



SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLGERMANIUM(IV) DIORGANOPHOSPHINODITHIOATES: CRYSTAL AND MOLECULAR STRUCTURES OF $\text{Ph}_3\text{GeS(S)PR}_2$ ($\text{R} = \text{Me, Ph}$)

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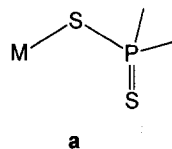
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Abstract—The first triphenylgermanium diorganophosphinodithioates, $\text{Ph}_3\text{GeS(S)PR}_2$ ($\text{R} = \text{Me, Et, Ph}$), were synthesized by metathesis reactions between Ph_3GeCl and the ammonium or sodium salt of the corresponding dithio acid. The compounds were characterized by IR, MS and multinuclear NMR (^1H , ^{13}C , ^{31}P) spectroscopy. The solid state molecular structures of $\text{Ph}_3\text{GeS(S)PR}_2$ ($\text{R} = \text{Me, Ph}$) were determined by X-ray diffractometry. Both compounds are monomeric, with the monometallic monoconnective (monodentate) 1,1-dithio ligand and slightly distorted, tetrahedral coordination geometry at the germanium atom.

1,1-Dithiophosphorus anions, i.e. phosphorodithioates, $(\text{RO})_2\text{PS}_2^-$, or phosphinodithioates, R_2PS_2^- , are well known to exhibit monometallic biconnective (bidentate) and bimetallic biconnective or triconnective (bridging) coordination patterns, involving both sulphur atoms in bonding to metal atoms, but monometallic monoconnective (monodentate) coordination (**a**) is rare.¹ In Main Group triorganometallic derivatives monometallic monoconnective coordination of diorganophosphorodithioato ligands was found by X-ray diffractometry in $\text{Ph}_3\text{GeS(S)P(OMe)}_2$,² $\text{Ph}_3\text{SnS(S)P(OEt)}_2$ ³ and $\text{Ph}_3\text{PbS(S)P(OEt)}_2$.⁴ Although a series of germanium(IV) and phenylgermanium(IV) phosphorodithioates, $\text{Ph}_n\text{Ge[S(S)P(OMe)}_2]_{4-n}$ ($n = 0-3$), have been investigated in detail and several crystal structures have

been determined,^{2,5,6} only a germanium(II) phosphinodithioate, $\text{Ge(S}_2\text{PMe}_2)_2$, has been structurally investigated.⁷



On the other hand, X-ray structural studies have revealed that changes from phosphorodithioato to phosphinodithioato ligands, or in the organic group for the same type of ligand, can result in modification of the coordination pattern of the 1,1-dithio ligand and/or in the coordination polyhedron around the central metal atom.^{8,9}

As an extension of our previous studies on metal derivatives of 1,1-dithiophosphorus ligands, we report the synthesis and spectroscopic characterization of triphenylgermanium(IV) diorgano-

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phosphinodithioates, $\text{Ph}_3\text{GeS(S)PR}_2$ ($\text{R} = \text{Me, Et, Ph}$), and the single-crystal molecular structure of the methyl and phenyl derivatives, containing monometallic monoconnective 1,1-phosphinodithioato groups.

EXPERIMENTAL

The starting materials were prepared according to literature methods: Ph_3GeCl ,¹⁰ $\text{Me}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$,¹¹ $\text{Et}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$ ¹² and $\text{Ph}_2\text{PS}_2\text{NH}_4$.¹³ Elemental analyses (C, H) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). IR spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded on KBr discs using a Perkin–Elmer 282B spectrophotometer. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument. ^1H , ^{13}C and ^{31}P NMR spectra were obtained at room temperature in CDCl_3 solution using a Varian VXR-300S spectrometer operating at 300, 75.4 and 121.4 MHz, respectively. TMS and H_3PO_4 85% were used as external standards.

