

# Metal-oxygen versus metal-sulfur bonding of the ambident monothiophosphinato ligand in some triphenylmetal(IV) derivatives, $Ph_3M[OSPR_2]$ (M = Ge, Sn, Pb). Crystal structures of $Ph_3Ge[O(S)PPh_2]$ and $[Ph_2Sn\{O(S)PPh_2\}$ ( $\mu$ -OH)]<sub>2</sub>

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Abstract—Diorganomonothiophosphinato-triphenylmetal(IV) derivatives,  $Ph_3M(OSPR_2)$  (M = Ge, Sn, Pb; R = Me, Et, Ph), were prepared and investigated. The IR and multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) NMR spectra are discussed in relation to the M—O and/or M—S bonding of the ambident  $OSPR_2^-$  ligand. The crystal and molecular structures of  $Ph_3Ge[O(S)PPh_2]$  (1) and  $[Ph_2Sn\{O(S)PPh_2\}(\mu-OH)]_2$  (2) were determined by Xray diffractometry. The asymmetric unit for  $Ph_3Ge[O(S)PPh_2]$  contains two independent molecules. The monothiophosphinato group is bonded to germanium only through oxygen (av. Ge—O 1.826, Ge…S 3.892 Å), leading to a tetrahedral coordination around the germanium atom. The crystal of  $[Ph_2Sn\{O(S)PPh_2\}(\mu-OH)]_2$  consists of dimeric units built up through Sn—O—Sn bridges involving the oxygen atom of the hydroxy groups. The monothiophosphinato group is again monodentate  $[Sn(1)-O(1) 2.089(3), Sn(1) \cdots S(1)$  (nonbonding) 4.164 Å] and the coordination geometry around tin is trigonal bipyramidal, with the O(1) atom of the phosphorous ligand and the O(2') atom of a bridging hydroxy group in axial positions. Copyright © 1996 Elsevier Science Ltd

Keywords: monothiophosphinato ligand; organogermanium(IV); organotin(IV); organolead(IV) compounds.

In contrast to the large amount of research work concerned with metal derivatives of dithiophosphorus ligands [1, 2], there are comparatively few investigations of the related monothiophosphinates. In the free acids (a) the presence of O—H groups was established by X-ray diffractometry. The corresponding  $[R_2PSO]^-$  anion is an ambident nucleophile and can exhibit primary coordination through either oxygen

(b) or sulfur (c), depending on the "hard/soft" acid character of the metallic centre.

Thus, X-ray diffraction studies show that in N(CH<sub>2</sub> CH<sub>2</sub>O)<sub>3</sub>SiO(S)PPh<sub>2</sub> [5] or Me<sub>3</sub>Sb[O(S)PPh<sub>2</sub>]<sub>2</sub> [6] the diphenylmonothiophosphinato ligand is attached to the metal only through oxygen, while in the gold complex [(C<sub>6</sub>F<sub>3</sub>)<sub>2</sub>Au{S(O)PPh<sub>2</sub>}(CH<sub>2</sub>PPh<sub>2</sub>Me) [7] it is linked only through the sulfur atom. Moreover, this type of ligand not only could exhibit monometallic monoconnective (monodentate) coordination, but also could act in a monometallic biconnective (bidentate) fashion or in various bridging patterns (bi-

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metallic biconnective or triconnective, trimetallic tetraconnective). Thus, anisobidentate coordination with primary bonds to oxygen (d) or to sulfur (e), or isobidentate coordination (f), is, in principle, possible. Secondary bonds  $[M \cdots S \text{ in } (\mathbf{d}) \text{ and } M \cdots O \text{ in } (\mathbf{e})]$ are longer than covalent bond lengths but shorter than van der Waals interatomic distances. Generally, with borderline Lewis acids, both oxygen and sulfur atoms of the  $[R_2PSO]^-$  unit are involved in the coordination to the metallic centre (Table 1), as established by single-crystal X-ray diffraction studies. When such compounds are dissolved the crystal lattice is generally destroyed and the weak intra- or intermolecular chalcogen-metal interactions observed in the solid state are probably broken. In this case the magnitude of the <sup>31</sup>P NMR chemical shift is indicative of the coordination pattern of the [R<sub>2</sub>PSO]<sup>-</sup> ligand, i.e. monodentate coordination with primary bonds through the oxygen or the sulfur atom, or a biconnective pattern involving both chalcogen atoms.

We now report the synthesis and spectroscopic characterization of triphenylmetal(IV) diorganomonothiophosphinates,  $Ph_3M[OSPR_2]$  (M = Ge, Sn, Pb; R = Me, Et, Ph), and the crystal and molecular structures of  $Ph_3Ge[O(S)PPh_2]$  and  $[Ph_2Sn\{O(S)PPh_2\}(\mu-OH)]_2$ .

#### **EXPERIMENTAL**

The starting materials were prepared according to literature methods: Ph<sub>3</sub>GeCl [14], Na[OSPMe<sub>2</sub>] · 1.5H<sub>2</sub>O, Na[OSPEt<sub>2</sub>] · 3H<sub>2</sub>O[15], and NH<sub>4</sub>[OSPPh<sub>2</sub>] [6,16]. Ph<sub>3</sub>ECl (E = Sn, Pb) were commercial products. Ph<sub>3</sub>Sn[OSPEt<sub>2</sub>] and Ph<sub>3</sub>Sn[OSPPh<sub>2</sub>] were prepared as previously described [8,9]. Infrared spectra were run in the range 4000–400 cm<sup>-1</sup> on a Perkin– Elmer 283B spectrometer, as KBr disks. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Varian Gemini 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. The chemical shifts are reported in ppm relative to TMS and 85% H<sub>3</sub>PO<sub>4</sub>, respectively.

Preparation of the title compounds,  $Ph_3M[OSPR_2]$  (Table 2)

A reaction mixture containing triphenylmetal chloride,  $Ph_3MCl$ , and the corresponding sodium or ammonium diorganomonothiophosphinate,  $M^1[OS PR_2] \cdot nH_2O$  (excess was used for R = Me, Et) in 50 cm<sup>3</sup> organic solvent was stirred at room temperature for 8 h. The insoluble solid (the resulting  $M^1Cl$  and the excess starting materials) was filtered off, the clear filtrate was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then the solvent was evaporated to dryness in a rotary evaporator. The remaining solid product was recrystallized from organic solvents. When oily products were obtained (M = Ge, R = Me, Et), treatment with n-hexane led to the title compounds as white solids.

### Crystal structure determinations

Colourless block crystals of  $Ph_3Ge[O(S)PPh_2]$  (1) and  $[Ph_2Sn{O(S)PPh_2}(\mu-OH)]_2$  (2) were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated  $Mo-K_{\alpha}$  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 range  $8.56 < 2\theta < 11.50^{\circ}$  for 1 and  $8.40 < 2\theta < 14.58^{\circ}$  for 2 corresponded to a monoclinic and triclinic cell, respectively, whose dimensions are given in Table 3. The systematic absences (h0l, l = 2n+1; 0k0, k = 2n+1) were observed for 1. Based on statistical analyses of intensity distributions and the successful solution and refinement of the structure, the space group was determined to be P-1 for 2.

