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The X-ray crystal structure of (diphenylmonothiophosphinato)triphenyltin(IV), $[Ph_3Sn(OSPPh_2)]_n$, exhibiting a polymeric chain supramolecular self-assembly†

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Abstract—The molecular structure of (diphenylmonothiophosphinato)triphenyltin(IV) was determined by X-ray diffractometry. The diphenylmonothiophosphinato ligand is bimetallic biconnective leading to a polymeric $[SnSPO]_n$ chain: Sn(1)—S(1) [2.785(3) Å] and Sn(1)—O(1′) [2.172(6) Å]. The coordination geometry about tin is trigonal bipyramidal with chalcogen atoms in apical positions [O(1′)—Sn(1)—S(1) 176.6(2)°] and carbon atoms of the phenyl groups attached to the metal in equatorial positions. The bridging pattern of the ambident monothio ligand is discussed in terms of partial bond orders and compared with those observed in other related organotin(IV) derivatives. © 1997 Elsevier Science Ltd

Keywords: organotin; diphenylmonothiophosphinato; supramolecular.

The ambident monothiophosphinato ligands, $[R_2SPO]^-$, might exhibit primary coordination through either oxygen (**a**) or sulfur (**b**), depending on the 'hard/soft' acid character of the metallic center. The second chalcogen atom of the ligand moiety is generally also involved in weak ('secondary interactions') or strong coordinative bonds to the same metal atom (symmetric or asymmetric monometallic biconnective pattern) or to a neighbouring metal atom (bimetallic biconnective or triconnective, trimetallic tetraconnective patterns) [1].

In a previous paper [1] we have reported on the synthesis of $Ph_3Sn(OSPR_2)$ (R = Me, Et, Ph) derivatives and their spectroscopic behavior. On the basis of infrared and NMR data, either monomeric (**c**) or polymeric (**d**) structures involving chelating or bridging monothiophosphinato ligand, respectively, have been suggested in solution and in solid state.

We now report on the crystal and molecular structure of (diphenylmonothiophosphinato)triphenyltin(IV), which exhibits chain polymeric structure of the type (**d**).

EXPERIMENTAL

The compound was prepared as described previously [1] and crystals suitable for X-ray diffraction investigation were obtained from a $CHCl_3$/*n*-hexane solvent mixture.

Crystal structure determination

A colourless block crystal of $Ph_3SnOSPPh_2$ (**1**) was mounted on glass fibre and sealed with epoxy glue. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation, operating at 50 kV and 35 mA. Cell constants and an orientation matrix for data collection, obtained from 24 carefully centred reflections in the

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† Dedicated to Professor Ionel Haiduc on the occasion of his 60th birthday.

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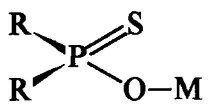
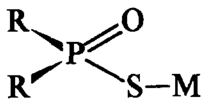


a



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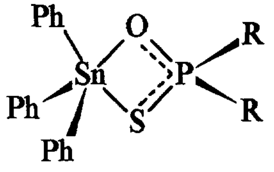

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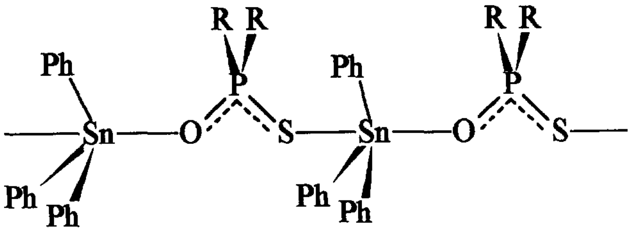


d

range $8.66 < 2\theta < 14.28°$, corresponded to a monoclinic cell, whose dimensions are given in Table 1.

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.17° with a takeoff angle of 6.0°. Scans of $(1.31 + 0.30 \tan\theta)°$ were made at speed of 32.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 4 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. The diameter of the incident beam collimator was 1.0 mm, and the crystal to detector distance was 285.0 mm.

