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Synthesis and characterisation of dialkyltin 2,3-bis(diphenylphosphino)maleic acid adducts

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Abstract

The novel dialkyltin 2,3-bis(diphenylphosphino)maleic acid adducts (R_2Sn)(O,O′-dpmaa) [**1a**, R = Me; **1b**, R = Bu; dpmaa = bis(diphenylphosphino)maleic acid] were synthesised from dpmaa and R_2SnCl_2 or Bu_2SnO. They were fully characterised by elemental analysis, IR- and multinuclear NMR-spectroscopies as well as X-ray crystallography [in the case of **1a** as its $Ph_2P(O)(CH_2)_2P(O)Ph_2$ adduct]. Both were found to be cyclic trimers in the solid state that dissolve in the case of **1b** into an equilibrium mixture of oligomers.

Keywords: Dialkyltin carboxylates; Cyclic trimer; 2,3-Bis(diphenylphosphino)maleic acid adducts; X-ray

1. Introduction

The self-assembly of organic ligands coordinated to metal ions or organometallic substances has been extensively studied [1]. The increasing interest in the field is mainly due to the potential relevance of such complexes to catalysis [2]. Another important objective is the synthesis of new, highly water soluble metal complexes useful in biological systems. Organo-tin compounds show a spectrum of biological effects and have been studied as fungicides, bactericides, acaricides and wood-preservatives [3]. Organo-tin compounds have also been studied as anti-tumour drugs and were reported to exhibit lower toxicity than the related platinum drugs [4]. Although the first testing of organotin compounds as anti-tumour agents was carried out in 1929, the application of organotin compounds did not attract much attention until the late 1980s [4].

Diorganotin(IV) complexes of adenine and glycylglycine were reported by Barbieri et al. [5]. Testing on these compounds revealed that the complex species is transported into the tumour cells. Saxena and Tandon [6] indicated that the presence of highly electronegative groups in diorganotin complexes could greatly enhance their activity. The organic group R in diorganotin compounds R_2SnX_2 determines the potential anti-tumour activity [7]. One of the most promising groups in substituted salicylic acids with diorganotin oxides appeared to be di-*n*-butyltin [7].

The solid-state structures of trialkyltin(IV) carboxylates can be either monomeric [8], oligo- and polymeric [9] or cyclooligomeric [10], whereby the oligo- and polymeric structures are formed through intermolecular Sn–O–C=O → Sn bonds. Since these bonds are relatively weak, a discrete molecular structure can be expected in solution. Because of interest in the creation of oligo- and polymeric structures with strong binding interactions between the repeating units, we became interested in the chemistry of diorganotin(IV) derivatives of dicarboxylic acids, and the literature search shows that the first complexes of this type were prepared more than 50 years ago [11]. Since then, various diorganotin(IV) moieties, mainly dimethyl and di-*n*-butyltin(IV), have been combined with the most common

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dicarboxylic acids, such as oxalic [12], malonic [13], succinic [13], adipic [13], maleic [14], phthalic [15,16], and terephthalic acid [16]. The resulting complexes were used as PVC stabilisers [17], catalysts for transesterification reactions [18], catalysts for polyurethane polymerisations [18], and in RTV silicone curing reactions [19]. A series of diorganotin(IV) derivatives of dicarboxylic acids have been tested also as anti-tumour agents [20]. However, a conclusive characterisation of diorganotin(IV) derivatives of dicarboxylic acids with respect to their structures in solution is not trivial, since they are frequently insoluble due to their polymeric or oligomeric nature, and for the case that they are soluble, they are often involved in dynamic equilibria with fast ligand exchange reactions [21].

Monodentate and bidentate phosphines are amongst the most common ligands in coordination chemistry. During our ongoing investigations in the coordination chemistry of metal-phosphine complexes [22], we became interested in the coordination behaviour of 2,3-bis(diphenylphosphino)maleic acid. Combination of the dialkyltin moiety with 2,3-bis(diphenylphosphino)maleic acid would give potentially new ligands for the synthesis of hetero-bimetallic compounds. Here, we report on our results on the solution- and solid-state study of dimethyltin(IV)- and di-*n*-butyltin(IV)-2,3-bis(diphenylphosphino)maleic acid adducts, which both form trinuclear macrocyclic structures in the solid state. The here presented adducts form the first examples of tin carboxylates containing two phosphine functionalities.

2. Results and discussion

2.1. Synthesis

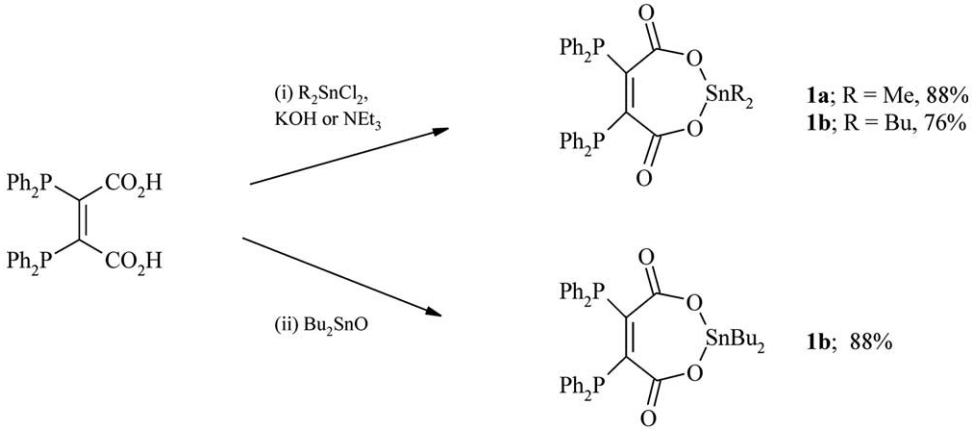
The tin complexes **1** were synthesised from the reaction of 2,3-bis(diphenylphosphino)maleic acid (dpmaa) and one equivalent of R_2SnCl_2 in the presence of two equivalents of base (KOH or NEt_3) in benzene at room temperature (Scheme 1(i)). Complex **1b** was alternatively obtained from the equilibrium reaction of dpmaa and Bu_2SnO by azeotropic removal of water (Scheme 1(ii)). Both compounds were yellow solids, moderately stable in moist air and soluble in polar organic solvents, but insoluble in hydrocarbons.