The data were collected at a temperature of  $23 \pm 1^{\circ}$ C using the  $\omega - 2\theta$  scan technique to a maximum of  $2\theta$  value of 50.0°. The  $\omega$  scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° for compound 1 and 0.35° for 2, with a take-off angle of 6.0°. Scans of  $(1.37+0.30 \tan \theta)^{\circ}$  for 1 and  $(1.68+0.30 \tan \theta)^{\circ}$  for 2

	Single-crystal X-ray diffractometry data Molecular dimensions Coordination (Å) pattern				ata		
Compound					Coordination pattern	 δ( <sup>31</sup> Ρ) (ppm)	Ref.
N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> SiO(S)PPh <sub>2</sub>	PO PS	1.549(3) 1.934(1)	Si—O Si····S	1.700(3) 4.044 <sup>b,c</sup>	monometallic monoconnective	63.2ª	[5]
$Me_3Sb[O(S)PPh_2]_2$	PO PS	$1.55(1)^d$ $1.95(2)^d$	Sb—O Sb···S	$2.111(5)^d$ $3.96(5)^{c,d}$	monometallic monoconnective	75.3 <sup>e</sup>	[6]
$(C_6F_5)_2Au\{S(O)PPh_2\}\$ $(CH_2PPh_2Me)$	РО	1.467(18)	Au…O	4.055 <sup>b,c</sup>	monometallic	45.9 <sup>e</sup>	[7]
	P—S	2.026(12)	Au—S	2.363(7)	monoconnective		
$Me_2Sn[O(S)PEt_2]_2$	Р—О	$1.57(4)^{d}$	Sn-O	$2.06(8)^{d}$	monometallic		[8]
	P—S	$1.98(1)^{d}$	$\mathbf{Sn}\cdots\mathbf{S}$	$3.29(17)^{df}$	biconnective		
$[Me_2Sn{O(S)PPh_2}_2]_n$	P(1)-O(1)	1.554(8)	Sn(1) - O(1)	2.041(8)	bimetallic		[9]
	P(1)—S(1)	1.984(4)	$\frac{\mathrm{Sn}(1)\cdots\mathrm{S}(1)}{\mathrm{Sn}(1a)-\mathrm{S}(1)}$	3.901(3) <sup>f</sup> 2.939(3) <sup>g</sup>	biconnective		
	P(2)O(2)	1.538(9)	Sn(1) - O(2)	2.081(8)	monometallic		
	P(2) - S(2)	1.957(5)	$Sn(1) \cdots S(2)$	3.530(4) <sup>f</sup>	biconnective		
[Me <sub>3</sub> SnOSPMe <sub>2</sub> ] <sub>n</sub>	P—O(1) P—S(1)	1.505(7) 1.997(3)	$Sn(1) \longrightarrow O(1)$ $Sn(1) \cdots S(1)$ $Sn(1a) \longrightarrow S(1)$	2.267(6) $5.180^{b,c}$ 2.737(3)	bimetallic biconnective	76.6	[10]
[Ph <sub>2</sub> SbOSPPh <sub>2</sub> ],	P—O(1) P—S(1)	1.504(3) 2.010(3)	Sb - O(1) $Sb \cdots S(1)$ Sb(1a) - S(1)	2.299(3) 4.524 <sup>b,c</sup> 2.753(1)	bimetallic biconn <del>e</del> ctive	51.7 <sup>e,f</sup>	[11]
[Me <sub>2</sub> TIOSPPh <sub>2</sub> ] <sub>n</sub>	PO(1) P\$(1)	1.487(7) 1.994(3)	$Tl(1) \cdots O(1) Tl(1) - S(1) Tl(1a) - O(1) Tl(1b) \cdots S(1) $	3.143(7) <sup>g</sup> 2.919(3) 2.509(7) <sup>h</sup> 3.402(3)	trimetallic tetraconnective	60.3 <sup>e</sup>	[12]

Table 1. Single-crystal X-ray diffraction and <sup>31</sup>P NMR data (solution) for some metal monothiophosphinates

"In CD<sub>3</sub>CN.

<sup>b</sup> Calculated from published atomic coordinates.

<sup>c</sup>Non-bonding distance.

<sup>d</sup> Averaged values; esds for average bond lengths are calculated from the equation  $\sigma = \left\{ \left[ \sum_{i=1}^{i=N} (x_i - x)^2 / (N-1) \right] \right\}^{1/2}$ , where is *i*th bond length and x is the mean of the *n* equivalent bond lengths [13]  $x_i$  is *i*th bond length and x is the mean of the *n* equivalent bond lengths [13].

<sup>e</sup> In CDCl<sub>3</sub>.

<sup>f</sup>This work.

<sup>g</sup>Weak intramolecular metal-sulfur interaction.

<sup>h</sup>Intermolecular interaction.

were made at a speed of  $32.0^{\circ} \text{ min}^{-1}$  (in  $\omega$ ). The weak reflections  $[I < 10.0\sigma(I)]$  were rescanned (maximum of four 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 10,281 reflections for compound 1 and 4277 for 2 that were collected, 9971 and 4047, respectively, were unique ( $R_{int} = 0.153$  and 0.061). 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).

The linear absorption coefficient for  $Mo-K_{a}$  is 12.84  $cm^{-1}$  for compound 1 and 12.88  $cm^{-1}$  for 2. An empirical absorption correction, based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.76 to 1.00 for 1 and 0.64 to 1.00 for 2. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods [17]. The non-hydrogen atoms, other than carbon, were refined anisotropically. The hydrogen atom attached to oxygen in compound 2 was found from the Fourier map and its position then fixed. The hydrogen atoms attached to carbon were included in their idealized positions with C-H set at 0.95 Å. Their isotropic thermal parameters were set at 1.2 times that of the atom to which they were attached. The final cycle of full-matrix least-squares refinement [18] was based on 2677 observed reflections for 1 and 2967 for 2  $[I > 3.00\sigma(I)]$  and 314 variable parameters for 1 and 262 for 2.

