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Crystal Structures of $[Bu_2Sn(O_2PPh_2)_2]$, $[Ph_2Sn(O_2PPh_2)_2]$, and $[PhClSn(O_2PPh_2)OMe]_2$. Raman Spectra of $[Ph_2Sn(O_2PPh_2)_2]$ and $[PhClSn(O_2PPh_2)OMe]_2$

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Abstract. $[(n\text{-}Bu)_2Sn(O_2PPh_2)_2]$ (**1**), and $[Ph_2Sn(O_2PPh_2)_2]$ (**2**) have been synthesized by the reactions of R_2SnCl_2 (R=n-Bu, Ph) with HO_2PPh_2 in Methanol. From the reaction of Ph_2SnCl_2 with diphenylphosphinic acid a third product $[PhClSn(O_2PPh_2)OMe]_2$ (**3**) could be isolated. X-ray diffraction studies show **1** to crystallize in the monoclinic space group $P2_1/c$ with a = 1303.7(1) pm, b = 2286.9(2) pm, c = 1063.1(1) pm, β = 94.383(6)°, and Z = 4. **2** crystallizes triclinic in the space group $P\bar{1}$, the cell parameters being a = 1293.2(2) pm, b = 1478.5(4) pm, c = 1507.2(3) pm, α = 98.86(3)°, β = 109.63(2)°, γ = 114.88(2)°, and Z = 2. Both compounds form arrays of eight-membered rings $(SnOPO)_2$ linked at the tin atoms to form chains of infinite length. The dimer **3** consists of a like ring, in which the tin atoms are bridged by methoxo groups. It crystallizes triclinic in space group $P\bar{1}$ with a = 946.4(1) pm, b = 963.7(1) pm, c = 1174.2(1) pm, α = 82.495(6)°, β = 66.451(6)°, γ = 74.922(6)°, and Z = 1 for the dimer. The Raman spectra of **2** and **3** are given and discussed.

Keywords: Tin; Crystal structure; Raman spectra; Diphenylphosphinates; Methoxo bridges

1 Introduction

Organotin complexes with ligands derived from phosphorus-based acids have attracted considerable attention due to their structural diversity as well as their possible applications as catalysts and biocides [1].

Diorganotin bis(diorganophosphinates) $[R_2Sn(O_2PRR'_2)_2]$ (R,R′= alkyl, aryl) have been synthesized by a variety of methods including among others the treatment of R_2SnCl_2 with sodium or ammonium salts of the phosphinic acids and condensation of R_2SnO with HO_2PR_2 [1]. Diorganotin bis(diorganophosphinates) obtained from such reactions are usually high melting powders and insoluble in organic solvents .

We have found that crystals suitable for X-ray crystallographic studies can be isolated from the reactions of R_2SnCl_2 with HO_2PR_2 in methanol at ambient temperature. Accordingly, the crystal structures of $[Me_2Sn(O_2PPh_2)_2]$ [2], $[Et_2Sn(O_2PPh_2)_2]$ [3], $[Et_2Sn(O_2PMe_2)_2]$, and $[Ph_2Sn(O_2PMe_2)_2]$ [4] have been determined.

In these polymeric compounds the diorganophosphinate groups behave as bidentate bridges between the tin atoms leading to $(SnOPO)_4$ sixteen-membered rings for $[Et_2Sn(O_2PMe_2)_2]$ and to $(SnOPO)_2$ eight-membered rings for $[R_2Sn(O_2PPh_2)_2]$ (R = Me, Et) and $[Ph_2Sn(O_2PMe_2)_2]$. Similar polymeric structures with O_2PR_2 double bridges and $(PbOPO)_2$ eight-memebered rings were also found in analogous organolead compounds $[Ph_2Pb(O_2PMe_2)_2]$ and $[Ph_2Pb(O_2PPh_2)_2]$ [2]. By contrast, crystal structures of dimethyltin bis(dialkyldithiophosphinates) $[Me_2Sn(S_2PR_2)_2]$ (R = Me [5], Et [6]) show monomeric distorted octahedral configuration with chealating anisobidentate $S_2PR_2^-$ ligands.