2.2. Spectroscopic studies

Complex formation and Sn–O bond formation in the products was evident in the IR spectrum from the absence of an ν(OH) absorption band at around 3500 cm^{-1} and the appearance of strong ν(CH) bands in the alkyl region (2900–3100 cm^{-1}) attributed to the alkyl groups of the tin moiety. The differences ($\Delta\nu$, Table 1) between antisymmetric and symmetric carboxylate stretching frequencies have previously been used to deduce the bonding mode of metal carboxylates [23]. Large $\Delta\nu$ values were related to an unidentate bonding mode ($\Delta\nu > 200$–$260\ cm^{-1}$; cf. $\Delta\nu$ for dpmaa in Table 1) and a small $\Delta\nu$ ($\Delta\nu < 200\ cm^{-1}$) to a bidentate chelating or bridging bonding mode [23]. Between the two extremes exists a bonding mode that is commonly referred to as anisobidentate where one metal oxygen contact is significantly shorter than the other. This region is not very well defined and was more recently shown to extend considerably beyond $\Delta\nu = 260\ cm^{-1}$ [24]. The tin complexes **1** were found to have both in the solid state as well as in solution $\Delta\nu$ values around 260 cm^{-1} which is therefore consistent with an anisobidentate coordination of the tin atoms.

Complex formation was also confirmed in the ^1H NMR spectrum of **1** by the absence of the OH signal at around δ 3 and the presence of signals of expected intensity in the alkyl region of the spectrum.

The chemical shift values in the ^{31}P NMR spectrum of the complexes were not surprisingly similar to that of the free ligand (Table 1) indicating that tin coordination to the carboxylate had only a negligible effect on the electronic environment of the phosphorus atoms. The butyl-derivative **1b**, however, showed unexpectedly two distinct signals at δ −8.5 and δ −10.1. Repeated recrystallisation of **1b** and powder-XRD analysis confirmed the purity of **1b** and the absence of free dpmaa. Dilution experiments of a saturated solution of **1b** in $CDCl_3$ that was stepwise diluted, revealed that the ratio of the two peaks changed



Scheme 1. Synthesis of dialkyltin(IV) dicarboxylates.

Table 1
Selected spectroscopic data of compounds **1**

Compound	$\Delta\nu$ (solid) (cm^{-1})	$\Delta\nu$ ($CHCl_3$) (cm^{-1})	δ (^{31}P, $CDCl_3$)	δ (^{119}Sn, $CDCl_3$)	δ (^{119}Sn, dmso)
dpmaa	509	–	−11.7	–	–
1a	264	257	−8.7	−83.3	–[a]
1b	253	258	−8.5, −10.1	−102.3	−116.5

[a] Not observed: signal presumably very broad as evident from ^{31}P NMR spectrum.

from 6:1 (saturated solution) to about 0.8:1. Variable temperature analysis showed further that the signal at δ −8.5 resolved into three broad signals at δ −7.4, δ −9.0 and δ −15.1 at 213 K (coalescence temperature 233 K), while the signal at δ −10.1 remained essentially unaffected. In a tentative interpretation of these results the signal at δ −8.5 was assigned to a trimeric species (**1b** was found to be a trimer in the solid state, see below) whose different phosphorus environments or different conformers (cf. the existence of different polymorphs in the solid state) were partially resolved at lower temperature. The signal at δ −10.1 is consistent with a second species, possibly a monomer, in equilibrium with the trimer (equilibrium was established fast as there was no visible time dependence in the ratio of the intensities of the two signals at room temperature when a sample of **1b** was measured immediately after preparation and then again after a period of 15 h), whose ^{31}P NMR spectrum was not influenced by temperature and whose formation from the trimer, in agreement with the dilution experiments, should be favoured at lower total concentration of **1b**. The presence of several oligomers in solutions of tin carboxylates has been described previously [13,25].

The ^{31}P NMR spectrum of the methyl derivative **1a** at room temperature showed, in contrast, only a single line at δ −8.7 similar to the postulated trimeric species of **1b** and a dent in the baseline at δ −11.3. Cooling of the sample resulted in significant line broadening (64 Hz) at 223 K but gave no further evidence of the existence of more than one species in solution.