The standard deviations of an observation of unit weight [19] were 1.97 and 1.53 for compounds 1 and

	Starting materials				
Ph <sub>3</sub> MCl g (mmol)	$M^{1}[OSPR_{2}] \cdot nH_{2}O$ g (mmol)	Reaction solvent	Product [yield : g(%)]	M.p. (°C)	Recryst. solvent
Ph <sub>3</sub> GeCl	Na[OSPMe <sub>2</sub> ] • 1.5H <sub>2</sub> O	CHCl <sub>3</sub>	Ph <sub>3</sub> Ge[OSPMe <sub>2</sub> ]	85-87	
1.13 (3.33)	0.85 (5.35)		1.00 (75)		
Ph <sub>3</sub> GeCl	$Na[OSPEt_2] \cdot 3H_2O$	CHCl <sub>3</sub>	Ph <sub>3</sub> Ge[OSPEt <sub>2</sub> ]	5557	CHCl <sub>3</sub>
1.13 (3.33)	1.14 (5.33)		1.00 (67)		-
Ph <sub>3</sub> GeCl	NH <sub>4</sub> [OSPPh <sub>2</sub> ]	C <sub>6</sub> H <sub>6</sub>	Ph <sub>3</sub> Ge[OSPPh <sub>2</sub> ]	136-137	cyclohexane
0.34(1.00)	0.25 (1.00)		0.47 (87)		•
Ph <sub>3</sub> SnCl	Na[OSPMe <sub>2</sub> ] · 1.5H <sub>2</sub> O	CHCl <sub>3</sub>	Ph <sub>3</sub> Sn[OSPMe <sub>2</sub> ]	296	
0.84 (2.18)	0.051 (3.27)		0.72 (72)		
Ph <sub>3</sub> PbCl	$Na[OSPMe_2] \cdot 1.5H_2O$	CHCl <sub>3</sub>	Ph <sub>3</sub> Pb[OSPMe <sub>2</sub> ]	dec.	
0.95 (2.00)	0.51 (3.20)		0.63 (57)		
Ph <sub>3</sub> PbCl	$Na[OSPEt_2] \cdot 3H_2O$	CHCl <sub>3</sub>	Ph <sub>3</sub> Pb[OSPEt <sub>2</sub> ]	dec.	
0.95 (2.00)	0.68 (3.18)		0.92 (80)		
Ph <sub>3</sub> PbCl	NH <sub>4</sub> [OSPPh <sub>2</sub> ]	CHCl <sub>3</sub>	Ph <sub>3</sub> Pb[OSPPh <sub>2</sub> ]	145-147	CHCl <sub>3</sub> /hexane
0.48 (1.00)	0.25 (1.00)		0.60 (89)		-7

Table 2. Preparation of Ph<sub>3</sub>M[OSPR<sub>2</sub>]

Table 3. Crystal data and details of structure refinement for  $Ph_3Ge[O(S)PPh_2]$  (1) and  $[Ph_2Sn\{O(S)PPh_2\}(\mu-OH)]_2$  (2)

	1	2
Formula	C <sub>30</sub> H <sub>25</sub> GeOPS	$C_{48}H_{42}O_4P_2S_2Sn_2$
Crystal size (mm)	$0.42 \times 0.33 \times 0.24$	$0.31 \times 0.24 \times 0.23$
M	537.15	1046.30
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	<i>P</i> -1
a (Å)	19.515(8)	11.098(4)
$b(\mathbf{A})$	14.990(7)	12.395(7)
$c(\mathbf{A})$	20.889(7)	9.844(4)
α (°)		108.09(4)
β (°)	117.37(3)	92.49(4)
γ (°)		114.33(3)
$V(Å^3)$	5426(4)	1149(1)
Z	8	1
$D_{\text{calc}} (\text{g cm}^{-3})$	1.32	1.51
$\mu (Mo-K_{\alpha}) (cm^{-1})$	12.84	12.88
<i>F</i> (000)	2208.00	524.00
$R = \Sigma( F_{\rm o}  -  F_{\rm c} ) / \Sigma  F_{\rm o} $	0.0549	0.032
$R' = [\Sigma w ( F_{\rm o}  -  F_{\rm c} )^2 / \Sigma w F_{\rm o}^2]^{1/2}$	0.0347	0.0255
Goodness-of-fit, $S = [\Sigma( F_o  -  F_c )/\sigma]/(N_o - N_v)$	1.97	1.53

2, respectively. The weighting scheme was based on counting statistics and included a factor (p = 0.004 for 1 and 0.003 for 2) to downweight the intense reflections. Plots of  $\Sigma w(|F_o| - |F_c|)^2$  versus  $|F_0|$ , 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 0.41 and -0.40 for 1 and 0.67 and -0.53 eÅ<sup>-3</sup> for 2.

Neutral-atom scattering factors were taken from Cromer and Waber [20]. Anomalous dispersion effects were included in  $F_c$  [21]; the values for  $\Delta f$  and  $\Delta f'$ were those of Creagh and McAuley [22]. All calculations were performed using the TEXSAN [23] crystallographic software package.

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

## **RESULTS AND DISCUSSION**

The title compounds were prepared as colourless, crystalline solids, by reacting the sodium or ammonium salts of the diorganomonothiophosphinate with the appropriate triphenylmetal(IV) chloride, in chloroform or benzene, according to Eq. (1):

$$M^1 = NH_4; \quad R = Ph \tag{1}$$

The triphenylgermanium(IV) and triphenyltin(IV) derivatives are stable compounds and can be stored in the solid state in the absence of air and moisture for months. An old sample of  $Ph_3Sn[O(S)PPh_2]$  stored for years in a sealed flask showed no sign of decomposition as proved by NMR analysis. In contrast, the triphenyllead(IV) monothiophosphinates are quite unstable. Thus, for R = Me and Et, the solid compounds become grey in about 24 h.

