $[R_3Sn(O_2ER'_2)]$ by a chloro ligand gives a class of compounds, some structures of which are already known for E=P and As [6, 7]. With methyl groups at at the tin and arsen atoms parallel chains with strong intermolecular interactions are formed, whereas in the diethyltin compound the structure is governed by intramolecular forces, leading to strongly folded chains [6]. Chlorodibutyltindimethylarsinate (**2**) is isostructural to the diethyl compound − it crystallizes in the space group $P2_1/m$ with the polymer chain lying in the mirror plane and running along the x-direction (Fig. 2). Same as in $[Et_2ClSn(O_2AsMe_2)]$ an extremely short Sn-O bond (Sn-O(2), 203 pm) is found for one oxygen atom, caused by a *trans* interaction with the loose contact of the tin atom with O(2)′ of the next asymmetric unit (Sn−O(2)′ 307 pm) (Table 4). Alternating [O-Sn−O-Sn−] motifs like this are well known from analogous carboxylates [22, 23], where the Sn-O distances are more equalized. The bond Sn-Cl (259 pm) is slightly shorter than in $[Et_2ClSn(O_2AsMe_2)]$, (Sn-Cl 262 pm) [6], which correlates with the weaker interaction Sn−O(2)′ (307 pm compared with 304 pm in the diethyl compound).

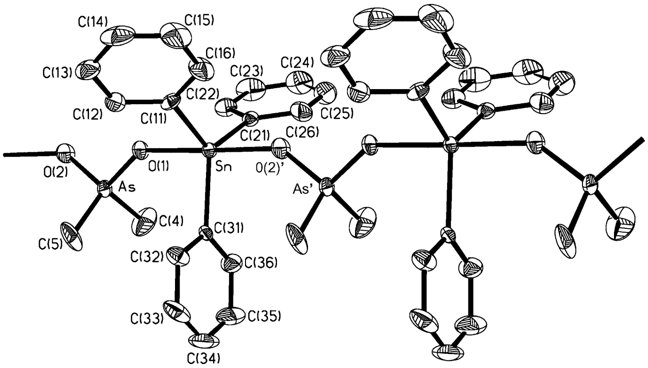

Fig. 1 Perspective view [27] of a section of the chains in **1**. Atom numbering is given for the asymmetric unit and for some adjacent atoms (probability level 50 %).

Table 3 Bond lengths/pm and angles/° for $[Ph_3Sn(O_2AsMe_2)]$ (**1**)

Sn-C(11)	215.2(2)	C(11)-Sn-C(21)	122.4(1)
Sn-C(21)	216.6(2)	C(11)-Sn-C(31)	118.3(1)
Sn-C(31)	215.2(2)	C(21)-Sn-C(31)	119.3(1)
Sn-O(1)	216.5(4)	C(11)-Sn-O(1)	89.1(2)
Sn-O(2)′	217.1(4)	C(11)-Sn-O(2)′	89.2(2)
As-O(1)	167.3(4)	C(21)-Sn-O(1)	91.6(1)
As-O(2)	166.0(4)	C(21)-Sn-O(2)′	88.9(1)
As-C(4)	188.0(5)	C(31)-Sn-O(1)	91.1(1)
As-C(5)	192.1(6)	C(31)-Sn-O(2)′	90.1(2)
		O(1)-Sn-O(2)′	178.3(2)
		O(1)-As-O(2)	106.4(2)
		O(1)-As-C(4)	110.7(2)
		O(1)-As-C(5)	109.5(3)
		O(2)-As-C(4)	112.0(2)
		O(2)-As-C(5)	109.0(3)
		C(4)-As-C(5)	109.2(3)
		As-O(1)-Sn	141.0(2)
		As′-O(2)′-Sn	143.6(2)

Symmetry transformations used to generate equivalent atoms (see figure 1):
El′ −1+x, y, z