The ^{119}Sn NMR spectra of **1a** and **1b** showed a single broad signal (Table 1) on the lower side or just outside the region (δ −90 to −190) [21] associated with five coordinated tin and similar to those of related compounds such as $[1,2\text{-}(Bu_2SnO_2C)_2C_6H_4]_n$ (δ −139) or $[1,3\text{-}(Bu_2SnO_2C)_2\text{-}C_6H_4]_3$ (δ −161) [25]. This is consistent with the previously described anisobidentate coordination (coordination number 5 as average between 4 and 6) of the carboxylic acid group found in the IR spectrum and the molecular structure of **1b** in the solid state (see below). ^{119}Sn NMR-spectroscopic shift values above δ −90 or below δ −190 were found to indicate tin complexes with coordination number 4 or 6, respectively [21]. The negligible influence of the solvent on the ^{119}Sn NMR spectrum of the complexes in a non-polar as compared to a polar solvent (Table 1) indicated that the average coordination number of the complexes was independent of the solvent. A shift of δ 30 ppm and more to higher field strength in the ^{119}Sn NMR spectrum of four and five coordinate tin compounds as a result of a change from a non-polar to a polar NMR solvent has been attributed to an increase in coordination number of the tin complexes in polar solvents [21]. Variable temperature experiments showed that the ^{119}Sn NMR spectrum of **1b** resolved in agreement with the complex behaviour discussed for the ^{31}P NMR spectrum into three broad signals at δ −96.6, −104.2 and −196.3.

2.3. Crystallographic studies

A considerable number of diorganotin(IV) carboxylates has been crystallographically characterised in the last two decades and several structural types have been identified [26]. These included (i) monomeric structures [27] with a six-coordinate tin atom and chelating carboxylate groups, (ii) polymeric structures [24,25,27b,28] with bridging carboxylate groups, (iii) dimeric structures [29] similar to the monomeric type but with an additional interaction between tin atoms and oxygen atoms of adjacent monomers, and (iv) more recently a cyclic trimer [25].

The repeated recrystallisation of **1b** in diethyl ether gave several batches of the dibutyltin-derivative, two of which were characterised by X-ray crystallography and found to represent two different polymorphs of **1b**. While numerous attempts to obtain crystals of **1a** suitable for X-ray diffraction from solvents such as Et_2O, CH_2Cl_2 or $CHCl_3$ were unsuccessful, co-crystals **1a** · $[Ph_2P(O)(CH_2)_2P(O)Ph_2]_{1/6}$ of **1a** and $Ph_2P(O)(CH_2)_2P(O)Ph_2$ were obtained from diethyl ether (or a mixture of Et_2O and CH_2Cl_2) solution by slow evaporation of the solvent. All three structures are cyclic trimers [in the case of **1a** bridged by $Ph_2P(O)(CH_2)_2P(O)Ph_2$] and crystallise with one or in the case of **1a** · $[Ph_2P(O)(CH_2)_2P(O)Ph_2]_{1/6}$ three molecules of diethyl ether per trimer. The molecular structures of **1a** and **1b** are illustrated in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 2.

The backbone of all three structures is a trimeric 21-membered macrocycle that is formed as a result of dpmaa binding to the tin atoms in a bridging anisobidentate bonding mode. The coordination geometry of the tin atoms (except Sn1c of **1a**) may be described as highly distorted octahedral or bicapped tetrahedral with the coordinative bound carbonyl oxygen atoms O2a, O4a, O2b, O4b, O2c and O4c capping the faces. The Sn–O bond distances to the latter are much longer [ranging from 2.350(3)–2.846(3) Å] than that to the covalently bound oxygen