In solution, however, the stability of the title tin and lead compounds is lower. Thus, a CHCl<sub>3</sub> solution of Ph<sub>3</sub>Pb[OSPPh<sub>2</sub>] kept in the refrigerator turned orange and a red solid product deposited within days. Attempts to grow crystals of Ph<sub>3</sub>Sn[OSPR<sub>2</sub>] for X-ray diffractometry investigations have failed, and only for R = Ph were some crystals separated that proved (NMR data, X-ray diffractometry) to be the unexpected hydroxo-bridged diphenyltin(IV) dimer,  $[Ph_2Sn{O(S)PPh_2}(\mu-OH)]_2$ . Indeed the magnitude of  ${}^{3}J_{SnH}$  [<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.3 (m, P-C<sub>6</sub>H<sub>5</sub>, Sn-C<sub>6</sub>H<sub>5</sub>, -meta + para), 7.66 (dd,  ${}^{3}J_{HH}$  7.7,  ${}^{4}J_{HH}$  1.2,  ${}^{3}J_{SnH}$  85.9 Hz, Sn-C<sub>6</sub>H<sub>5</sub>, -ortho), 7.80 (ddd,  ${}^{3}J_{HH}$  7.6,  ${}^{4}J_{HH}$ 1.4,  ${}^{3}J_{PH}$  13.5 Hz, P-C<sub>6</sub>H<sub>5</sub>, -ortho)] and of  ${}^{2}J_{SnC}$  and  ${}^{3}J_{\text{SnC}}$  [<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  127.96 (d,  ${}^{3}J_{\text{PC}}$  12.8 Hz, P- $C_{\rm m}$ ), 128.79 (s, <sup>3</sup>J<sub>SnC</sub> 94.9 Hz, Sn- $C_{\rm m}$ ), 130.43 (s, P- $C_{\rm p}$ ), 130.67 (s, Sn- $C_{\rm p}$ ), 130.75 (d, <sup>2</sup> $J_{\rm PC}$  11.0 Hz, P- $C_{\rm 0}$ ), 135.84 (s,  ${}^{2}J_{\text{SnC}}$  65.0 Hz, Sn-C<sub>0</sub>). 138.48 (d,  ${}^{1}J_{\text{PC}}$  106.7 Hz, P- $C_i$ ], 139.19 (s, Sn- $C_i$ ) are consistent with the presence of only two phenyl groups attached to tin (cf. <sup>13</sup>C NMR data for PH<sub>2</sub>SnCl<sub>2</sub>;  ${}^{2}J_{SnC}$  63,  ${}^{3}J_{SnC}$  90Hz, and for  $Ph_3SnCl$ : <sup>2</sup> $J_{SnC}$  49, <sup>3</sup> $J_{SnC}$  68 Hz) [24]. Moreover, the <sup>31</sup>P resonance of the hydroxo-bridged diphenyltin(IV) derivative was found to be surrounded by satellites due to phosphorous-tin coupling [<sup>31</sup>P NMR  $(CDCl_3)$ :  $\delta$  68.1 (s, <sup>2</sup>J<sub>PSn</sub> 126.0 Hz)], a pattern that was not observed for the Ph<sub>3</sub>Sn[OSPR<sub>2</sub>] compounds. The same hydroxobridged derivative was obtained upon attempted monocrystal growth of Ph<sub>2</sub>Sn [OSPPh<sub>2</sub>]<sub>2</sub>, described previously [9]. This is in line with a previous report that bis(diorganomonothiophosphinato)diorganotin(IV) derivatives, R<sub>2</sub>Sn[OSP (OR')2]2, are sensitive to atmospheric moisture and a monothiophosphinato group is readily hydrolysed to give  $[R_2Sn{O(S)P(OR')_2}(\mu-OH)]_2$  or  $[R_2Sn{O(S)P(OR')_2}(\mu-OH)]_2$  $(S)P(OR')_2\}_2O]_2$ , depending on the nature of the R groups on the tin or phosphorous atoms [25, 26]. In our case the same compound was formed both by hydrolytic splitting of a phenyl group from Ph<sub>3</sub>Sn

 $[OSPPh_2]$  or a monothiophosphinato group from  $Ph_2Sn[OSPPh_2]_2$ . Crystal samples of both origins were subjected to complete X-ray diffraction analysis in two different, independent laboratories (by J.E.D. and F.C.) and the results were practically identical. The data reported here are for the sample obtained from  $Ph_3Sn[OSPPh_2]$  (J.E.D.'s laboratory).

The compounds were investigated by IR and multinuclear NMR spectroscopy and the crystal and molecular structure of  $Ph_3Ge[O(S)PPh_2]$  and  $[Ph_2Sn\{O(S)PPh_2\}(\mu-OH)]_2$  were determined by X-ray diffractometry.

#### Infrared spectra

The analysis of the infrared spectra was focused on the v(PO) and v(PS) stretching vibrations that proved to be a useful tool in establishing the coordination pattern of the monothiophosphinato ligand. The IR data for the present compounds are listed in Table 4, and compared with data for the corresponding O- and S-alkyl esters of the monothiophosphinic acids and their sodium or ammonium salts.

The infrared spectra of the O-R' esters,  $R_2P(S)OR'$ , exhibit medium to very strong absorption bands in the regions of  $1040-990 \text{ cm}^{-1}$  and 590-580 $cm^{-1}$  (R = Me, Et) or 630 cm<sup>-1</sup> (R = Ph) which were assigned to single bond P-O(R) and double bond P=S stretching vibrations. For the S-R' esters,  $R_2P(O)SR'$ , the absorption bands corresponding to the double bond P=0 and single bond P-S(R)stretching vibrations are shifted, as expected, to higher (1200-1180 cm<sup>-1</sup>) and lower [520-510 cm<sup>-1</sup> (R = Me, Et) or 570 cm<sup>-1</sup> (R = Ph)] wavenumbers, respectively. The infrared spectra of the sodium or ammonium salts exhibit absorption bands at intermediate values between those observed for the O-R' and S-R' esters, corresponding to a delocalization of the  $\pi$  electrons over the PSO fragment.

All triphenylgermanium(IV) derivatives exhibit medium to strong bonds at about 906 and 660-620  $cm^{-1}$  which clearly indicate the coordination of the monothiophosphinato ligand only through the oxygen atom. Therefore, it is reasonable to propose a monomeric structure (g) for  $Ph_3Ge[O(S)PR_2]$  in the solid state. In contrast, for triphenyltin(IV) and -lead(IV) analogues the positions of the bands assigned to the phosphorus-oxygen and phosphorous-sulfur stretching vibrations (Table 4) suggest bidentate behaviour of the monothiophosphinato ligand, i.e. coordination through both oxygen and sulfur atoms, thus leading to an increase of the coordination number of the central metal atom from four to five. As a result either monomeric h or polymeric i structures might be considered for  $\{Ph_3M[OSPR_2]\}_n$ (M = Sn, Pb) in the solid state. In this case, on the basis of infrared data it is impossible to distinguish between isobidentate and anisobidentate coordination, and to assign a primary coordination of

Compound	v(P—O)	$v(\mathbf{P}\cdots\mathbf{O})$	v(P=O)	v(P—S)	$v(\mathbf{P}\cdots\mathbf{S})$	v(P==S)	Ref
Me <sub>2</sub> P(S)OMe	1038					581	[27]
Me <sub>2</sub> P(O)SMe			1184	510			[27]
Me <sub>2</sub> PSONa		1075vs			562s		[28]
Ph <sub>3</sub> GeOSPMe <sub>2</sub>	960vs					617vs	This work
Ph <sub>3</sub> SnOSPMe <sub>2</sub>		1080vs			545s		This work
Ph <sub>3</sub> PbOSPMe <sub>2</sub>		1110vs			535vs		This work
Et <sub>2</sub> P(S)OPr <sup>n</sup>	990s					580m	[29]
Et <sub>2</sub> P(O)SPr <sup>n</sup>			1180s	520m			[29]
Et <sub>2</sub> PSONa		1084vs			553ms		[28]
Ph <sub>3</sub> GeOSPEt <sub>2</sub>	965s					622m	This work
Ph <sub>3</sub> SnOSPEt <sub>2</sub>		1100s			535m		This work
Ph,PbOSPEt,		1100vs			530m		This work
Ph <sub>2</sub> P(S)OMe	1027vs					635s	[30]
Ph <sub>2</sub> P(O)SMe			1200vs	568vs			[30]
Ph <sub>2</sub> PSONH <sub>4</sub>		1045s			628vs		[31]
		1051s					
Ph <sub>3</sub> GeOSPPh <sub>2</sub>	965vs					660m	This work
Ph <sub>3</sub> SnOSPPh <sub>2</sub>		1063s			595s		This work
Ph <sub>3</sub> PbOSPPh <sub>2</sub>		1055s			590s		This work

Table 4. Infrared data for Ph<sub>3</sub>M[OSPR<sub>2</sub>] derivatives and related compounds

the monothiophosphinato ligand through oxygen or sulfur respectively. Single-crystal X-ray diffractometry investigations have confirmed a structure of type **g** for  $Ph_3Ge[O(S)PPh_2]$ (see below) and of type **i** for the { $Me_3Sn[OSPMe_2]$ }<sub>n</sub> analogue [10].