Of the 5257 reflections which were collected, 5001 were unique. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

Table 1. Crystallographic data for $[Ph_3SnOSPPh_2]_n$

Molecular formula	$C_{30}H_{25}OPSSn$
Crystal size (mm)	0.25 × 0.25 × 0.30
M	583.25
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.728(4)
b (Å)	13.818(3)
c (Å)	16.774(2)
b (°)	95.29(2)
V (Å^3)	2706(1)
Z	4
D_{calc} (g cm^{-3})	1.43
μ(Mo-Kα) (cm^{-1})	10.98
F(000)	1176.00

The linear absorption coefficient for Mo-Kα is 10.98 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.94 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [2]. The non-hydrogen atoms, other than carbon, were refined anisotropically and the hydrogen atoms were included in their idealized positions with C—H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [3] was based on 2289 observed reflections ($I > 3.00\sigma(I)$) and 157 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0528$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.0446$.

The standard deviation of an observation of unit weight [4] was 1.78. The weighting scheme was based on counting statistics and included a factor ($p = 0.006$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.95 and -0.82 e Å^{-3}, respectively.

Neutral-atom scattering factors were taken from Cromer and Waber [5]. Anomalous dispersion effects were included in F_c [6], the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [7]. All calculations were performed using the TEXSAN [8] crystallographic software package of Molecular Structure Corp.

Additional material available from the Cambridge Crystallographic Data Center comprises the final atomic coordinates of the non-hydrogen atoms, H-atom coordinates, thermal parameters and all of the bond lengths and angles. Structure factor tables are available from the authors.

Calculation of Pauling bond order

The formula proposed by Pauling [9] for calculating the bond orders of partial bonds is given by $d_n - d = -0.60 \log n$, where d_n is the bond length for bond number n, and d is the length of the single bond of the same type. Based on the C—C single bond of 1.54 Å, Pauling's formula gives a bond length of 1.36 Å for $n = 2$; 1.72 Å for $n = 0.5$; and 1.90 Å for $n = 0.25$. These give percentage increases in bond length for the partial bonds of approximately 12 and 23%, respectively for $n = 0.5$ and 0.25. It is reasonable to assume that similar relationships relating bond order to interatomic distances for the much longer secondary interactions or partial bonds involving Sn and S should utilize percentage differences 'normalized' to 1.54 as follows rather than absolute differences. Pauling's relationship, which can be written as $n = 10^X$, where $X = (d - d_n)/0.6$, can be modified to allow for percentage differences 'normalized' to 1.54 to give $X = [1.54(d - d_n)/d]/0.6$ or $X = 2.57(d - d_n)/d$. Based on the assumption that in tin(IV) compounds the appropriate Sn—S single bond length is 2.458 Å found in $\mathrm{Ph_3Sn{-}S({=}S)P(OEt)_2}$ [10], typical calculated values of the lengths of Sn···S partial bonds for various values of n are as follows: 2.458 ($n = 1.0$), 2.58 (0.75), 2.75 (0.50), 3.03 (0.25) and 3.41 Å ($n = 0.10$). Similarly, based on a Sn—O single bond length of 1.955 Å found in $\mathrm{Ph_3Sn{-}O{-}SnPh_3}$ [11], typical calculated values of the lengths of Sn···O partial bonds for various values of n are as follows: 1.955 ($n = 1.0$), 2.05 (0.75), 2.18 (0.50), 2.41 (0.25) and 2.72 Å ($n = 0.10$). Both scales are compatible with the sum of the respective van der Waals radii [12]. These values are apparently underestimating the bond order relative to other modes of calculation that have been proposed [13].

RESULTS AND DISCUSSION

The solid state structure of (diphenylmonothiophosphinato)triphenyltin(IV) was determined by single-crystal X-ray diffractometry. The ORTEP diagram of the molecular unit $\mathrm{Ph_3SnOSPPh_2}$ is shown in Fig. 1. In the crystal the molecular units are associated into polymeric chains through bridging monothiophosphinato groups which act as bimetallic biconnective bridges between the tin atoms. Selected bond distances and angles are listed in Table 2 and polymeric association is shown in Fig. 2.