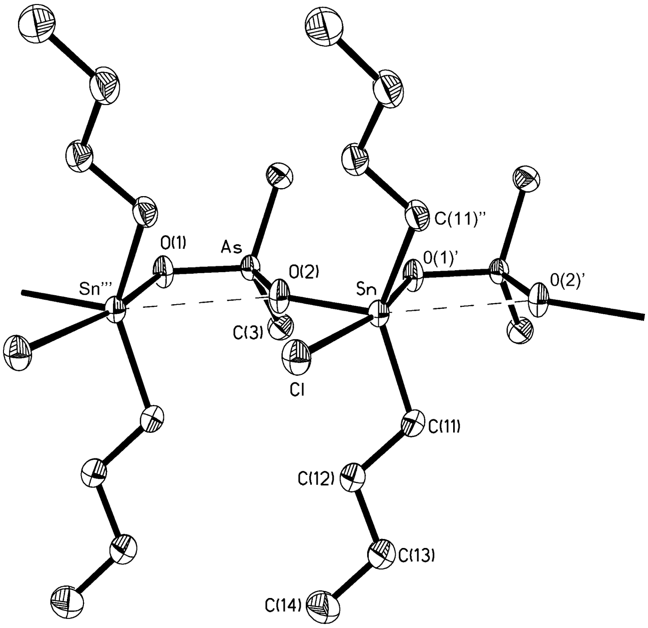

Fig. 2 ORTEP view [27] of two asymmetric units of **2** and the equivalents generated by the mirror plane (thermal ellipsoids drawn at 50 % level).

Table 4 Bond lengths/pm and angles/° for $[(n\text{-}Bu)_2ClSn(O_2AsMe_2)]$ (**2**)

Sn-O(1)′	218.2(2)	O(1)′-Sn-O(2)	82.93(8)
Sn-O(2)	203.1(2)	O(1)′-Sn-C(11)	94.80(6)
Sn‴-O(2)	306.7(2)	O(1)′-Sn-Cl	164.72(6)
Sn-C(11)	213.3(2)	O(2)-Sn-C(11)	110.93(6)
Sn-Cl	258.77(7)	O(2)-Sn-Cl	81.78(6)
As-O(1)	168.4(2)	C(11)-Sn-C(11)″	137.9(1)
As-O(2)	170.2(2)	C(11)-Sn-Cl	90.66(6)
As-C(3)	190.3(2)	Sn-O(1)′-As′	117.8(1)
C(12)-C(13)	152.4(3)	Sn-O(2)-As	136.9(1)
C(11)-C(12)	152.4(3)	Sn-C(11)-C(12)	115.8(1)
C(13)-C(14)	152.7(4)	C(11)-C(12)-C(13)	112.0(2)
		C(12)-C(13)-C(14)	112.8(2)
		O(1)-As-O(2)	102.0(1)
		O(1)-As-C(3)	111.21(8)
		O(2)-As-C(3)	110.28(8)
		C(3)-As-C(3)″	111.5(1)

Symmetry transformations used to generate equivalent atoms:
El′ x−1, y, zEl″ x, 1.5−y, z

Cleaving off one substituent R from the unit [$R_2ClSn(O_2AsMe_2)$] (e.g. for R = Ph, leaving as benzene) gives a chain closing to a centrosymmetric dimer of the formula [$RClSn(O_2AsR'_2)(\mu\text{-}OMe)]_2$ (**3**) with $(Sn\text{-}O\text{-}As\text{-}O)_2$ 8-membered rings, in which the charge defect at the tin atom is made up for by methanolate bridges (Fig. 3) as found for the corresponding phosporus compound [9]. They originate from the solvent methanol which provides the proton for the leaving hydrocarbon. Tin and oxygen atoms are coplanar with a maximal deviation of 16 pm of the best plane from which the arsen atoms have a distance of 56 pm. The coordination polyhedron of the tin atom is a distorted octahedron in which by the asymmetry of the methanolate bridges one of the Sn-O bond lengths is 217 pm compared with 210 pm of the others and accounts for the relatively short Sn-Cl bond (242 pm) (cf. **2**) in *trans* position. Like in the analogous phosphinate the bridging O atom has a pyramidal configuration with a sum of the bond angles of 348° (bond lengths and angles are summarized in Table 5).