### NMR spectra

All of the triphenylmetal(IV) derivatives were investigated in solution by multinuclear NMR spectroscopy. Their <sup>1</sup>H NMR spectra (Table 5) exhibit two sets of resonances corresponding to the organic groups attached to phosphorous and metal atoms, respectively. For the protons of the diorganomonothiophosphinato ligands only one resonance with the expected splitting pattern owing to the proton–proton and phosphorous–proton couplings was observed for the P-CH<sub>3</sub> (doublet), P-CH<sub>2</sub>- CH<sub>3</sub> (doublet of triplets), P-CH<sub>2</sub>-CH<sub>3</sub> (doublet of quartets), P-C<sub>6</sub>H<sub>5</sub> (*ortho*-H, doublet of multiplets), respectively. This indicates the equivalence of the organic groups attached to the same phosphorous atom on the NMR time-scale. The phenyl groups attached to the metal atom exhibit two multiplet resonances for the *ortho* and *meta*+*para* protons. In the case of Ph<sub>3</sub>Sn<sup>IV</sup> and Ph<sub>3</sub>Pb<sup>IV</sup> derivatives the resonance of the *ortho* protons is surrounded by satellites caused by the tin-proton and lead-proton couplings, with the expected magnitude of the <sup>3</sup>J(SnH) (*ca*, 60 Hz) and <sup>3</sup>J(<sup>207</sup>PbH) (*ca* 105 Hz) coupling constants.

The <sup>13</sup>C NMR spectra (Table 6) show the expected downfield resonances for the carbon atoms of the phenyl groups attached to the metal. For the tin and lead derivatives the signals for the *ortho* and *meta* carbons are surrounded by satellites due to the metalcarbon couplings, with a magnitude of the <sup>2</sup>J(MC)



	P	'n₃M		Р	Et	H	PPh
Compound	ortho	meta + para	РМе	CH <sub>2</sub>	CH3	ortho	meta + para
Ph <sub>3</sub> GeOSPMe <sub>2</sub>	7.74dd	7.48m	1.74d	<u> </u>			
	${}^{3}J_{\rm HH}$ 7.6		${}^{2}J_{\rm PH}$ 13.2				
	<sup>4</sup> J <sub>нн</sub> 2.0						
Ph <sub>3</sub> SnOSPMe <sub>2</sub>	7.77dd	7.44s,br	1.67d				
· ·	${}^{3}J_{\rm HH}$ 6.4	,	${}^{2}J_{\rm PH}$ 13.2				
	<sup>4</sup> J <sub>1111</sub> 2.8						
	${}^{3}J_{8-11}$ 61.8						
Ph <sub>2</sub> PbOSPMe <sub>2</sub>	7.82d	7.54dd (meta)	1.63d				
1 11.31 0 0 0 1 1.102	<sup>3</sup> Jun 7.1	<sup>3</sup> Jun 7.5	$^{2}J_{\rm PH}$ 13.1				
	$^{3}/_{mu}$ 106.0	7 41t (nara)	5 PH 1911				
	0 P6H 100.0	$^{3}J_{\rm HH}$ 7.5					
Ph <sub>3</sub> GeOSPEt <sub>2</sub>	7.73dd	7.46m		1.84dq	1.09dt		
· ·	${}^{3}J_{\rm HH}$ 7.7			$^{2}J_{\rm PH}$ 12.5	${}^{3}J_{\rm PH}$ 19.7		
	4J <sub>µµ</sub> 1.8			${}^{3}J_{\rm HH}$ 7.4	${}^{3}J_{\rm HH}$ 7.4		
Ph <sub>2</sub> SnOSPEt <sub>2</sub>	7.80d	7.45m		1.82da	1.07dt		
2	${}^{3}J_{\mu\mu}$ 6.0			<sup>2</sup> J <sub>рн</sub> 12.0	<sup>3</sup> Ј <sub>РН</sub> 19.5		
	<sup>3</sup> J <sub>5-11</sub> 57.8			<sup>3</sup> Jun 7.7	${}^{3}J_{\rm HH}$ 7.7		
Ph <sub>2</sub> PbOSPEt <sub>2</sub>	7.86d	7.51dd (meta)		1.79da	1.07dt		
	<sup>3</sup> J 6.8	<sup>3</sup> Jun 7.1		$^{2}J_{\rm BH}$ 11.8	<sup>3</sup> J <sub>pu</sub> 19.3		
	${}^{3}I_{\rm mu}$ 104 9	7 40t ( $para$ )		<sup>3</sup> J76	<sup>3</sup> J76		
	PBH IVII	$^{3}J_{m}, 7.1$		• HH 110	CHH / C		
Ph.GeOSPPh.	7 66dd	7 37m <sup>a</sup>				7 81ddd	7 37m"
1.1,000,00,1.1.2	<sup>3</sup> J 7 7					$^{3}J_{\rm ru}$ 13.7	
	<sup>4</sup> <i>L</i> <sub>m</sub> 1.8					<sup>3</sup> <i>L</i> 8 0	
	CHH 1.0					<sup>4</sup> L16	
Ph.SnOSPPh.	7 65d	7 29mª				7 70dd	7.29m"
1 113011001 1 112	$^{3}L_{1}$ 67	7.29111				${}^{3}I_{-1}$ 13.4	7.2711
	$^{3}L$ 54 7					${}^{3}L74$	
Ph.PhOSPPh.	777d	7 38mª				7 72dd	$7.38m^{a}$
1 1132 00001 1 112	${}^{3}L71$	7.5011				${}^{3}L_{1}$ 13.1	7.50m -
	$^{3}L$ 105.6					<sup>3</sup> <i>I</i> 72	
	JP6H 103.0					JHH 7.5	

#### Table 5. <sup>1</sup>H NMR data for Ph<sub>3</sub>M[OSPR<sub>2</sub>] derivatives

" Resonances for M-Ph and P-Ph overlapped.

and  ${}^{3}J(MC)$  corresponding to a triphenylmetal moiety. No resonances suggesting the presence of a Ph<sub>2</sub>Sn derivative were observed in the spectrum of Ph<sub>3</sub>Sn[OSPPh<sub>2</sub>]. Regardless of the nature of the metal atom in the Ph<sub>3</sub>M moiety, the <sup>13</sup>C NMR spectra show only one set of signals for each carbon atom of the OSPR<sub>2</sub> ligand, thus indicating the equivalence of the organic groups attached to the same phosphorous atom on the NMR time-scale. These resonances exhibit the expected doublet pattern caused by the phosphorous–carbon couplings.