In the molecular fragment the monothiophosphinato group is attached to tin through the sulfur atom [Sn(1)—S(1) 2.785(3) Å]. The *anti* conformation of the SnSPO fragment (torsion angle Sn(1)S(1)P(1)O(1) 120.0°) places the O(1) atom far away from any interaction with the Sn(1) atom [Sn(1)···O(1) (non-bonding) 5.082 Å]. This oxygen atom is involved in strong coordination to a tin atom of a neighbouring molecule [Sn(1″)—O(1) 2.172(6) Å], thus leading to the polymeric chain structure shown in Fig. 2. In the ligand moiety the phosphorus–oxygen bond is shorter [P(1)—O(1) 1.517(6) Å], while the phosphorus–sulfur bond is longer [P(1)—S(1) 2.002(4) Å], than single P—O bond and double P=S bond, respectively, found in the free acid, $\mathrm{Ph_2P(S)OH}$ [P—O 1.563(7), P=S 1.931(5) Å] [14], or in the O—Me ester, $\mathrm{Ph_2P(S)OMe}$ [P—O 1.60(2), P=S 1.936(6) Å] [15]. This behavior is consistent with a delocalization of the π-electrons over the SPO system. The geometry around the phosphorus atom is a distorted tetrahedron with bond angles ranging from C(19)—P(1)—C(25) 105.1(5)° to S(1)—P(1)—O(1) 112.8(3)°.

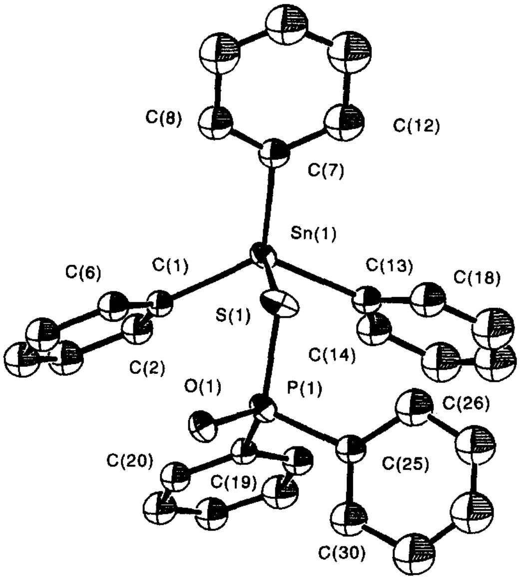


Fig. 1. ORTEP plot of the molecule $\mathrm{Ph_3SnOSPPh_2}$ showing bonding through sulfur with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity.

The environment about the tin atom is distorted trigonal bipyramidal, a geometry that is often found in triorganotin(IV) complexes of phosphorus-based acids [16,17]. The O and S atoms occupy the apical positions [O(1′)—Sn(1)—S(1) 176.6(2)°], while the carbon atoms of the phenyl groups are in the equatorial plane. The Sn(1)C(1)C(7)C(13) system is basically planar [the deviations from the best equatorial plane are: Sn(1) −0.015, C(1) 0.005, C(7) 0.005, C(13) 0.005 Å], with the C—Sn—C angles ranging from 114.8(4) to 126.4(4)°.

The resulting polymeric catena $[\mathrm{SnSPO}]_n$ has a helical conformation (Fig. 3a), with SPO fragments placed alternatively on each side of a coplanar arrangement of Sn atoms. The differences in the polymeric chain structure of the title compound and the methyl analogue, $[\mathrm{Me_3SnOSPMe_2}]_n$ (Fig. 3b) [18], are reflected in the torsion angles (Table 3). There are not many metallo-organic compounds of main group metals that form such helical structures, some examples being $[\mathrm{Li(THF)_2PHMes}]_n$ [19], $[\mathrm{LiNPr^{i}_2}]_n$ [20],

Table 2. Selected bond lengths (Å) and angles (°) for $[Ph_3SnOSPPh_2]_n$

Sn(1)—O(1′)^a	2.172(6)	O(1′)—Sn(1)—S(1)	176.6(2)
Sn(1)—S(1)	2.785(3)	O(1′)—Sn(1)—C(1)	91.1(3)
Sn(1)—C(1)	2.151(9)	O(1′)—Sn(1)—C(7)	93.6(3)
Sn(1)—C(7)	2.16(1)	O(1′)—Sn(1)—C(13)	87.2(3)
Sn(1)—C(13)	2.11(1)	S(1)—Sn(1)—C(1)	91.6(3)
		S(1)—Sn(1)—C(7)	83.3(3)
P(1)—O(1)	1.517(6)	S(1)—Sn(1)—C(13)	93.0(3)
P(1)—S(1)	2.002(4)	C(1)—Sn(1)—C(7)	118.9(4)
P(1)—C(19)	1.813(9)	C(1)—Sn(1)—C(13)	126.4(4)
P(1)—C(25)	1.83(1)	C(7)—Sn(1)—C(13)	114.8(4)
		Sn(1)—S(1)—P(1)	114.0(1)
		Sn(1)—O(1′)—P(1′)	159.6(4)
		S(1)—P(1)—O(1)	112.8(3)
		S(1)—P(1)—C(19)	112.8(3)
		S(1)—P(1)—C(25)	109.7(4)
		O(1)—P(1)—C(19)	107.0(4)
		O(1)—P(1)—C(25)	109.7(4)
		C(19)—P(1)—C(25)	105.1(5)