X-ray diffraction studies of triorganotin diorganophosphinates show that $[R_3SnO_2PR_2]$ exhibit chain polymeric structures for $[Me_3SnO_2PMe_2]$ [7] and $[Bu_3SnO_2PPh_2]$ [8] and a tetrameric structure for $[Me_3SnO_2PPh_2]$ [9] and the related lead complex $[Me_3PbO_2PPh_2]$ [10]. The R_3M (M = Sn, Pb) groups are axially bridged by O-P-O linkages to form trigonal bipyramids at the metal atoms. Moreover, chain polymeric structures with $OSPR_2$ bridges were also reported for $[Me_3SnOSPMe_2]$ [11] and $[Ph_3SnOSPPh_2]$ [12]. The chalcogen atoms are in apical positions in the resulting trigonal bipyramidal configuration.

Continuing our work on the preparation and structural studies of organotin diorganophosphinates, we describe the synthesis and crystal structures of$[Bu_2Sn(O_2PPh_2)_2]$ (**1**),

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[$Ph_2Sn(O_2PPh_2)_2$] (**2**), and [$PhClSn(O_2PPh_2)OMe$]$_2$ (**3**). The Raman spectra of **2** and **3** are given and discussed.

Table 1 Raman frequencies (1200−100 cm^{-1}) of **2** and **3**

[$Ph_2Sn(O_2PPh_2)_2$] (**2**)	[$PhClSn(O_2PPh_2)OMe$]$_2$ (**3**)	
1195 vw		δ(CH)-Ph in-plane
1180 vw		
1155 vw	1161 w	
1139 s		νas(PO_2) in-phase
1134 w	1127 w	δ(CH)-Ph in-plane
1083 vw		
1073 vw	1076 w	
1066 vw		
1026 s	1030 w	νs(PO_2)
1020 vw	1021 vw	δ(CH)-Ph in-plane
	1004 w	ν($O\text{-}CH_3$)
1003 vs	998 vs	Ph ring breathing
997 s		
843 vw		
757 vw	753 vw	δ(CH)-Ph out-of-plane
	736 vw	
730 vw	729 vw	
723 vw		
700 m-s	704 w	
697 m-s	696 w	
668 vw		
657 s	662 s	δ(C-C) out-of-plane
617 m	618 w-m	(C-C-C) bend in-plane
	616 w	δ(CH)-Ph out-of-plane
	555 vw	
545 vw	543 w	
	480 w	ν(Sn-O-Sn)
466 vw		
458 vw		
446 vw	434 vw	δ(PO_2)
	412 w	
403 vw	401 w	
395 vw	393 vw	
350 vw	366 vw	δ(CPO)
	338 w	
	313 s	ν(Sn-Cl)
291 vw		
	273 m	
260 vw	254 w	
244 vw		
233 vw	229 vw	
221 w		νs($SnPh_2$)
	215 w	ν(SnPh) in-phase
208 w-m	196 w	
	191 w	δ(SnO_2) δ(SnPh) δ(PPh)
	183 m	
	173 s	
157m	147 w	
136 w	140 w	

2 Results and Discussion

Treatment of Bu_2SnCl_2 with HO_2PPh_2 in methanol at ambient temperature gave [$Bu_2Sn(O_2PPh_2)_2$] (**1**) (eq.(1)) as white needles. The reaction of Ph_2SnCl_2 with HO_2PPh_2 under similar conditions afforded needle-like crystals of [$Ph_2Sn(O_2PPh_2)_2$] (**2**) (eq.(1)) along with [$PhClSn(O_2PPh_2)$-OMe]$_2$ (**3**) (eq.(2)) crystallizing as colorless blocks. Crystals suitable for X-ray structure determination were isolated from these reactions.

$$R_2SnCl_2 + 2\ HO_2PPh_2 \rightarrow [R_2Sn(O_2PPh_2)_2] + 2\ HCl\ (R = n\text{-}Bu, Ph) \quad (1)$$

$$2\ Ph_2SnCl_2 + 2\ HO_2PPh_2 + 2\ HOMe \rightarrow [PhClSn(O_2PPh_2)OMe]_2\ (\mathbf{3}) + 2\ HPh + 2\ HCl \quad (2)$$

[$R_2Sn(O_2PPh_2)_2$] (R = Bu, Ph) can be synthesized by treatment of R_2SnCl_2 with the sodium [13] or ammonium [14] salts of diphenylphosphinic acid and by oxidation of $R_2Sn(PPh_3)_2$ with an ethanolic solution of H_2O_2 [15]. In addition, **1** can also be prepared by the reaction of $Bu_2Sn(OCOMe)_2$ with Ph_2POCl in toluene [16] and by the reaction of$Bu_2SnCl_2$with $NMe_4O_2PPh_2.H_2O$ in ethanol [17].