Preparation of (dimethylphosphinodithioato)triphenylgermanium, $\text{Ph}_3\text{GeS(S)PMe}_2$ (1)

$\text{Me}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$ (0.23 g, 1.25 mmol) was added to a solution of Ph_3GeCl (0.42 g, 1.25 mmol) in 25 cm^3 of benzene. The reaction mixture was stirred under reflux for 6 h, and then filtered to remove the resulting NaCl. The solvent was removed from the clear filtrate on a rotary evaporator, leading to a colourless oily product. Addition of 20 cm^3 of n-hexane produced, after 24 h, colourless crystals which were recrystallized from cyclohexane. Yield 0.40 g (74%), m.p. $126\text{--}128^\circ\text{C}$. Found: C, 56.2; H, 5.0. Calc. for $\text{C}_{20}\text{H}_{21}\text{GePS}_2$: C, 56.0, H, 4.9%. IR (KBr): $\nu_{\text{as}}(\text{PS}_2)$ 600vs, $\nu_{\text{s}}(\text{PS}_2)$ 453vs, $\nu(\text{GeS})$ 385ms. ^1H NMR: 1.80d (6H, P—CH_3 , $^2J_{\text{PH}}$ 12.8), 7.45m (9H, $\text{Ge—C}_6\text{H}_5$, *meta+para*), 7.77m (6H, $\text{Ge—C}_6\text{H}_5$, *ortho*). ^{13}C NMR: 29.82d (P—CH_3 , $^1J_{\text{PC}}$ 56.2), 128.49s (C_m), 130.20s (C_p), 134.37s (C_i), 135.05s (C_o). ^{31}P NMR: 53.5s. MS (m/z , (%)): 430 (3), M^+ ; 353 (28), $\text{Ph}_2\text{GeS}_2\text{PMe}_2^+$; 337 (3), Ph_3GeS^+ ; 305 (100), Ph_3Ge^+ ; 151 (12), PhGe^+ ; 93 (5), Me_2PS^+ .

Preparation of (diethylphosphinodithioato)triphenylgermanium, $\text{Ph}_3\text{GeS(S)PEt}_2$ (2)

The synthesis was carried out as described above for the methyl derivative, using $\text{Et}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$ (0.42 g, 2 mmol) and Ph_3GeCl (0.68 g, 2 mmol) in 25 cm^3 of acetone. The product was recrystallized from cyclohexane. Yield 0.68 g (75%), m.p. $80\text{--}82^\circ\text{C}$. Found: C, 57.4; H, 5.4. Calc. for $\text{C}_{22}\text{H}_{25}\text{GePS}_2$: C, 57.8; H, 5.5%. IR (KBr): $\nu_{\text{as}}(\text{PS}_2)$

584 vs, $\nu_{\text{s}}(\text{PS}_2)$ 447vs, $\nu(\text{GeS})$ 408ms. ^1H NMR: 1.12dt (6H, $\text{P—CH}_2\text{—CH}_3$, $^3J_{\text{PH}}$ 21.7, $^3J_{\text{HH}}$ 7.4), 1.76ddq (2H, $\text{P—CH}_2\text{—CH}_3$, $^2J_{\text{PH}}$ 10.9, $^3J_{\text{HH}}$ 7.4, $^2J_{\text{HH}}$ 14.6), 1.86 ddq (2H, $\text{P—CH}_2\text{—CH}_3$, $^2J_{\text{PH}}$ 10.9, $^3J_{\text{HH}}$ 7.4, $^2J_{\text{HH}}$ 14.6), 7.42m (9H, $\text{Ge—C}_6\text{H}_5$, *meta+para*), 7.76m (6H, $\text{Ge—C}_6\text{H}_5$, *ortho*). ^{13}C NMR: 7.73d ($\text{P—CH}_2\text{—CH}_3$, $^2J_{\text{PC}}$ 7.0), 32.15d ($\text{P—CH}_2\text{—CH}_3$, $^1J_{\text{PC}}$ 53.1), 128.73s (C_m), 130.42s (C_p), 135.31s (C_i), 135.46s (C_o). ^{31}P NMR: 77.2s. MS (m/z , (%)): 458 (8), M^+ ; 381 (100), $\text{Ph}_2\text{GeS}_2\text{PEt}_2^+$; 337 (2), Ph_3GeS^+ ; 305 (93), Ph_3Ge^+ ; 151 (8), PhGe^+ ; 121 (15), Et_2PS^+ .