^{a}Symmetry equivalent position (1/2-*x*, *y*-1/2, 3/2-*z*) is denoted by prime.

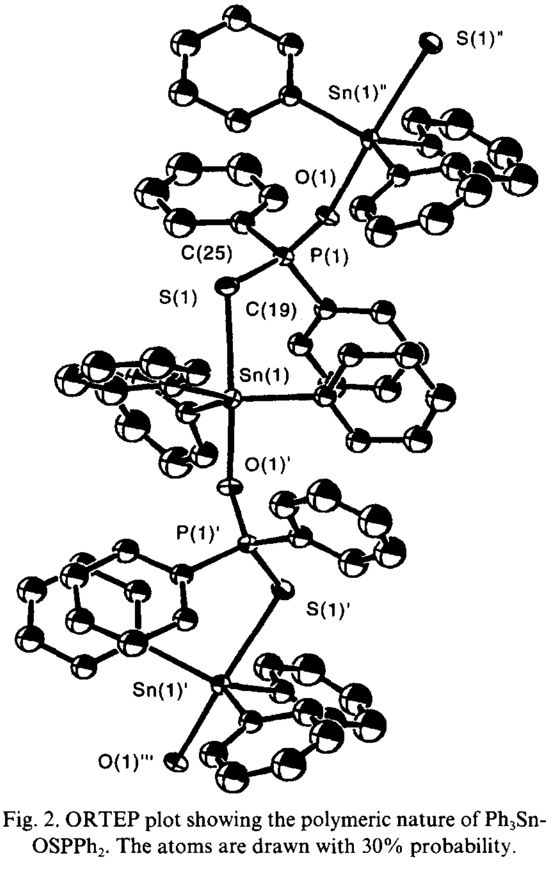


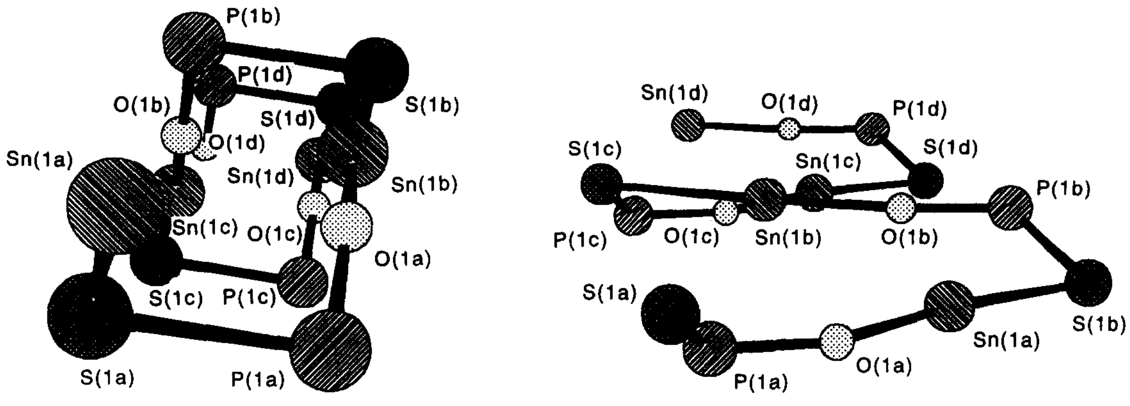
Fig. 2. ORTEP plot showing the polymeric nature of Ph_3Sn-$OSPPh_2$. The atoms are drawn with 30% probability.

$[Ph_2SbO_2PPh_2]_n$, $[Ph_2SbOSPPh_2]_n$ [21a,c], $[Ph_2SbS_2P(OPr^i)_2]_n$ [21b,c], $[Et_2BiOR]_n$ (R=Ph, C_6F_5) [22], or $[Pb_2BiNCS]_n$ [23].