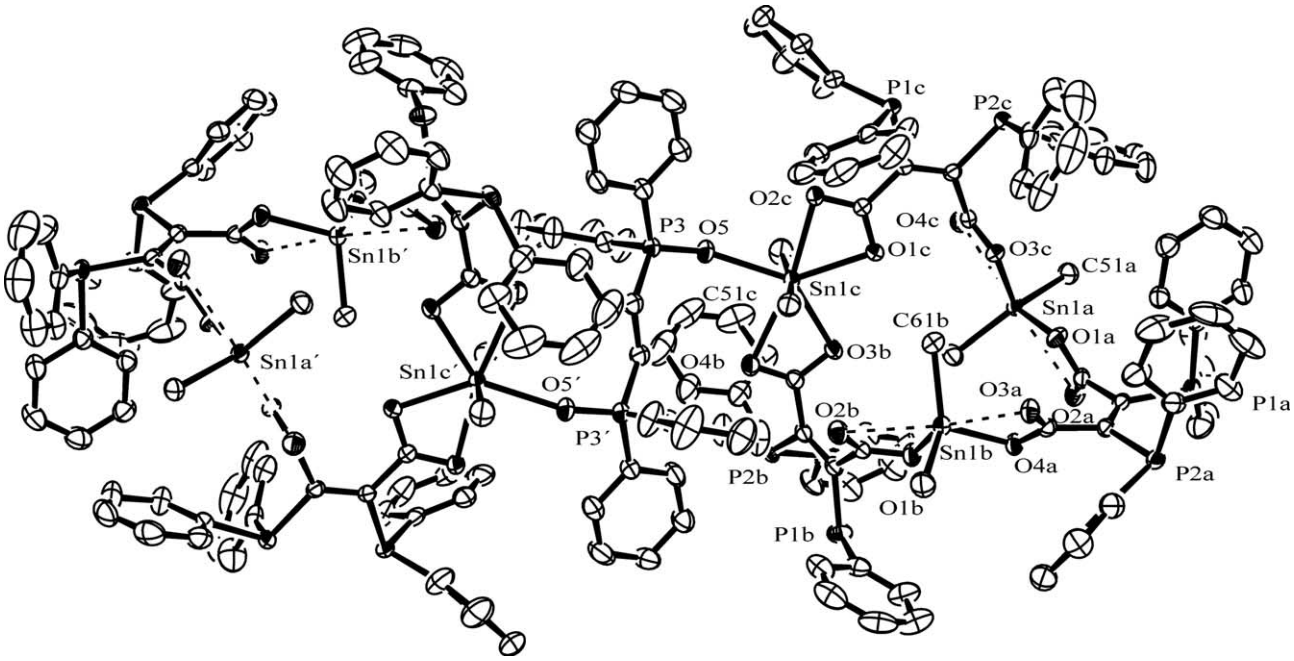


Fig. 1. ORTEP diagram of **1a** · $[Ph_2P(O)(CH_2)P(O)Ph_2]_{1/6}$ drawn at 50% probability. H-atoms have been omitted for clarity. Atoms labelled with prime (′) were generated by the symmetry transformation: $-x+1$, $-y+2$, $-z+1$.

atoms [ranging from 2.070(3)–2.166(3) Å]. The 'normal' tetrahedral angles around the tin atoms are in the range of 100.3(2)° to 111.8(2)°, while the remaining two sets of angles show the effect of the capping resulting in much more acute [79.3(1)–86.4(1)°] and obtuse angles [129.4(1)–146.5(2)°]. The octahedral view of the geometry is evident from the planarity of the SnO_4 fragment (largest deviation from planarity ranging from 0.018 to 0.081 Å in **1b** but 1.0 Å in **1a**) and the large C–Sn–C angles. The covalent Sn–C and Sn–O distances show little variation and are similar to those described in the literature [24–29]. The coordinative Sn–O distances (Table 2) show much larger variations which is in agreement with the wide range of values (2.46–3.11 Å) reported for that type of bond in trialkyl- and dialkyltin carboxylates [26–30]. The difference in Sn–O bond distances is also reflected in the disparity of the two associated CO distances of the carboxylate groups, one representing a C–O single [1.283(4)–1.307(5) Å] and one a C═O double bond [1.209(5)–1.260(5) Å].

In the case of **1a** two trimers are bridged via the O atoms of a $Ph_2P(O)(CH_2)_2P(O)Ph_2$ molecule that has an inversion centre in the middle of the central C–C bond. The additional coordination of the O atom of the $Ph_2P(O)(CH_2)_2$-$P(O)Ph_2$ results in a pentagonal bipyramidal coordination of Sn1c, with five oxygen atoms in the equatorial plane [largest deviation from plane for O4b (0.126 Å)] and the two methyl groups (C51c and C61c) in axial position [C51c–Sn1c–C61c 170.2(1)°]. The bonding mode of the carboxylic acid group is approximately bidentate as is evident from the similarity of the Sn–O bonds [2.251(2)–2.518(2) Å] and the close to identical CO bond distances [1.254(4)–1.271(4) Å] that are in agreement with delocalisation in those groups.

A comparison of the two polymorphs of **1b** reveals the main difference to be the different contact distances for Sn1a–O2a (2.848 versus 2.574 Å) and Sn1c–O2c (2.413 versus 2.549 Å) and a different arrangement of the phenyl groups of the phosphine ligands (Fig. 2). This is evident from an overlap of the two polymorphs that shows a root mean square (RMS) difference of 0.29 Å for the backbone of the molecule excluding butyl and phenyl groups other then α- and *ipso*-C atoms (Fig. 3) as compared to a RMS value of 2.78 Å for the whole molecule.

The molecular structure of the related trimeric dibutyltin(IV) isophthalate $[1,3\text{-}(Bu_2SnO_2C)_2C_6H_4]_3$ [25] differs from that of **1a** and **1b** in the ring size (24-membered) and the near-planarity of the ring. This creates a cavity in the isophthalate derivate that is occupied by a butyl group of a neighbouring trimer. Adjacent trimers are further connected to long chains by an interaction between the tin atoms in one trimer with a carbonyl group of an adjacent trimer hereby increasing the coordination number around tin to seven (cf. **1a**). The macrocycle in **1a** and **1b** is in contrast puckered in such a way that the space inside the macrocycle is occupied by the alkyl substituents of each trimer hereby minimising steric interactions between the butyl and the phenyl groups. There are no close contacts other than van der Waals interactions in **1a** and **1b**.

3. Experimental

3.1. General procedures and reagents

All manipulations were carried out using standard Schlenk techniques under argon [31]. Solvents were dis-