Preparation of (diphenylphosphinodithioato)triphenylgermanium, $\text{Ph}_3\text{GeS(S)PPh}_2$ (3)

A reaction mixture consisting of $\text{Ph}_2\text{PS}_2\text{NH}_4$ (0.27 g, 1 mmol) and Ph_3GeCl (0.34 g, 1 mmol) in 25 cm^3 of benzene, was stirred under reflux for 6 h, and then filtered to remove the resulting NH_4Cl . The clear filtrate was concentrated on a rotary evaporator to $ca\ 5\text{ cm}^3$, 20 cm^3 of n-hexane were added, and the mixture was stored in a refrigerator. After 48 h colourless-greenish crystals of the title compound had deposited and were filtered. Recrystallization from cyclohexane led to colourless, well-shaped crystals. Yield 0.45 g (82%), m.p. $131\text{--}132^\circ\text{C}$. Found: C, 64.8; H, 4.7. Calc. for $\text{C}_{30}\text{H}_{25}\text{GePS}_2$: C, 65.1; H, 4.5%. IR (KBr): $\nu_{\text{as}}(\text{PS}_2)$ 647vs, $\nu_{\text{s}}(\text{PS}_2)$ 522vs, $\nu(\text{GeS})$ 380m. ^1H NMR: 7.32m (15H, $\text{P—C}_6\text{H}_5$, $\text{Ge—C}_6\text{H}_5$, *meta+para*), 7.63 (6H, $\text{Ge—C}_6\text{H}_5$, *ortho*), 7.85dd (4H, $\text{P—C}_6\text{H}_5$, *ortho*, $^3J_{\text{PH}}$ 14.6, $^3J_{\text{HH}}$ 7.5). ^{13}C NMR: 128.05d ($\text{C}_m(\text{P})$, $^3J_{\text{PC}}$ 12.8), 128.18s ($\text{C}_m(\text{Ge})$), 129.83s ($\text{C}_p(\text{Ge})$), 130.91s ($\text{C}_p(\text{P})$), 131.02d ($\text{C}_o(\text{P})$, $^2J_{\text{PC}}$ 11.4), 134.29s ($\text{C}_i(\text{Ge})$), 135.15s ($\text{C}_o(\text{Ge})$), 137.20d ($\text{C}_i(\text{P})$, $^1J_{\text{PC}}$ 84.7). ^{31}P NMR: 56.1s. MS (m/z , (%)): 554 (2), M^+ ; 477 (53), $\text{Ph}_2\text{GeS}_2\text{PPh}_2^+$; 337 (4), Ph_3GeS^+ ; 305 (100), Ph_3Ge^+ ; 217 (79), Ph_2PS^+ ; 151 (11), PhGe^+ .

X-Ray crystal structure determination

Crystals of **1** and **3**, suitable for X-ray diffraction investigation, were obtained from cyclohexane/n-hexane solvent mixture using the diffusion method. Data were collected at room temperature on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-K_α radiation and the full-matrix least-squares refinement was performed with the SHELXTL-PC program system.¹⁴ Details of crystal data, measurement of intensities, and data processing are summarized in Table 1. The structures were solved by direct methods (SIR92)¹⁵ and difference Fourier synthesis revealed the positions for the other non-hydrogen atoms. All non-hydro-

Table 1. Crystal data for Ph₃GeS(S)PMe₂ (**1**) and Ph₃GeS(S)PPh₂ (**3**)