For all (diorganomonothiophosphinato)triphenylmetal(IV) the <sup>31</sup>P NMR spectra are seen as singlets. The magnitude of <sup>31</sup>P chemical shift of diorganomonothiophosphinic acid derivatives can be used to distinguish between the  $R_2P(=S)O$ ,  $R_2P(=O)$  S or [ $R_2PSO$ ] structure of the coordinated ligands. Thus, the resonance for the S ester is shifted about 40–60 ppm to higher field, as expected, compared with the signal observed for the free acid (which contains an O—H group) and its O—Me ester, for the same R group attached to phosphorous. The resonances for the corresponding sodium or ammonium salts have intermediate values between these two extremes. A comparison of the <sup>31</sup>P chemical shifts of the Ph<sub>3</sub>M derivatives with those of the free acids, their O— and S—Me esters and their sodium or ammonium salts is given in Table 7 and reveals interesting results. Thus, for all Ph<sub>3</sub>Ge<sup>IV</sup> derivatives the <sup>31</sup>P chemical shift is of the same magnitude as observed for the corresponding free acid or its O—Me ester. This behaviour is consistent with monodentate coordination of the monothiophosphinato moiety only through its oxygen atom, structure **g** found in the solid state for Ph<sub>3</sub>Ge[O(S)PPh<sub>2</sub>] and indicated by the IR spectra, being also preserved in solution.

For the  $Ph_3M^{IV}$  (M = Sn, Pb) derivatives, with one exception, the <sup>31</sup>P chemical shift has an intermediate magnitude between those observed for the O— and S—Me esters of the corresponding mono-thiophosphinic acid. Taking into account the presence of only one set of <sup>1</sup>H and <sup>13</sup>C resonances, respectively,

ompound 1,GeOSPMe <sub>2</sub> 1,SnOSPMe <sub>2</sub> 1,PbOSPMe <sub>2</sub> 1,GeOSPEt <sub>2</sub> 1,SnOSPEt <sub>2</sub> 1,GeOSPPt <sub>2</sub> 1,GeOSPPh <sub>2</sub>	C <sub>1</sub> 134.43s 139.05s 150.09s 134.44s 134.44s 139.05s 139.05s 137.92s	Ph. C <sub>o</sub> 134.76s 134.76s 134.76s 134.76s 134.76s 137.10s 134.82s 134.82s 134.82s 134.82s 134.82s 134.76s 137.27s 134.76s 137.27s 136.75s 136.72s 136.72s 136.72s 136.72s 136.72s 136.72s 136.72s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.75s 137.7	<sup>3</sup> M C <sup>m</sup> 128.63s 128.63s <sup>3</sup> J <sub>5ac</sub> 62.2 130.18s 130.18s 130.18s 130.18s 130.18s 130.18s 128.54s 128.54s 128.54s 128.79s 123.40s 123.40s 123.40s 123.40s	C <sub>p</sub> 130.74s 128.89s 128.89s 128.89s 129.53s 129.93s 129.39s 129.39s 120.05s	PMe 26.43d JPc 74.2 25.43d JPc 71.8 25.28d JPc 71.2	PE CH <sub>2</sub> CH <sub>2</sub> U <sub>Fe</sub> 71.5 28.36d <sup>1</sup> J <sub>Fe</sub> 68.4 28.36d <sup>1</sup> J <sub>Fe</sub> 67.5	t CH <sub>3</sub> 7.31d <sup>2</sup> J <sub>PC</sub> 4.3 6.86d 6.88d 6.88d <sup>2</sup> J <sub>PC</sub> 4.6	C, 132.98d 1J <sub>PC</sub> 110.2 137.96d	C <sub>a</sub> C <sub>a</sub> 125.80d <sup>2</sup> J <sub>PC</sub> 11.4 130.71d <sup>2</sup> J <sub>PC</sub> 11.6	Ph C <sub>m</sub> C <sub>m</sub> 123.02d 127.98d 3J <sub>PC</sub> 13.5	C <sub>p</sub> 4. <sub>125.82d</sub> 130.79s
3PbOSPPh2	155.35s	137.13s <sup>2</sup> J <sub>PbC</sub> 86.0	130.06s <sup>3</sup> J <sub>PbC</sub> 101.5	129.49s				138.38d <sup>1</sup> J <sub>PC</sub> 112.6	130.77d <sup>2</sup> J <sub>PC</sub> 10.8	128.09d <sup>3</sup> J <sub>PC</sub> 12.9	130.85s

Compound	δ[P(==S)O]	$\delta$ [PSO]	$\delta$ [P(==O)S]	Ref
Me <sub>2</sub> P(S)OH	87.9ª			[32]
Me <sub>2</sub> P(S)OMe	94.3ª			[32]
Me <sub>2</sub> P(O)SMe			45.9	[33]
Me <sub>2</sub> PSONa		63.9 <sup><i>b</i>,<i>c</i></sup>		This work
Ph <sub>3</sub> GeO(S)PMe <sub>2</sub>	84.3 <sup>a</sup>			This work
Ph <sub>3</sub> SnOSPMe <sub>2</sub>		68.1br <sup>a</sup>		This work
Ph <sub>3</sub> PbOSPMe <sub>2</sub>		55.6ª		This work
Et <sub>2</sub> P(S)OH	99.7 <sup>d</sup>			[32]
$Et_2P(S)OMe$	108.8 <sup>a</sup>			[34]
$Et_2P(O)SMe$			58.6	[33]
Et <sub>2</sub> PSONa <sup>b</sup>		77.9 <sup>c,e</sup>		This work
Ph <sub>3</sub> GeO(S)PEt <sub>2</sub>	98.4 <sup>a</sup>			This work
Ph <sub>3</sub> SnOSPEt <sub>2</sub>		83.2 <sup>a</sup>		This work
Ph <sub>3</sub> PbOSPEt <sub>2</sub>		71.2 <sup>a</sup>		This work
Ph <sub>2</sub> P(S)OH	<b>76.0</b> ⁴			This work
Ph <sub>2</sub> P(S)OMe	83.5			[33]
$Ph_2P(O)SMe$			42.8	[33]
Ph₂PSONH₄		58.1 <sup>b</sup>		This work
Ph <sub>3</sub> GeO(S)PPh <sub>2</sub>	71.9ª			This work
Ph <sub>3</sub> SnOSPPh <sub>2</sub>		64.9 <sup>a</sup>		This work
Ph <sub>3</sub> PbS(O)PPh <sub>2</sub>			48.1 <sup>a</sup>	This work

Table 7. <sup>31</sup>P NMR data for Ph<sub>3</sub>M[OSPR<sub>2</sub>] derivatives and related compounds

"In CDCl<sub>3</sub>.