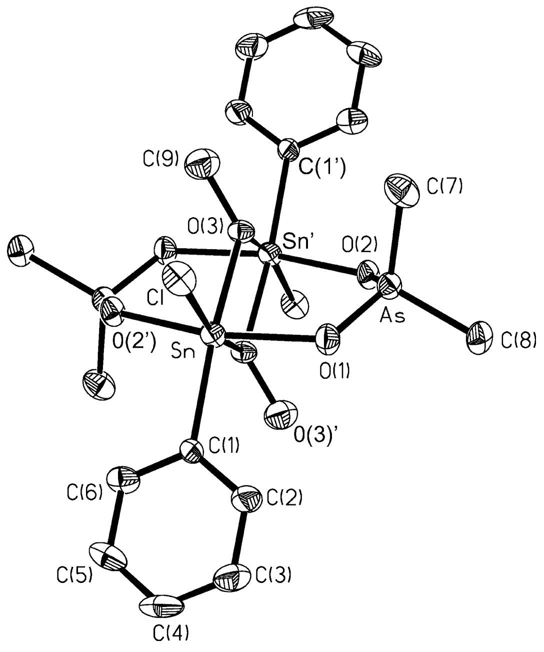

Fig. 3 Perspective view of a dimer of **3** [27]. Atoms of the asymmetric unit are numbered along with some relevant equivalent atoms (all atoms drawn as 50 % probability ellipsoids).

3 Experimental Section

The chemical reagents employed were obtained from commercial sources and were used without further purification. $Na(O_2AsMe_2)$ was formed by treating HO_2AsMe_2 with an equimolar amount of sodium methoxide in methanol and used as methanol solution.

Infrared spectra were measured using KBr pellets on a Bruker instrument IFS 88. The Raman spectra were recorded using a Jobin Yvon Labram HR 800 instrument with 632.8 nm helium neon Laser excitation.

Mass spectra were measured on Varian MAT CH 7A (EI 70 eV) (**1**) and on Finnigan MAT S (**2**, **3**).

Table 5 Bond lengths/pm and angles/° for [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**3**)

Sn-O(1)	210.4(4)	O(1)-Sn-O(2)′	163.7(2)
Sn-O(2)′	209.5(4)	O(1)-Sn-O(3)	82.1(2)
Sn-O(3)	210.7(4)	O(1)-Sn-O(3)′	85.3(2)
Sn-O(3)′	217.4(5)	O(2)′-Sn-O(3)	83.7(2)
Sn-C(1)	214.8(3)	O(2)′-Sn-O(3)′	83.3(2)
Sn-Cl	242.1(2)	O(3)-Sn-O(3)′	74.5(2)
As-O(1)	168.3(5)	O(1)-Sn-C(1)	95.7(2)
As-O(2)	169.7(4)	O(2)′-Sn-C(1)	96.8(2)
As-C(7)	190.0(8)	O(3)-Sn-C(1)	169.2(2)
As-C(8)	190.0(7)	O(3)′-Sn-C(1)	94.8(2)
O(3)-C(9)	146.6(9)	O(1)-Sn-Cl	94.0(2)
		O(2)′-Sn-Cl	94.1(2)
		O(3)-Sn-Cl	91.1(1)
		O(3)′-Sn-Cl	165.6(1)
		C(1)-Sn-Cl	99.6(2)
		O(1)-As-O(2)	113.3(2)
		O(1)-As-C(7)	110.8(3)
		O(1)-As-C(8)	106.2(3)
		O(2)-As-C(7)	110.4(3)
		O(2)-As-C(8)	106.2(3)
		C(7)-As-C(8)	109.7(3)
		C(9)-O(3)-Sn	122.5(4)
		C(9)-O(3)-Sn′	120.1(4)
		Sn-O(3)-Sn′	105.5(2)
		As-O(2)-Sn′	124.4(3)
		As-O(1)-Sn	125.1(2)

Symmetry transformation used to generate equivalent atoms:
El′ 1−x, 1−y, 1−z

Synthesis of [$Ph_3Sn(O_2AsMe_2)$] (1)

A solution of 0.11 g $Na(O_2AsMe_2)$ (0.70 mmol) in 5 mL methanol was added to 0.27 g (0.70 mmol) Ph_3SnCl in 15 mL methanol. After one week a precipitate was formed, which was filtered off and the mother liquor was set aside in an open flask. After one week crystals of [$Ph_3Sn(O_2AsMe_2)$] (**1**) (10 mg) were formed and filtered off.

Synthesis of [$Bu_2ClSn(O_2AsMe_2)$] (2)

A solution of 0.5 g (3.6 mmol) HO_2AsMe_2 in 10 mL methanol was added to 0.6 g (2.0 mmol) Bu_2SnCl_2 in 15 mL methanol. After two weeks a very small quantity of crystalline substance was formed, which was filtered off. The filtrate was set aside in an open flask at ambient temperature. After two days crystals of [$Bu_2ClSn(O_2AsMe_2)$] (**2**) were formed and filtered off (250 mg).