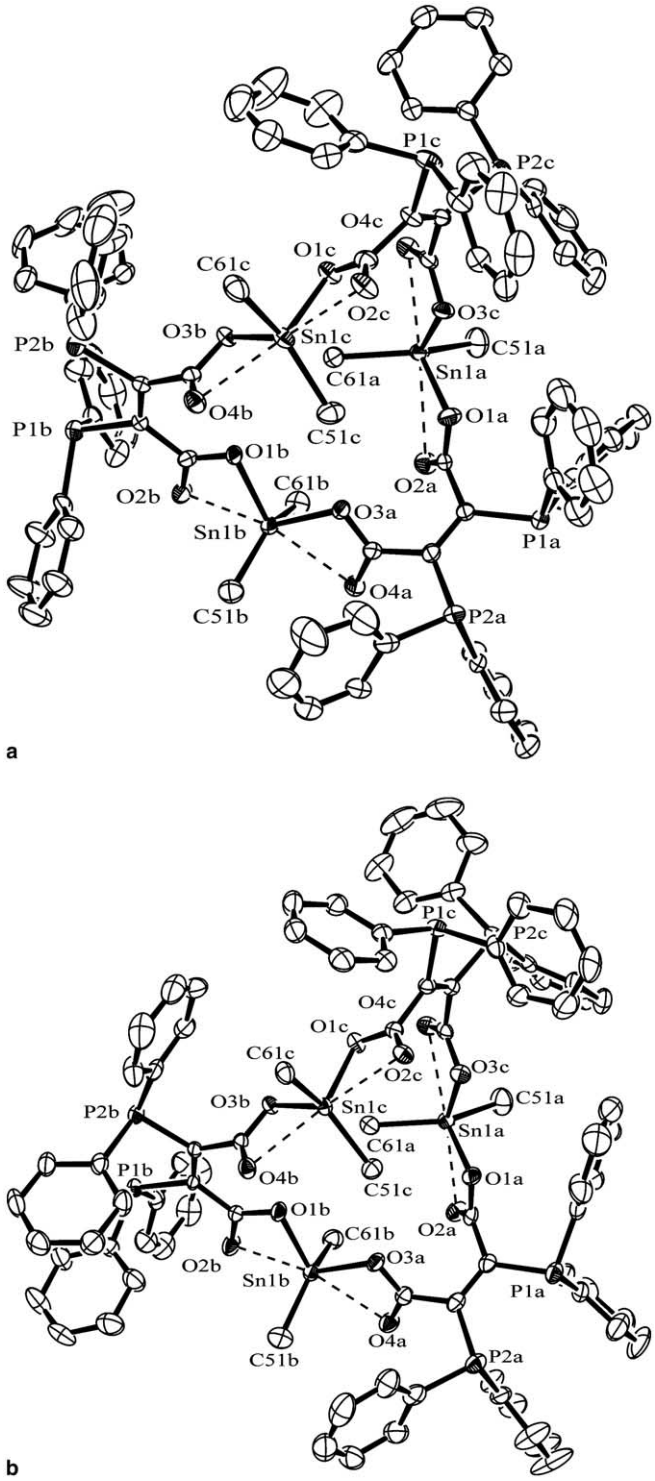


Fig. 2. ORTEP diagram of polymorphs A (a) and polymorphs B (b) of compound **1b** drawn at 50% probability level. H-atoms and β-, γ- and δ-carbon atoms of the Sn-butyl groups have been omitted for clarity and the backbone of both polymorphs has been orientated in such a way as to emphasise their similarity.

tilled from the appropriate drying agent prior to use [32]. 2,3-Bis(diphenylphosphino)maleic acid (dpmaa) was obtained by the hydrolysis of the anhydride. 2,3-Bis(diphenylphosphino)maleic anhydride was synthesised according to the literature procedure [33]. All other reagents were obtained from Sigma-Aldrich and stored under argon. NMR spectra were recorded on either a Bruker DRX 400 (^{1}H, 400.13 MHz; ^{31}P, 162.0 MHz; ^{119}Sn, 149.2), a Bruker Avance 300 (^{1}H, 300.13 MHz; ^{13}C, 75.5 MHz) or a Bruker AC 200 (^{1}H, 200.13 MHz) spectrometer. NMR spectra were referenced internally to residual solvent resonances (^{1}H and ^{13}C) or externally to 85% H_3PO_4 (^{31}P) or $SnMe_4$ (^{119}Sn). Infrared spectra were recorded on a Bruker Vectro 22 spectrometer. FAB-MS spectra were collected using a VG70-SEQ instrument in positive ion mode. Elemental analyses were determined by the Institute for Soil, Climate and Water, Pretoria, South Africa. The following abbreviations are used throughout Section 3: bs, broad singlet; m, multiplet; mm, multiple multiplets; q, quartet; s, singlet; t, triplet. Coupling constants (*J*) are given in Hz.

3.2. Synthesis of compound *1a*

Triethyl amine (0.25 cm^3, 1.58 mmol) was added to a solution of 2,3-bis(diphenylphosphino)maleic acid · 2Et_2O (0.50 g, 0.79 mmol) in benzene (25 cm^3). The reaction mixture was stirred for 15 min and a solution of dimethyltin dichloride (0.17 g, 0.79 mmol) in benzene (20 cm^3) was then added dropwise over a period of 15 min. The yellow reaction mixture was then stirred for 16 h. The volatiles were removed in vacuo to give a yellow powder. The residue was partitioned between chloroform (15 cm^3) and water (20 cm^3). The organic layer was separated, washed with water (20 cm^3), dried over $MgSO_4$, filtered and concentrated in vacuo to give the title compound as a yellow powder (0.56 g, 88%). Elemental analysis: Calc. for $C_{30}H_{26}O_4P_2Sn$: C, 57.09; H, 4.15%. Found: C, 56.88; H, 4.62%. IR (KBr, cm^{-1}): 1323 s [ν_s(C–O)], 1580 s [ν_{as}(C=O)], 2912 m, 2930 m, 3000 m, 3049 m [ν(C–H)]; ^{1}H NMR ($CDCl_3$): δ 0.25 [bs, CH_3, ^2J(^{119}Sn–^{1}H) 77.8 Hz, 6H], 7.32–7.23 (m, *o* and *m*-Ar, 16H), 7.43 (bs, *p*-Ar, 4H); ^{13}C NMR ($CDCl_3$): δ 3.3 (s, CH_3), 128.3 [t, Ar, ^2J(^{19}P–^{13}C) 3.6 Hz], 128.8 [s, (*p*-Ar)], 133.9 [t, Ar, ^1J(^{19}P–^{13}C) 10.7 Hz], 134.5 [t, Ar, ^2J(^{19}P–^{13}C) 2.4 Hz], 149.8 (s, C=C), 174.3 [t, C=O, ^2J(^{19}P–^{13}C) 3.7 Hz]; ^{31}P NMR ($CDCl_3$): δ −8.7 (s); ^{119}Sn NMR ($CDCl_3$): δ −83.3; FAB-MS ($M^+ + H$) 632 *m*/*z* (8%).