It is worth noting, that on the basis of Mössbauer and vibrational spectra chain polymeric structures, with bridging O_2PPh_2 ligands and octahedral geometry around tin have been suggested for **1** and **2** [14, 16−18].

The formation of [$PhClSn(O_2PPh_2)OMe$]$_2$ (**3**) indicates that Sn-Cl and Sn-C bonds of Ph_2SnCl_2 are cleaved. In our previous studies on the reactions of HO_2PMe_2 with Ph_2SnCl_2 [4] as well as HO_2PPh_2 with R_2SnCl_2 (R = Me [2], Et [3]), fission of only Sn-Cl bonds has been observed leading to the corresponding diorganotin bis(diorganophosphinates). Consequently, the Sn-Cl bonds are cleaved favorably compared to the Sn-C bonds in such acidolysis reactions.

On the other hand, the reaction of Ph_3PbCl with HO_2PMe_2 and HO_2PPh_2 in methanol cause break of Pb-Cl and Pb-C bonds to give [$Ph_2Pb(O_2PMe_2)_2$] and [$Ph_2Pb(O_2PPh_2)_2$], respectively [2].

Raman Spectra

The IR and Raman spectra of [$Bu_2Sn(O_2PPh_2)_2$] (**1**) were previously given and discussed [16]. The observed Raman frequencies (1200-100 cm^{-1}) of **2** and **3** (Table 1) are assigned by comparison with the Raman spectra of [$Ph_3SnO_2PPh_2$] [19], [$Bu_2Sn(O_2PPh_2)_2$] [16] and other related organotin complexes [3, 8].

The ν(PO_2) frequencies are assigned in the region between 1200-1000 cm^{-1} which is consistent with bidentate bridge O_2PPh_2 ligands. The bands at 1004, 480 and 313 cm^{-1} in the Raman spectrum of **3** are ascribed to ν($O\text{-}CH_3$), ν(Sn-O-Sn) and ν(Sn-Cl), respectively. The absence of these bands in the Raman spectrum of **2** supports this assignment. The Raman spectrum of the dimeric complex [$Sn_2Cl_6(OH)_2(H_2O)_2$].$4H_2O$ shows ν(Sn-O-Sn) at 482 cm^{-1} [20]. The region of 480 to 530 cm^{-1} is given for such ν(Sn-O-Sn) modes in the dimeric compounds containing bridging alkoxy groups [21].

The Raman spectra of **2** and **3** display the characteristic very strong bands due to the phenyl ring breathing at 1003 and 998 cm^{-1}, respectively. The bands at 617 cm^{-1} in the Raman spectrum of **2** and at 618 cm^{-1} in the Raman spectrum of **3** are assigned to the phenyl (C-C-C) bending-in-plane vibrations.

Corresponding modes appear at 618-621 cm^{-1} in the Raman spectra of [Ph_3SnO_2PRR'] (RR′ = Me_2, MePh, Ph_2) [19], [$Bu_2Sn(O_2PRR')_2$] (RR′ = MePh, Ph_2) [16], [$Et_2Sn(O_2PPh_2)_2$] [3], and $Bu_3SnO_2PPh_2$ [8].

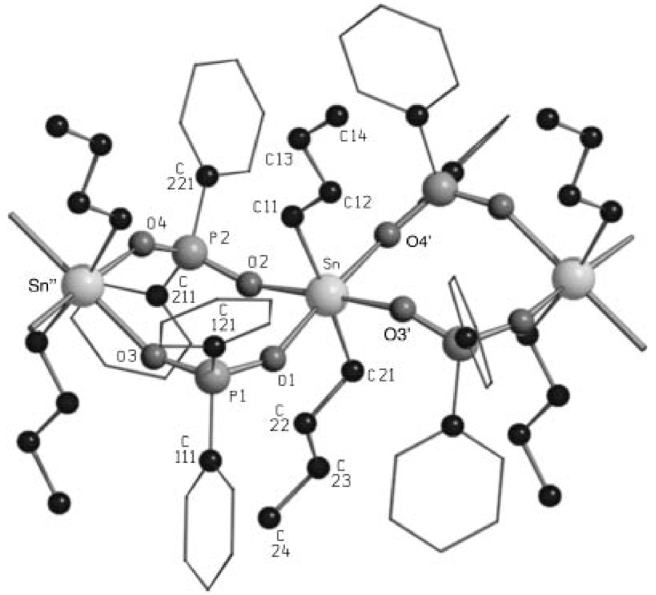

Figure 1 Perspective view [27] of a section of a chain in **1**. Atom-numbering is given for the asymmetric unit excepting phenyl groups