<sup>b</sup> In CD<sub>3</sub>OD.

 $\delta = 62.4$  in CD<sub>3</sub>OD [32].

<sup>d</sup> In CD<sub>3</sub>COCD<sub>3</sub>.

 $\delta = 67.7 \text{ in } \text{CD}_3\text{COCD}_3 [32].$ 

for both organic groups attached to phosphorous, this suggests that the ligand coordinates to the metallic centre through both chalcogen atoms and has fluxional behaviour in solution according to the following scheme: Crystal and molecular structure of Ph<sub>3</sub>Ge[O(S)PPh<sub>2</sub>]

The solid state structure of  $Ph_3Ge[O(S)PPh_2]$  was determined by single-crystal X-ray diffractometry. The asymmetric unit contains two, very similar, inde-



In contrast, for M = Pb, R = Ph the <sup>31</sup>P chemical shift displays a value of  $\delta$  48.1, which compares very well with that of the S—Me ester,  $Ph_2P(=O)SMe$  (cf.  $\delta$  42.8). This indicates that the structural formulation of this compound in solution should be  $Ph_3PbS(O)PPh_2$ , with a monodentate ligand attached to lead only through the sulfur atom.

On the basis of the above data we conclude that <sup>31</sup>P NMR can distinguish not only between the monodentate and bidentate coordination pattern of the monothiophosphinato ligands, but also between the  $R_2P(=S)O$ — or  $R_2P(=O)S$ — nature in the former situation. In addition, these data confirm the versatility of the monothiophosphinato ligand, i.e. its capacity to coordinate through oxygen to a "hard" metallic centre, to involve both chalcogen atoms, or to coordinate only through the sulphur atoms to a "soft" metallic centre. pendent monomeric molecules, which are separated by normal van der Waals distances. Selected bond distances and angles for both molecules 1a and 1b are listed in Table 8, but in the subsequent discussion we will refer only to molecule 1a (Fig. 1) (the same considerations can be used to describe molecule 1b).

The monothiophosphinato ligand is coordinated through the oxygen atom in a clearly monodentate pattern. The phosphorous-oxygen and phosphorous-sulphur bond distances are characteristic for single P-O [1.563(7) Å] and double P=S [1.931(5) Å] bonds [cf. 1.582(2) and 1.956(1) Å in the free Ph<sub>2</sub>P(S)OH acid, [35] or 1.60(2) and 1.936(6) Å in its O-Me ester, Ph<sub>2</sub>P(S)OMe [36]. The tetrahedral geometry around the phosphorous atoms in both ligands is distorted with an O(1)-P(1)-S(1) angle [116.7(3)°] of the same magnitude as in the free Ph<sub>2</sub>P(S)OH acid [O-P-S 115.4(1)°] [35].

Table 8. Relevant interatomic distances (Å) and bond angles (°) for  $Ph_3Ge[O(S)PPh_2]$ (1)

	Molecule	( <b>1a</b> )		Molecule	(1b)
Ge(1)-O(1)	1.825(7)		Ge(2)-O(2)	1.826(8)	
Ge(1) - C(1)	1.91(1)		Ge(2) - C(31)	1.90(1)	
Ge(1) - C(7)	1.93(1)		Ge(2)-C(37)	1.91(1)	
Ge(1) - C(13)	1.92(1)		Ge(2)C(43)	1.93(1)	
$Ge(1) \cdots S(1)$	3.843(4)		$Ge(2) \cdots S(2)$	3.940(4)	
P(1)—O(1)	1.563(7)		P(2)O(2)	1.562(8)	
P(1) - S(1)	1.931(5)		P(2)S(2)	1.920(5)	
P(1)-C(19)	1.79(1)		P(2)-C(49)	1.80(1)	
P(1)—C(25)	1.79(1)		P(2)—C(55)	1.78(1)	
O(1)-Ge(1)-	C(1)	112.4(4)	O(2)Ge(2)	C(31)	112.4(4]
O(1)-Ge(1)-	C(7)	102.5(4)	O(2)-Ge(2)-	C(37)	102.5(4)
O(1)-Ge(1)-	C(13)	103.6(4)	O(2)—Ge(2)—	C(43)	101.7(4)
C(1)-Ge(1)-	C(7)	111.2(6)	C(31)-Ge(2)-	-C(37)	113.6(6)
C(1)-Ge(1)-	C(13)	114.8(5)	C(31)Ge(2)	-C(43)	113.4(5)
C(7)Ge(1)	C(13)	111.5(5)	C(37)Ge(2)	-C(43)	112.2(5)
Ge(1)-O(1)-	P(1)	132.2(5)	Ge(2)-O(2)-	P(2)	132.6(5)
O(1)—P(1)—S	(1)	116.7(3)	O(2)P(2)S(	(2)	116.8(4)
O(1)-P(1)-C	(19)	104.6(5)	O(2)-P(2)-C	(49)	102.7(5)
O(1)-P(1)-C	(25)	101.2(6)	O(2)—P(2)—C	(55)	105.4(6)
S(1)-P(1)-C	(19)	114.2(5)	S(2) - P(2) - C(2)	(49)	113.5(5)
S(1)-P(1)-C(	(25)	114.3(5)	S(2)—P(2)—C(	(55)	113.5(5)
C(19)-P(1)-C	C(25)	104.2(6)	C(49)P(2)C	C(55)	103.5(6)



Fig. 1. ORTEP plot of the molecule Ph<sub>3</sub>Ge[O(S)PPh<sub>2</sub>] (1a).

The Ge(1)--O(1) bond length is slightly longer [1.825(7) Å] than in  $(Ph_3Ge)_2O$  [average 1.77(5) Å] [37], and close to the sum of the covalent radii of Ge and O,  $\Sigma_{cov}(Ge, O) = 1.95$  [38]. The Ge(1)--O(1)--P(1) angle of 132.2(5)° is slightly less

than the Ge-O-Ge angle of 135.7(7)° in (Ph<sub>3</sub>Ge)<sub>2</sub>O [37]. The relative position of the sulfur atom double bonded to phosphorous with respect to the germanium atom is similar to that observed in the dithiophosphinato analogues,  $Ph_3Ge[S(S)PR_2]$  (R = Me, Ph) [39], i.e. the monothiophosphorus ligand is twisted to bring the non-bonded sulfur atom much closer to the germanium atom, thus leading to a syn conformation of the Ge-O-P=S fragment. This situation contrasts to that observed in the dithiophosphinato derivative, Ph<sub>3</sub>GeS(S)P(OMe)<sub>2</sub>, for which the non-bonded sulfur atom is twisted as far as possible from the germanium atom (Ge  $\cdots$  S 5.253 Å) [40]. The magnitude of the germanium-sulfur distances [Ge(1)  $\cdots$  S(1) 3.843(4) and Ge(2)  $\cdots$  S(2) 3.940(4) Å in molecules 1a and 1b, respectively] is in the range of van der Waals distances and too large to suggest any significant secondary interaction between these atoms.