3.3. Synthesis of compound 1a · [$Ph_2P(O)(CH_2)_2P(O)Ph_2$]$_{1/6}$

A mixture of **1a** (0.172 g, 0.27 mmol) and a slight excess (stoichiometric ratio of **1a**:P-oxide = 6:1.13) of $Ph_2P(O)(CH_2)_2P(O)Ph_2$ (0.022 g, 0.051 mmol) was dissolved in a 1:1 mixture of Et_2O and CH_2Cl_2. Slow evaporation of the solvents resulted in the formation of yellow crystals of the adduct (0.14 g, 74%). M.p. (decomp.): 135–140 °C Elemental analysis: Calc. for $C_{206}H_{180}O_{26}P_{24}Sn_6 \cdot (CH_2Cl_2)$ (^{1}H NMR spectroscopy and an uncompleted

Table 2
Selected bond distances (Å) and bond angles (°) of compounds **1a** and **1b**

	1a[a]	**1b** (A)	**1b** (B)		**1a**	**1b** (A)	**1b** (B)
Sn1a–O1a	2.069(2)	2.070(3)	2.093(3)	Sn1a–O2a	2.723(2)	2.846(3)	2.574(3)
Sn1a–O3c	2.071(2)	2.092(3)	2.096(3)	Sn1a–O4c	2.673(2)	2.596(3)	2.637(3)
Sn1a–C51a	2.097(3)	2.130(5)	2.104(4)	Sn1a–C61a	2.101(3)	2.120(5)	2.094(4)
Sn1b–O1b	2.081(2)	2.166(3)	2.165(3)	Sn1b–O2b	2.737(2)	2.374(3)	2.350(3)
Sn1b–O3a	2.117(2)	2.122(3)	2.134(3)	Sn1b–O4a	2.445(2)	2.561(3)	2.536(3)
Sn1b–C51b	2.104(3)	2.117(5)	2.108(5)	Sn1b–C61b	2.102(3)	2.114(5)	2.121(4)
Sn1c–O1c	2.258(2)	2.166(3)	2.119(3)	Sn1c–O2c	2.341(2)	2.414(3)	2.551(3)
Sn1c–O3b	2.251(2)	2.129(3)	2.130(3)	Sn1c–O4b	2.518(2)	2.566(3)	2.566(3)
Sn1c–C51c	2.108(4)	2.116(5)	2.118(4)	Sn1c–C61c	2.106(4)	2.105(5)	2.120(4)
Sn1c–O5	2.346(2)	–	–				
O1a–C1a	1.304(4)	1.295(5)	1.296(5)	O2a–C1a	1.225(4)	1.230(6)	1.255(5)
O3a–C4a	1.300(4)	1.307(5)	1.290(5)	O4a–C4a	1.244(4)	1.238(5)	1.247(5)
O1b–C1b	1.297(4)	1.298(5)	1.299(4)	O2b–C1b	1.228(4)	1.241(5)	1.260(5)
O3b–C4b	1.271(4)	1.297(5)	1.283(4)	O4b–C4b	1.254(4)	1.209(5)	1.239(5)
O1c–C1c	1.268(4)	1.292(6)	1.298(5)	O2c–C1c	1.258(4)	1.251(6)	1.234(5)
O3c–C4c	1.292(4)	1.297(5)	1.296(5)	O4c–C4c	1.228(4)	1.241(6)	1.248(5)
O1a–Sn1a–O3c	80.7(1)	79.4(1)	82.5(1)	O1b–Sn1b–O3a	81.5(1)	85.6(1)	86.2(1)
O1a–Sn1a–C51a	107.5(1)	104.2(2)	110.2(2)	O1b–Sn1b–C51b	104.7(1)	101.0(2)	106.1(2)
O1a–Sn1a–C61a	109.4(1)	107.7(2)	108.4(1)	O1b–Sn1b–C61b	105.0(1)	110.2(2)	103.7(1)
O3c–Sn1a–C51a	109.0(1)	111.8(2)	102.6(1)	O3a–Sn1b–C51b	110.5(1)	102.9(2)	102.2(2)
O3c–Sn1a–C61a	110.1(1)	107.3(3)	104.7(2)	O3a–Sn1b–C61b	106.2(1)	100.4(2)	102.3(1)
C51a–Sn1a–C61a	129.4(1)	133.0(2)	134.9(2)	C51b–Sn1b–C61b	135.5(2)	142.1(2)	142.3(2)
O1c–Sn1c–O3b	79.3(1)	86.4(1)	84.0(1)				
O1c–Sn1c–C51c	93.9(1)	104.1(2)	104.3(1)				
O1c–Sn1c–C61c	94.0(1)	102.0(2)	104.0(1)				
O3b–Sn1c–C51c	95.9(1)	102.6(2)	101.8(1)				
O3b–Sn1c–C61c	91.3(1)	100.3(2)	105.3(1)				
C51c–Sn1c–C61c	170.2(2)	146.5(2)	142.4(2)				
O2c–Sn1c–C51c	89.1(1)	–	–				
O2c–Sn1c–C61c	90.5(1)	–	–				
O4b–Sn1c–C51c	86.1(1)	–	–				
O4b–Sn1c–C61c	92.6(1)	–	–				
O5-Sn1c–C51c	87.8(1)	–	–				
O5-Sn1c–C61c	82.5(1)	–	–				