The band at 221 cm^{-1} in the Raman spectrum of **2** is attributed to $\nu_s(SnPh_2)$ and the band at 215 cm^{-1} in the Raman spectrum of **3** is assigned to $\nu(SnPh)$ in-phase. The $\nu_{as}(SnPh_2)$ of the trans $SnPh_2$ group in **2** and the $\nu(SnPh)$ out-of-phase in the centrosymmetric dimer **3** are Raman inactive.

Structural results

In the diorgano tin phosphinates with eight-membered ring chain structures reported in the past [2−4] three structural types occur with the chains running along or parallel to cell edges, principally differing in the positions of the heavy atoms and the ring conformations. Compounds **1** and **2** represent two new types, one of them also containing chains parallel to the c-axis (**1**), the other being distinguished by chains along space diagonal [111] (**2**).

In **1**, which more resembles the species already known, the tin atoms lie on general positions close to the c glide plane, so the eight-membered rings are generated by glide reflection of the asymmetric unit $[R_2Sn(O_2PR_2)_2]$, leading to a distorted boat conformation with the SnO_4 best planes tilted against each other by an angle of about 47.3 degrees (see Fig 1). Somewhat unexpectedly the best planes of the n-butyl groups do not meet at a right angle like the phenyl substituents in some cases [2, 4] nor are parallel like ethyl and phenyl groups in other examples [2, 3], but are set at an angle of about 55.8°.

A somewhat remarkable arrangement of the chains is found in **2**. There are two different tin atom sites one of which (Sn(1)) lies on the origin of the triclinic cell, the other (Sn(2)) taking a general position close to $\frac{1}{3},\frac{1}{3},\frac{1}{3}$. As a result two kinds of rings with principally different, but similar chair-like conformation occur: ring 1 (see Fig. 2) connecting tin atoms Sn(1) and Sn(2), not subject to any nontrivial symmetry, and ring 2, centrosymmetric, connecting Sn(2) with its inverse equivalent. So the succession of rings in the chain along the the space diagonal of the unit cell is (ring 1, ring 2, ring1′ etc). Compared with the dibutyl tin compound ring bending is much weaker − the largest distance of a ring atom from the best planes is 35 pm, and the SnO_4 − planes of Sn(1) and Sn(2) just intersect with an angle of about 15.5°. Phenyl group order around the tin atoms is parallel at centrosymmetric Sn(1) and roughly rectangular (79,2°) at Sn(2).

In spite of strongly differing ring conformations most bond lengths in **1** and **2** are restricted to narrow ranges (tables 2 and 3). P-O distances range from 149.9 to 151.2 pm, Sn-C distances are between 212.3 pm (aliphatic)