The distortion from tetrahedral angles around Ge is not large but all C—Ge—C angles are greater than those for all tetrahedral angles (Table 8). In each independent molecule two O—Ge—C angles are well below all tetrahedral angles, while the third one is of the same value as the C—Ge—C angles. In comparison, the tetrahedral distortion is slightly less for the two germanium centres in (Ph<sub>3</sub>Ge)<sub>2</sub>O [37], with the average C—Ge—C angle still larger than that for all tetrahedral angles at 111.4°, but only one O—Ge—C angle in each half of the molecule significantly less, at 101.9(7) and 103.5(7)°. The above is essentially as expected from Bent's rule [41], which seems to operate well for germanium compounds; according to this rule "more electronegative substituents 'prefer' hybrid orbitals having less *s* character, and more electropositive substituents 'prefer' those having more *s* character". Alteratively, the distortion of the tetrahedral coordination polyhedron at germanium might be owing to the spatial requirements of the phenyl groups attached to germanium and of the non-bonded sulfur atom.

# Crystal and molecular structure of $[Ph_2Sn{O(S) PPh_2}(\mu-OH)]_2$

The solid state structure of  $[Ph_2Sn{O(S)PPh_2}(\mu-OH)]_2$  was also determined by single-crystal X-ray diffractometry. Selected bond distances and angles are listed in Table 9. Figure 2 shows the ORTEP view of the molecular structure, with the atom-numbering scheme.

The monothiophosphinato ligand is monodentate and linked to tin through the oxygen atom. The tinsulfur interatomic distance is 4.164 Å, significantly longer than the sum of van der Waals radii of the corresponding atoms,  $\Sigma_{vdW}(Sn, S) = 4.0$  Å [38]. As a result, each tin atom is five coordinated, in a distorted trigonal bipyramidal geometry (Fig. 3). The axial positions are occupied by the O(1) atom of the monothiophosphinato ligand and the O(2') hydroxo oxygen



Fig. 2. ORTEP plot of the molecule [Ph<sub>2</sub>Sn{O(S)PPh<sub>2</sub>}(μ-OH)]<sub>2</sub> (2) (the atoms are drawn with 30% probability ellipsoids and hydrogen atoms are omitted for clarity).

of the other molecular unit of the dimer, with an O(1)—Sn(1)—O(2') angle of 156.76°, which reflects the distortion of the coordination polyhedron. The equatorial bond angles at tin range between 117.0 and 121.8°, and the O(2)Sn(1)C(1)C(7) system is basically planar [the deviations from the best equatorial plane are: Sn(1) - 0.079, O(2) 0.028, C(1) 0.025, C(7) 0.026Å]. The four-membered  $Sn_2O_2$  ring is planar. The O(1)P(1)S(1) and O(1')P(1')S(1') fragments are almost coplanar with the  $Sn_2O_2$  system, being sym-

$[Ph_2Sn\{O(S)PPh_2\}(OH)]_2 (2)^a$							
Sn(1)O(1)	2.089(3)	P(1)—O(1)	1.548(3)				
Sn(1)O(2)	2.024(3)	P(1) - S(1)	1.972(2)				
Sn(1)O(2')	2.174(3)	P(1)-C(13)	1.807(4)				
$Sn(1) \cdots S(1)^b$	4.164	P(1)—C(19)	1.799(4)				
Sn(1)-C(1)	2.116(4)	$O(1) \cdots S(1)^b$	2.993				
Sn(1)C(7)	2.122(4)	O(2)—H(21)	1.15				
		$S(1) \cdots H(21)$	1.96				
O(1)Sn(1)O(2)	86.8(1)	O(2') - Sn(1) - O(2)	70.0(1)				
O(1)Sn(1)C(1)	96.0(1)	O(2') - Sn(1) - C(1)	97.1(2)				
O(1) - Sn(1) - C(7)	96.0(2)	O(2')-Sn(1)-C(7)	95.1(2)				
O(1) - Sn(1) - O(2')	156.76(9)	C(1)— $Sn(1)$ — $C(7)$	117.0(2)				
		O(2) - Sn(1) - C(1)	120.5(2)				
		O(2)Sn(1)C(7)	121.8(1)				
Sn(1) - O(1) - P(1)	145.0(2)	Sn(1)O(2)H(21)	118.6				
Sn(1)-O(2)-Sn(1')	110.0(1)	Sn(1')-O(2)-H(21)	130.0				
O(1)-P(1)-S(1)	116.0(1)	S(1)P(1)C(13)	111.4(1)				
O(1) - P(1) - C(13)	106.4(2)	S(1) - P(1) - C(19)	110.4(1)				
O(1)-P(1)-C(19)	106.0(2)	C(13) - P(1) - C(19)	106.1(2)				
O(2)-H(21)···S(1)	157.3						

Table 9. Relevant interatomic distances (Å) and bond angles (°) for  $[Ph_2Sn{O(S)PPh_2}(OH)]_2 (2)^a$ 

<sup>a</sup> Symmetry equivalent position (1-x, 1-y, -z) is denoted by prime.

<sup>b</sup> Non-bonding distance.



Fig. 3. ORTEP plot of the core of the molecule  $[Ph_2Sn {O(S)PPh_2}(\mu-OH)]_2$  (2) showing the trigonal bipyramidal coordination around tin (the atoms are drawn with 50% probability ellipsoids and the phenyl rings, except for the carbon atoms attached to tin and phosphorous, are omitted for clarity).

metrically displaced on each side of the  $Sn_2O_2$  plane [the deviations from the best Sn(1)O(2)Sn(1')O(2')plane are: O(1) -0.057, P(1) -0.028, S(1) -0.028Å]. The equatorial planes at both tin atoms are almost perpendicular to the  $Sn_2O_2$  ring  $(OSnC_2/Sn_2O_2)$ dihedral angle 88.6°).

The monodentate character of the ligand is supported by the phosphorus-chalcogen distances [P(1)-O(1) 1.548(3), P(1)-S(1) 1.972(2) Å; for comparison see the above discussion of the molecular structure of the germanium compound]. The hydrogen bond interactions between the sulfur and hydroxo oxygen atoms within each molecular unit might account for the slightly longer phosphorus-sulfur bond distance. A similar hydrogen bond interaction was observed for the monothiophosphinato analogue,  $[Ph_2Sn{O(S)OPh_2}(\mu-OH)]_2$  [25], where the sulfur and hydroxo oxygen atoms within each molecular unit are brought together at 3.121 Å, compared with 3.050 Å in the present compound.

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