[a] Remaining O–Sn1c–O angles in **1a** have been omitted.

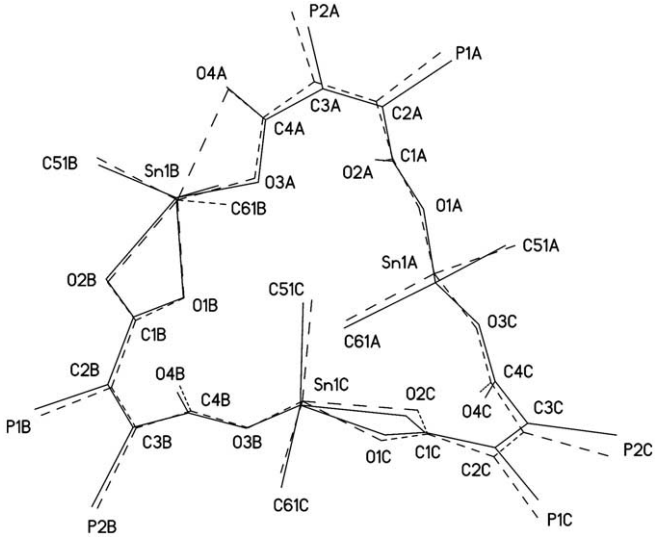


Fig. 3. Overlap of the backbone of both polymorphs of **1b** including only the α- and *ipso*-C atoms of the butyl and phenyl groups, respectively.

X-ray structure suggest the presence of CH_2Cl_2 which is lost on standing): C, 57.79; H, 4.26%. Found: C, 57.3; H, 4.47%.

The crystals used for single crystal analysis were obtained in a similar but less reproducible manner (a result of the limited solubility of the phosphine oxide in Et_2O) from a solution of the two starting materials in Et_2O. A ^{31}P NMR spectrum of the crystals in $CDCl_3$ at room temperature showed two signals at δ −8.7 and 33.3 in agreement with a dissociation of the adduct in solution into uncoordinated **1a** and free $[Ph_2P(O)\text{-}(CH_2)_2P(O)Ph_2]$.

3.4. Synthesis of compound *1b*

Method A. A solution of KOH (0.027 g, 0.85 mmol) in methanol was added to a solution of 2,3-bis(diphenylphosphino)maleic acid · $2Et_2O$ (0.25 g, 0.42 mmol) in thf (15 cm^3). The reaction mixture was stirred for 15 min. A thf solution of dibutyltin dichloride (0.13 g, 0.42 mmol)

was then added dropwise to the dpmaa solution over a period of 15 min at room temperature. The reaction mixture was stirred overnight. The solvent was removed in vacuo, the residue extracted into $CHCl_3$ (20 cm^3) and the solution was washed twice with deionised water (20 cm^3). The organic phase was separated, dried over $MgSO_4$ and then removed in vacuo to give a light yellow solid (0.22 g, 76%).

Method B. Dibutyltin oxide (0.60 g, 2.4 mmol) was added to a solution of 2,3-bis(diphenylphosphino)maleic acid · $2Et_2O$ (1.00 g, 1.58 mmol) in benzene (90 cm^3). The reaction mixture was heated under reflux for 30 min while continuously removing the formed water by azeotropic distillation in a Dean-Stark apparatus. The volatiles were evaporated in vacuo and the residue was recrystallised from diethyl ether to give the title compound as yellow crystals (1.20 g, 88%). Crystals suitable for X-ray analysis were grown from diethyl ether. Elemental analysis: Calc. for $C_{36}H_{38}O_4P_2Sn$: C, 60.45; H, 5.35%. Found: C, 60.37; H, 5.34%. IR (KBr, cm^{-1}): 1342 s [ν_s(C═O)], 1594 s [ν_{as}(C═O)], 2856 m, 2915 m, 2959 m, 3055 m [ν(C─H)]; ^1H NMR ($CDCl_3$): δ 0.73 [bs, CH_3(Bu) 6H], 0.92–1.13 [mm, CH_2 (Bu), 12H], 3.48 [q, OCH_2(solvent)], 7.07–7.31 (mm, *m*, *p*, *o*-Ar, 20H); ^{13}C NMR ($CDCl_3$): δ 13.5, 13.8 (s, CH_3), 15.3 [s, $CH_3(Et_2O)$], 23.8, 26.1, 26.35, 26.43, 27.0 (s, CH_2), 65.8 [s, $OCH_2(Et_2O)$], 127.9–128.1 (mm, *m*-Ar), 128.6–128.7 (mm, *p*-Ar), 133.9–134.3 (mm, *o*-Ar), 134.9, 135.3 (*ipso*-Ar) 151.0 (s, C═C), 172.2 [t, C═O, $^2J(^{31}P–^{13}C)$ 4.1 Hz], 174.2 [t, C═O, $^2J(^{31}P–^{13}C)$ 3.6 Hz]; ^{31}P NMR ($CDCl_3$): δ −8.6 (s) and −10.1(s); ^{119}Sn NMR($CDCl_3$): δ −102.3 (s); ^{119}Sn NMR(d_6-dmso): δ −116.5 (s); FAB-MS (M^+ − Bu) 660 *m*/*z* (12%).