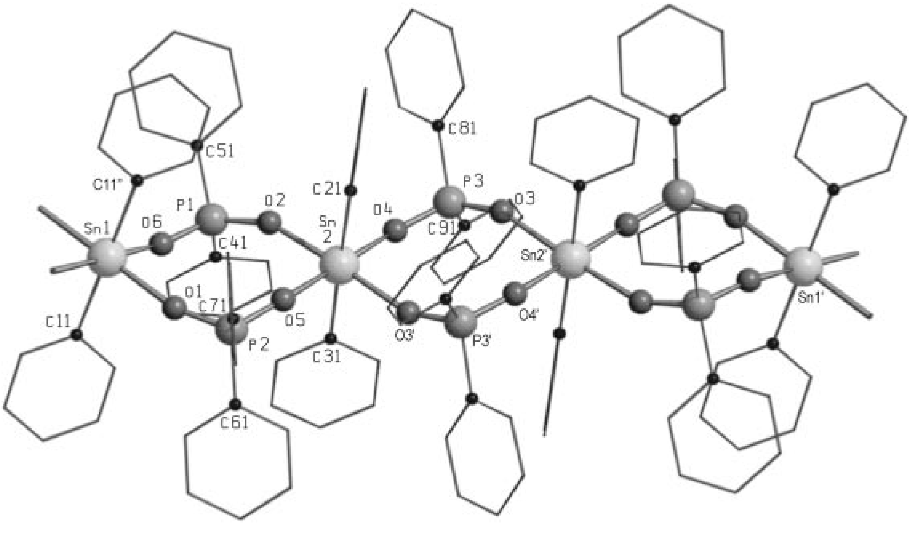

Figure 2 Succession of rings in the unit cell of **2** [27], a straight line Sn(1)-Sn(1)′ denoting space diagonal [111]. Atom numbering is given for an asymmetric unit and for some transformed atoms. For clarity phenyl substituents are drawn as simple hexagons.

Table 2 Selected bond lengths/pm and angles/° for $Bu_2Sn(O_2PPh_2)_2$ (**1**).

Sn-O(1)	220.4(3)	O(1)-Sn-O(2)	92.59(11)
Sn-O(2)	222.1(3)	O(1)-Sn-O(3)′	85.81(11)
Sn-O(3)′	219.3(3)	O(1)-Sn-O(4)′	176.00(11)
Sn-O(4)′	222.3(3)	O(2)-Sn-O(3)′	178.12(12)
Sn-C(11)	212.3(4)	O(2)-Sn-O(4)′	90.85(11)
Sn-C(21)	212.6(4)	O(3)′-Sn-O(4)′	90.72(11)
P(1)-O(1)	151.1(3)	C(11)-Sn-O(1)	91.47(14)
P(1)-O(3)	150.9(3)	C(11)-Sn-O(2)	88.18(13)
P(2)-O(2)	150.1(3)	C(11)-Sn-O(3)′	92.83(14)
P(2)-O(4)	150.3(3)	C(11)-Sn-O(4)′	90.68(14)
P(1)-C(111)	182.0(2)	C(21)-Sn-O(1)	90.49(15)
P(1)-C(121)	180.7(2)	C(21)-Sn-O(2)	83.88(14)
P(2)-C(211)	181.3(2)	C(21)-Sn-O(3)′	95.16(14)
P(2)-C(221)	181.3(3)	C(21)-Sn-O(4)′	87.84(15)
		C(11)-Sn-C(21)	171.9(2)
		P(1)-O(1)-Sn	150.2(2)
		P(1)-O(3)-Sn″	149.9(2)
		P(2)-O(2)-Sn	148.4(2)
		P(2)-O(4)-Sn″	148.8(2)
		C(12)-C(11)-Sn	117.6(3)
		C(22)-C(21)-Sn	114.7(3)
		O(1)-P(1)-O(3)	116.4(2)
		O(2)-P(2)-O(4)	117.8(2)
		C(111)-P(1)-C(121)	105.7(14)
		C(211)-P(2)-C(221)	105.3(2)

Symmetry transformations used to generate equivalent atoms:
El′ : x,−y+1/2,z+1/2 El″ : x,−y+1/2,z−1/2

Table 3 Selected bond lengths/pm and angles/° for $(Ph_2Sn)_3(O_2PPh_2)_6$ (**2**).