Synthesis of [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (3)

A solution of 0.26 g (1.6 mmol) of NaO_2AsMe_2 in 10 mL methanol was added to 0.56 g (1.6 mmol) of Ph_2SnCl_2 in 20 mL methanol. Directly after the addition a precipitate was formed. After one week the precipitate was filtered off and the mother liquor was set aside in an open flask at ambient temperature.

After nine days small crystals of [$PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**3**) (40 mg) were formed and filtered off.

X-ray structural investigations

Single crystals selected from the reaction products described above were handled in oil, mounted on glass threads and measured at −80 °C on Stoe diffractometers IPDS I (**1** and **3**) and IPDS II (**2**). Crystal data, experimental details and details about structure solution and refinement are comprehended in table 6. After data reduction [24] the reflections were subjected to absorption correction (numerical (**2**) and with equivalent reflections (**1**, **3**)). The structures were solved with direct methods (**1**, **2**) [25] and with the aid of Patterson syntheses (**3**) [25], and the models were refined by

Table 6 Crystal data, measurement, and structure refinement details for **1, 2,** and **3**

	1	**2**	**3**
Formula	$[Ph_3Sn(O_2AsMe_2)]$	$[(n\text{-}Bu)_2ClSn(O_2AsMe_2)]$	$[PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$
Formula weight	486.98	405.32	399.26
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/m$	$P\bar{1}$
a / pm	699.8(1)	480.6(1)	822.8(2)
b / pm	1961.4(2)	1992.7(2)	910.4(2)
c / pm	1433.6(2)	808.8(1)	929.2(2)
α /deg			77.04(3)
ß / deg	95.174(13)	103.726(5)	82.35(3)
γ / deg			68.69(3)
V / pm^3 x 10^{-4}	1959.7(4)	752.4(1)	630.9(3)
Cell determination	7166 (Θ 2.0 to 25.8)	10047	2775 (Θ 2.2 to 25.7)
ρ_{calc} / g x cm^{-3}	1.651	1.789	2.102
Z	4	2	2
F(000)	960	400	384
μ (MoK$_\alpha$) / cm^{-1}	29.88 cm^{-1}	40.41	48.24
Diffractometer type	IPDS I (Stoe)	IPDS II (Stoe)	IPDS I (Stoe)
Wavelength / pm	71.073	71.073	71.073
T / K	193(2)	192(2)	193(2)
Scan mode	phi scans	omega-scans	phi scans
hkl range	$-8 \le h \le 8$, $-23 \le k \le 24$, $-17 \le l \le 17$	$-6 \le h \le 6$, $-27 \le k \le 27$, $-11 \le l \le 10$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-11 \le l \le 10$
Theta range for data collection	1.76 to 25.99	2.04 to 29.28°	2.25 to 26.05°
Reflections collected	15312	11619	6289
Independent reflections	3809 [R(int)=0.1115)]	2089 [R(int)=0.0336]	2309 [R(int)=0.0817]
Reflections used for refinement	3809	2089	2309
Observed reflections	2223 [I>2sigma(I)]	1849 [I>2sigme(I)]	1398 [I>2sigme(I)]
Absorption correction	based on equivalent reflections	face-indexed	based on equivalent reflections
Programs used	XCAD4[24], SHELXS-97, SHELXL-97[25], PLATON[26], SHELXTL[27],		
Solution	Direct Methods/difmap	Direct Methods/difmap	Patterson Methods/difmap
Refinement	Full-matrix least-squares on F^2		
refined parameters	188	90	131
wR2 [all reflections]	0.0597	0.0444	0.0626
R1 [I>2sigma(I)]	0.0343	0.0211	0.0363
(shift/error)$_{max}$	0.002	0.018	-0.002
ρ_{fin} (max/min) / eÅ^{-1}	0.638/−0.525	0.385/−1.025	0.731/−0.799

successive refinement cycles and difference Fourier syntheses [25]. Hydrogen atoms were introduced into the models as part of rigid groups. Geometrical calculations were carried out by PLATON [26].

Crystallographic data (excluding structure Factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nrs. CCDC-659567 (**1**), CCDC-659568 (**2**), and CCDC-659569 (**3**). Details are available, free of charge, on application to CCDC, 12 Uniion Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk)

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