3.5. X-ray crystallography

Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved ω-scans of width 0.3°. Data was reduced with the program SAINT+ [34] and absorption corrections were made using the program SADABS [34]. The crystal structures were solved by direct methods using SHELXTL [35]. Non-hydrogen atoms were first refined isotropically, followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. Further crystallographic data are summarised in Table 3. Diagrams and publication material were generated using SHELXTL [35], PLATON [36] and ORTEP3 [37].

In the structure of **1a** one of the phenyl groups was found to be disordered (C11B–C16B). This was refined isotropically over two positions as C11B–C16B and C11D–C16D with site occupancies of 0.60(2) and 0.40(2),

Table 3
Crystal data and structure refinement details for **1a** and **1b**

	1a	**1b** (Polymorph A)	**1b** (Polymorph B)
Empirical formula	$C_{218}H_{210}O_{29}P_{14}Sn_6$	$C_{112}H_{124}O_{13}P_6Sn_3$	$C_{112}H_{124}O_{13}P_6Sn_3$
Formula weight	4439.58	2220.00	2220.00
Temperature (K)	173(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	13.5228(13)	15.1482(7)	15.4779(5)
b (Å)	25.780(3)	15.8531(8)	19.4003(7)
c (Å)	29.962(3)	24.6201(12)	35.4638(11)
α (°)	90	86.851(4)	90
β (°)	93.518(4)	80.508(3)	91.585(2)
γ (°)	90	63.835(3)	90
Volume ($Å^3$)	10425.5(18)	5232.9(5)	10644.9(6)
Z, calculated density ($Mg\ m^{-3}$)	2, 1.414	2, 1.409	4, 1.385
Absorption coefficient (mm^{-1})	1.414	0.863	0.848
F(000)	4520	2280	4560
Crystal size (mm)	0.44 × 0.22 × 0.22	0.26 × 0.20 × 0.18	0.30 × 0.30 × 0.22
θ Range (°)	1.04, 27.00	0.84, 26.00	1.15, 25.00
Index ranges	$-16 < h < 16$, $-31 < k < 32$, $-34 < l < 38$	$-18 \leqslant h \leqslant 18$, $-19 \leqslant k \leqslant 19$, $-29 \leqslant l \leqslant 30$	$-18 \leqslant h \leqslant 18$, $-22 \leqslant k \leqslant 22$, $-42 \leqslant l \leqslant 39$
Reflections collected/unique [R_{int}]	66839/22499 [0.063]	36940/20292 [0.063]	45573/18496 [0.060]
Completeness to 2θ (%)	98.8	98.6	98.7
Maximum and minimum transmission	0.8296 and 0.6976	0.8602 and 0.8068	0.8331 and 0.7880
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	22499/108/1206	20292/0/1169	18496/67/1253
Goodness-of-fit on F^2	1.048	1.001	1.061
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.037$, $wR_2 = 0.089$	$R_1 = 0.045$, $wR_2 = 0.125$	$R_1 = 0.039$, $wR2 = 0.102$
R indices (all data)	$R_1 = 0.053$, $wR2 = 0.098$	$R1 = 0.072$, $wR2 = 0.142$	$R1 = 0.055$, $wR2 = 0.111$
Largest difference peak and hole/e $Å^{-3}$	1.263 and −1.015	1.289 and −0.669	1.171 and −0.774

respectively. In addition, one of the diethyl ether molecules was also found to be disordered and was refined anisotropically in two positions with site occupancies of 0.501(11) and 0.499(11), respectively.

Polymorph A of **1b** contains disordered ether molecules (1 per main molecule). A treatment of SQUEEZE [38] accounted for 53 electrons per unit cell, less than the 84 electrons two ether molecules would account for, but not unexpected as the data collection was done at room temperature, allowing some of the solvent molecules to escape. Though coordinates of the ether molecules have not been added to the final structure, their contribution to $F(000)$, the sum formula and density has been accounted for with full occupancy.

Polymorph B of **1b** contains several disordered butyl groups. These have each been refined over two positions, using free variables for the occupancy of each position (the occupancies of the two positions being summed up to unity), as well as SADI and DFIX restraints on the molecular geometries of each disordered fragment.

The RMS difference values for the two polymorphs of **1b** were calculated with XP [35].

4. Supplementary material

Full crystallographic data (CCDC 267677 for **1a**, 267678 for polymorph A and 267679 for polymorph B of **1b**) have been deposited at the Cambridge Crystallographic Database Centre and are available on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web http://www.ccdc.cam.ac.uk).

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