A comparison of the molecular dimensions and structural patterns for the title compound and some related derivatives is summarized in Table 4. For the hydroxo-bridged dinuclear derivatives, $[R_2Sn\{O(S)R'_2\}(\mu\text{—}OH)]_2$ (R′ = Ph, OPh, OEt), regardless the nature of the organic groups attached to tin and to phosphorus, the monothio ligand is monometallic monoconnective and bonded to tin through the oxygen atom. It should be noted that in the tetranuclear derivative $([Me_2Sn\{O(S)P(OEt)_2\}]_2O)_2$, the monothio ligand exhibits a bimetallic biconnective (bridging) pattern involving only the oxygen atom [27]. For the diorganotin compounds, $Me_2Sn[O(S)PR_2]_2$, again the monothio ligand is bonded to tin through the oxygen atom, but secondary tin–sulfur interactions [significantly shorter than the sum of van der Waals radii, $\Sigma_{vdW}(Sn,S) = 4.0$ Å] [29] were also noted. The monomeric $Me_2Sn[O(S)PEt_2]_2$ exhibits only intramolecular Sn···S interactions leading to a distorted octahedral environment around tin. In the $[Me_2Sn\{O(S)PPh_2\}_2]_n$ derivative both weak intramolecular Sn···S (3.530 Å) and quite strong intermolecular Sn···S (2.939 Å) interactions were observed. The bridging pattern of one of the monothio ligands gives rise to a chain polymeric structure in which the coordination geometry at tin might be described either as trigonal bipyramidal or distorted octahedral (if the weak intramolecular Sn···S interaction is considered).

Triorganotin(IV) derivatives of 1,1-dithiolato ligands investigated so far by X-ray diffraction are monomers in solid state, the tin atom exhibiting either a tetrahedral geometry [monometallic monoconnective dithio ligand, e.g. $Ph_3SnS(S)P(OEt)_2$ [10], Sn-S 2.458, Sn···S (non-bonding) 5.326 Å], or a trigonal bipyramidal geometry [monometallic biconnective dithio ligand, e.g. $Me_3SnS_2CNMe_2$ [30] : Sn—S 2.47, Sn···S 3.16 Å].

By contrast, the triorganotin(IV) monothiophosphinates exhibit a chain polymeric structure



(a) (b)

Fig. 3. View of the polymeric catena down the polymer axix in (a) $[Ph_3SnOSPPh_2]_n$, and (b) $[Me_3SnOSPMe_2]_n$.

Table 3. Comparative torsion angles (°) and deviations from Sn_n plane (Å) in the polymeric catena of $[Ph_3SnOSPPh_2]_n$ and $[Me_3SnOSPMe_2]_n$

	$[Ph_3SnOSPPh_2]_n$ [this work]	$[Me_3SnOSPMe_2]_n$ [18]
Torsion angles		
SnOPS	−108.6	−152.7
SSnOP	−112.9	−161.1
PSSnO	−165.9	−178.4
OPSSn	−120.0	−17.8
Deviations from Sn$_n$plane		
P(1a)	−1.400	−1.248
S(1a)	−0.719	−0.790
O(1a)	−0.563	−0.689
P(1b)	1.400	1.248
S(1b)	0.719	0.790
O(1b)	0.563	0.689

due to the bimetallic biconnective (bridging) pattern of the phosphorus ligand, which involves both chalcogen atoms in strong interactions with different tin atoms. A question arises in this case, i.e. the relative strength of the tin–sulfur and tin–oxygen bonds. Partial bond orders for Sn—S and Sn—O bonds, calculated as shown in the Experimental section, give values of 0.46 (Sn—S) and 0.52 (Sn—O) for $[Ph_3SnOSPPh_2]_n$, and 0.51 (Sn—S) and 0.39 (Sn—O) for $[Me_3SnOSPMe_2]_n$, respectively. These values suggest the two chalcogen atoms of a ligand moiety are linked to two different tin atoms by fairly strong bonds of similar strength, which is consistent with an almost symmetrically bridged monothiophosphinato group. This behavior is clearly different from that observed in the polymeric $[Me_2Sn\{O(S)PPh_2\}_2]_n$, which also contains a bimetallic biconnective monothiophosphinato ligand; in this case the primary bond to tin is clearly through the Sn—O bond (2.041 Å, partial bond order $n = 0.77$), which is much stronger than the Sn—S bond (2.939 Å, partial bond order $n = 0.31$).