Sn(1)-O(1)	214.2(3)	O(1)-Sn(1)-O(6)″	91.78(11)
Sn(1)-O(6)	217.4(3)	O(1)-Sn(1)-O(6)	88.22(11)
Sn(2)-O(2)	217.8(3)	O(1)-Sn(1)-C(11)	87.88(10)
Sn(2)-O(3)′	218.0(3)	O(1)-Sn(1)-C(11)″	92.12(10)
Sn(2)-O(4)	218.9(3)	O(6)-Sn(1)-C(11)	87.70(9)
Sn(2)-O(5)	215.4(3)	O(6)″-Sn(1)-C(11)	92.30(9)
Sn(1)-C(11)	215.5(2)	O(5)-Sn(2)-O(2)	92.46(11)
Sn(2)-C(21)	215.0(2)	O(5)-Sn(2)-O(3)′	87.28(12)
Sn(2)-C(31)	213.1(2)	O(3)′-Sn(2)-O(4)	93.63(11)
P(1)-O(2)	151.2(3)	O(2)-Sn(2)-O(3)′	176.51(9)
P(1)-O(6)	150.4(3)	O(5)-Sn(2)-O(4)	178.83(10)
P(2)-O(5)	150.4(3)	O(2)-Sn(2)-O(4)	86.58(11)
P(2)-O(1)	149.9(3)	C(21)-Sn(2)-O(5)	88.45(9)
P(3)-O(3)	150.8(3)	C(21)-Sn(2)-O(4)	92.21(9)
P(3)-O(4)	150.6(3)	C(21)-Sn(2)-O(2)	89.66(9)
P(1)-C(41)	180.5(2)	C(21)-Sn(2)-O(3)′	93.81(9)
P(1)-C(51)	180.0(2)	C(31)-Sn(2)-O(2)	91.06(9)
P(2)-C(61)	180.0(2)	C(31)-Sn(2)-O(3)′	85.48(9)
P(2)-C(71)	180.9(2)	C(31)-Sn(2)-O(5)	92.93(9)
P(3)-C(81)	181.0(2)	C(31)-Sn(2)-O(4)	86.42(9)
P(3)-C(91)	180.8(2)		
C(31)-Sn(2)-C(21)	178.42(10)		
P(1)-O(6)-Sn(1)	154.9(2)		
P(1)-O(2)-Sn(2)	154.7(2)		
P(2)-O(5)-Sn(2)	158.3(2)		
P(2)-O(1)-Sn(1)	163.9(2)		
P(3)-O(4)-Sn(2)	151.8(2)		
P(3)-O(3)-Sn(2)′	157.5(2)		
O(6)-P(1)-O(2)	117.4(2)		
O(1)-P(2)-O(5)	116.3(2)		
O(4)-P(3)-O(3)	116.8(2)		
C(51)-P(1)-C(41)	106.49(13)		
C(61)-P(2)-C(71)	109.14(11)		
C(91)-P(3)-C(81)	103.98(11)		

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

Table 4 Selected bond lengths/pm and angles/° for $[PhClSn(O_2PPh_2)(OMe)]_2$ (**3**).

Sn-O(1)	211.71(12)	O(3)-Sn-O(2)	81.64(5)
Sn-O(2)	213.69(12)	O(1)-Sn-O(3)′	82.97(5)
Sn-O(3)	207.97(12)	O(2)-Sn-O(3)′	83.51(5)
Sn-O(3)′	216.13(13)	O(3)-Sn-O(1)	80.02(5)
Sn-Cl	239.30(5)	O(1)-Sn-O(2)	159.40(5)
Sn-C(11)	213.15(14)	O(3)-Sn-O(3)′	75.74(5)
P-O(1)′	153.15(13)	O(1)-Sn-Cl	94.00(4)
P-O(2)	153.21(14)	O(2)-Sn-Cl	95.89(4)
P-C(21)	180.8(2)	O(3)-Sn-Cl	91.87(4)
P-C(31)	179.9(2)	O(3)′-Sn-Cl	167.56(3)
O(3)-C(4)	144.5(2)	C(11) -Sn- O(1)	98.27(5)
		C(11)-Sn-O(2)	97.92(5)
		C(11)-Sn-O(3)′	93.17(5)
		C(11)-Sn-O(3)	168.89(5)
		C(11)-Sn-Cl	99.21(4)
		P′-O(1)-Sn	130.53(8)
		P-O(2)-Sn	126.63(7)
		C(4)-O(3)-Sn	123.96(11)
		C(4)-O(3)-Sn′	120.77(11)
		Sn-O(3)-Sn′	104.26(5)
		O(1)′-P-O(2)	116.76(7)
		O(1)′-P-C(21)	109.89(7)
		O(1)′-P-C(31)	106.50(6)
		O(2)-P-C(21)	108.15(7)
		O(2)-P-C(31)	107.88(6)
		C(31)-P-C(21)	107.26(6)

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

and 213.1 to 215.5 pm (aromatic), and P-C bonds have lengths from 179.9 to 182.0 pm, which are values in good accordance with the known species of $[R_2Sn(O_2PR_2{}')_2]_n$. An obvious exception is found for the Sn-O bonds which are significantly shorter in the phenyl compound **2** (214.2 to 218.9 pm) than in **1** (219.3 to 222.3 pm) which may be due to the electron-withdrawing power of the phenyl groups.

As shown by reaction schemes (1) and (2) Ph_2SnCl_2 reacts with HO_2PPh_2 not only to form [$Ph_2Sn(O_2PPh_2)_2$], but also undergoes a second reaction from which the dimeric $[PhClSn(O_2PPh_2)OMe]_2$ (**3**) results. Similar clusters have been prepared from n-$BuSn(OH)_2Cl$ and $(t\text{-}Bu)_2P(O)OH$ along with higher aggregated species [22] and from n-BuSn(O)OH and $(c\text{-}Hex)_2PO_2H$ as a mixture with other oligomers [23].

In the dimer **3** (Fig.3) two tin atoms related by an inversion centre are connected in bidentate fashion by two dimethyl phosphinate bridges and two methoxy groups, thus achieving a distorted octahedral coordination with axial angles of 159.5° (O(1)-Sn-O(2)), 168.9° (C11-Sn-O(3)), and 167.6° (Cl-Sn-O(3)′) (table 2). The phosphinates bridge almost symmetrically, whereas the Sn-O distances of the methoxo oxygen atoms differ significantly depending on the ligand in trans-position (208 and 216 pm (*trans* to the chloro ligand), respectively). As the corresponding bond lengths in related compounds with OH linked tin atoms [22, 23] are shorter and lie within a narrow range, this must be attributed to the *trans* effect of the chloro ligand. The centrosymmetric ring Sn_2O_2 is planar with pyramidal configuration at the oxygen atoms (sum of bond angles at oxy-

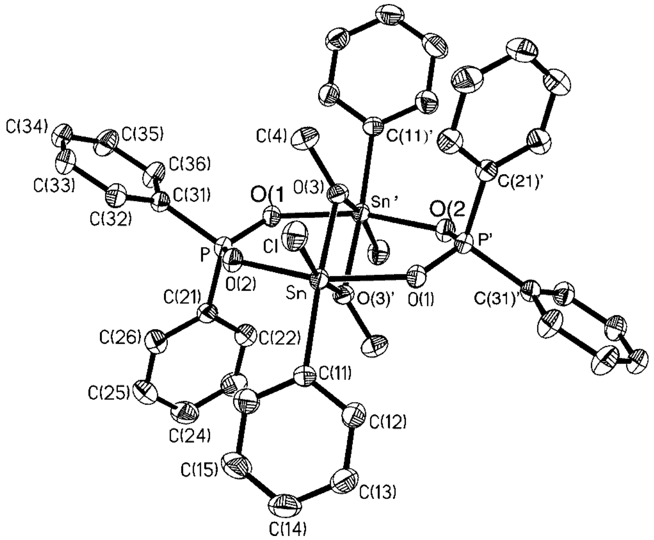

Figure 3 ORTEP perspective view [28] of a dimer of **3** at a 50 % probability level. Atoms of the asymmetric unit are numbered along with adjacent equivalent atoms.

gen is 349°), whilst in the eight-membered ring the maximal deviation of a ring atom from the best plane is 16 pm.

3 Experimental

The chemical reagents employed were obtained from commercial sources and were used without further purification. The Raman spectra were recorded using a Jobin Yvon Labram HR 800 instrument with 632.8 nm helium neon laser excitation.

*Synthesis of [$Bu_2Sn(O_2PPh_2)_2$] (**1**)*

A solution of 0.42 g (1.9 mmol) HO_2PPh_2 in 30 mL methanol was added to 0.60 g (2.0 mmol) Bu_2SnCl_2 in 10 mL methanol. Directly after the addition a small quantity of precipitate was formed, which was filtered off and the mother liquor was set aside at ambient temperature in a closed flask. After 14 d needle-like crystals (30 mg) of $Bu_2Sn(O_2PPh_2)_2$ (**1**) were formed and filtered off. Another portion of the white needles (135 mg) of **1** which separated from the mother liquor after partial evaporation of methanol at room temperature were filtered off, washed with methanol and dried.