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3. Least-squares: Function minimized: $\Sigma w(|F_o|$

Table 4. Comparative molecular dimensions and structural patterns for the title compound and some related derivatives

Compound	Molecular dimensions (Å)				Coordination pattern	Coordination geometry at Sn atom	Ref.
$[Ph_3SnOSPPh_2]_n$	P(1)—O(1)	1.517(6)	Sn(1)···O(1)	5.082^a	bimetallic	distorted	[this
	P(1)—S(1)	2.002(4)	Sn(1)—S(1)	2.785(3)	biconnective	trigonal bipyramidal	work]
			Sn(1)—O(1′)	2.172(6)			
$[Me_3SnOSPMe_2]_n$	P(1)—O(1)	1.505(7)	Sn(1)—O(1)	2.267(6)	bimetallic	distorted	[18]
	P(1)—S(1)	1.997(3)	Sn(1)···S(1)	$5.180^{a,b}$	biconnective	trigonal bipyramidal	
			Sn(1a)—S(1)	2.737(3)			
$Me_2Sn[O(S)PEt_2]_2$	P—O	$1.57(4)^c$	Sn—O	$2.06(8)^c$	monometallic	distorted octahedral	[24]
	P—S	$1.98(1)^c$	Sn···S	$3.29(17)^{c,d}$	biconnective	(skew trapezoidal)	
$[Me_2Sn\{O(S)PPh_2\}_2]_n$	P(1)—O(1)	1.554(8)	Sn(1)—O(1)	2.041(8)	bimetallic	distorted	[25]
	P(1)—S(1)	1.984(4)	Sn(1)···S(1)	3.901(3)	biconnective	trigonal bipyramidal	
			Sn(1a)—S(1)	$2.939(3)^e$		or	
	P(2)—O(2)	1.538(9)	Sn(1)—O(2)	2.081(8)	monometallic	distorted octahedral	
	P(2)—S(2)	1.957(5)	Sn(1)···S(2)	$3.530(4)^{d'}$	biconnective		
$[Ph_2Sn\{O(S)PPh_2\}(\mu\text{-}OH)]_2$	P(1)—O(1)	1.548(3)	Sn(1)—O(1)	2.089(3)	monometallic	distorted	[1]
	P(1)—S(1)	1.997(3)	Sn(1)···S(1)	4.164^a	monoconnective	trigonal bipyramidal	
			$Sn(1)—O(2)^f$	2.024(3)			
			$Sn(1)—O(2')^f$	2.174(3)			
$[Ph_2Sn\{O(S)P(OPh)_2\}(\mu\text{-}OH)]_2$	P(1)—O(1)	1.511(2)	Sn(1)—O(1)	2.151(2)	monometallic	distorted	[26]
	P(1)—S(1)	1.944(1)	Sn(1)···S(1)	3.947^a	monoconnective	trigonal bipyramidal	
			$Sn(1)—O(2)^f$	2.032(2)			
			$Sn(1)—O(2')^f$	2.198(2)			
$[Bu^t_2Sn\{O(S)P(OEt)_2\}(\mu\text{-}OH)]_2$	P(1)—O(1)	1.481(7)	Sn(1)—O(1)	2.121(7)	monometallic	distorted	[27]
	P(1)—S(1)	1.915(4)	Sn(1)···S(1)	4.110^a	monoconnective	trigonal bipyramidal	
			$Sn(1)—O(2)^f$	2.197(6)			
			$Sn(1)—O(2')^f$	2.018(6)			

[a] Non-bonding distance.

[b] Calculated from published atomic coordinates.

[c] Averaged values; E.s.d's for average bond lengths are calculated from the equation

$$\sigma = \left[\sum_{i=1}^{i=N} (x_i - x)^2/(N-1)\right]^{1/2},$$

where x_i is ith bond length and x is the mean of the N equivalent bond lengths [28].

[d] Weak intramolecular metal–sulfur interaction.

[e] Intermolecular interaction.

[f] Sn—O(H) bond.

$-|F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C+R^2B)+(pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp = Lorentz-polarization factor, and $p = p$ factor.

4. Standard deviation of an observation of unit weight: $\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)^{1/2}$, where N_0 = number of observations and N_v = number of variables.
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