*Synthesis of [$Ph_2Sn(O_2PPh_2)_2$] (**2**) and [$PhClSn(O_2PPh_2)OMe]_2$ (**3**)*

A solution of 0.43 g (2.0 mmol) HO_2PPh_2 in 50 mL methanol was added to a solution of 0.70 g (2.0 mmol) Ph_2SnCl_2 in 20 mL methanol. After few seconds a white precipitate was formed which was filtered off and the mother liquor was set aside at ambient tempera-

Table 5 Crystal data, measurement and structure refinement details for **1**, **2**, and **3**

	1	**2**	**3**
Formula	$Bu_2Sn(O_2PPh_2)_2$	$(Ph_2Sn)_{1.5}$ $(O_2PPh_2)_3$	$PhClSn(O_2PPh_2)(OMe)$
Formula weight	667.25	1060.85	479.45
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a / pm	1303.7(1)	1293.2(2)	946.4(1)
b / pm	2286.9(2)	1478.5(4)	963.7(1)
c / pm	1063.1(1)	1507.2(3)	1174.2(1)
α / deg		96.86(3)	82.495(6)
β / deg	94.383(6)	109.63(2)	66.451(6)
γ / deg		114.88(2)	74.922(6)
V / pm^3 x 10^{-4}	3.1603(4) x 10^5	2.3447(9) x 10^5	0.9474(1) x 10^5
Cell determination	12107 refl. $\theta = 1.8$ to 27.1°	8000 refl. $\theta = 8.95$ to 26.85°	6913 refl. $\theta = 1.8$ to 29.5°
ρ_{calc} / g x cm^{-3}	1.402	1.503	1.681
Z	4	2	2
F(000)	1368	1074	476
μ (MoK_α) / cm^{-1}	9.43	9.59	15.89
Diffractometer type	IPDS II (Stoe)	IPDS I (Stoe)	IPDS II (Stoe)
Wavelength / pm	71.073	71.073	71.073
T / K	192(2)	192(2)	192(2)
Scan mode	omega	phi	omega
hkl range	$-16\leq h\leq 13;-29\leq k\leq 28;-13\leq l\leq 13$	$-17\leq h\leq 17;-20\leq k\leq 20;-20\leq l\leq 20$	$-12\leq h\leq 12;-12\leq k\leq 13;-16\leq l\leq 16$
Theta range for data coll.	1.78 to 26.84	2.55 to 29.22°	1.89 to 29.15°
Reflections collected	17600	31427	16777
Independent reflections	6694 [R(int)=0.0844)	11598 [R(int)=0.074]	5064 (R(int)=0.0244)
Refl. used for refinement	6694	11598	5064
Observed reflections	4688 [I>2sigma(I)]	7342 [I>2sigma(I)]	4399 [I>2sigma(I)]
Absorption correction	based on equivalent reflections	numerical	based on equivalent reflections
Programs used	SHELXS-97[25], SHELXL-97[25], PLATON-89[26], SCHAKAL-97[27], SHELXTL[28]		
Solution direct/ difmap	Direct Methods, difmap	Patterson Methods	Direct Methods, difmap
Refinement		Full-matrix least-squares on F^2	
refined parameters	314	484	195
wR2 [all reflections]	0.0952	0.0782	0.0471
R1[I>2sigma(I)]	0.0440	0.0383	0.0209
$(shift/error)_{max}$	−0.002	−0.001	0.001
ρ_{fin} (max/min) / $eÅ^{-1}$	0.849 / −2.142	0.993 / −0.683	0.528 / −0.471

ture in a closed flask. After one month the white crystalline mixture (40 mg) of $[Ph_2Sn(O_2PPh_2)_2]$ (**2**) and $[PhClSn(O_2PPh_2)OMe]_2$ (**3**) was filtered off, washed with methanol and dried.

X-ray structural investigations

Single crystals of **1**, **2**, and **3** were taken from the filtrate of the reaction mixture after due time (see experimental section). All of them, the needles of **1** and **2** and the blocks of **3** were handled in oil, mounted on glass threads, and measured at −80 °C on Stoe Diffractometers IPDS I (**2**) and IPDS II (**1** and **3**) (see table 5 for crystal and experimental details and for structure solution and refinement). After data reduction [24] the data were corrected for absorption basing on equivalent reflections (**1** and **3**) and numerically (**2**). The structures were solved by direct methods (**1** and **3**) and by interpretation of Patterson maps (**2**) − refinement of the models was done by successive refinement cycles and difference Fourier syntheses [25]. For the input of hydrogen atoms at methyl, butyl and phenyl substituents a rigid group model with "riding" H atoms was applied. Geometrical calculations were carried out with PLATON [26].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nrs. CCDC-608554 (**1**), CCDC-608555 (**2**), and CCDC-608553 (**3**). Details are available, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

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