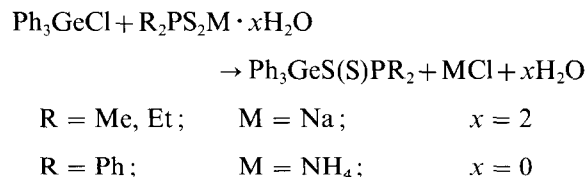
	1	3
Formula	C ₂₀ H ₂₁ GePS ₂	C ₃₀ H ₂₅ GePS ₂
<i>M</i>	429.0	553.2
Crystal size (mm)	0.42 × 0.40 × 0.36	0.50 × 0.50 × 0.40
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>P2₁2₁2₁</i>
<i>a</i> (Å)	13.208(2)	9.158(2)
<i>b</i> (Å)	12.919(2)	12.752(2)
<i>c</i> (Å)	24.054(2)	23.243(2)
<i>β</i> (°)	91.95(2)	
<i>V</i> (Å ³)	4101.9(6)	2714.5(6)
<i>Z</i>	8	4
<i>D</i> _{calc} (g cm ⁻³)	1.389	1.354
<i>μ</i> (Mo- <i>K_α</i>) (mm ⁻¹)	1.774	1.358
<i>F</i> (000)	1760	1136
Reflections collected	7193	4422
Independent reflections	3607 (<i>R</i> _{int} = 3.48%)	4422 (<i>R</i> _{int} = 0.00%)
Observed reflections	2483 (<i>F</i> > 4.0σ(<i>F</i>))	2467 (<i>F</i> > 4.0σ(<i>F</i>))
Absorption correction	—	Semi-empirical
Min./max. transmission		0.7513/0.8744
Weighting scheme	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0002 <i>F</i> ²	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0008 <i>F</i> ²
<i>R</i> ^a (%)	3.92	5.10
<i>wR</i> ^a (%)	3.70	5.35
Goodness-of-fit	1.05	0.99

^a*R* = Σ|Δ|/Σ|*F*_o|; *wR* = [Σ(*w*Δ²)/Σ(*wF*_o²)]^{1/2}; *S* = [Σ*w*Δ²/(N.O. - N.V.)]^{1/2} (where N.O. = number of observed reflections; N.V. = number of parameters refined); Δ = |*F*_o - *F*_c|.

gen atoms were refined anisotropically, and hydrogen atoms were calculated as a riding model with isotropic U. For compound **3** absolute conformation was determined by refinement of the *η* parameter (1.03(5)).

RESULTS AND DISCUSSION

The title compounds were prepared in good yields (75–85%) by the reaction of the sodium or ammonium salt of the appropriate phosphinodithioic acid with chlorotriphenylgermane, in benzene or acetone, according to:



These compounds are highly soluble in common organic solvents, which is consistent with monomeric, covalent structures, and rules out a polymeric or ionic nature. Spectroscopic characterization (IR, multinuclear NMR, mass spectra) as well as X-ray diffraction studies are also consistent with a monomeric structure.

The IR spectra of all the compounds exhibit, in addition to characteristic absorptions due to the triphenylgermanium moiety,^{2,16,17} strong bands assigned to asymmetric and symmetric stretching vibrations of the PS₂ group. The large values of the difference Δ = *v*_{as}(PS₂) - *v*_s(PS₂) (147, 137 and 125 cm⁻¹ for R = Me, Et and Ph, respectively) are consistent with a monometallic monoconnective coordination pattern of the 1,1-phosphinodithioato ligand.¹⁸ The Ge—S stretching vibration appears, as expected, close to 400 cm⁻¹.^{2,17}

The ³¹P NMR spectra are seen as sharp singlets, while the ¹H and ¹³C NMR spectra of all three compounds show the expected down-field resonances for aromatic proton and carbon atoms of the phenyl groups attached to germanium. In the case of compounds **1** and **3** the resonances for the organic groups bound to phosphorus exhibit the expected doublet pattern due to phosphorus—proton and phosphorus—carbon couplings, respectively. The pattern of the NMR spectra is consistent with the free rotation of the phosphinodithioato moiety around the Ge—S bond, i.e. the absence of any Ge···S(=P) secondary interaction in solution.

The alkyl region at room temperature in the ¹H NMR spectrum of the ethyl derivative **2** deserves

some special comments. At higher field the resonance for the methyl protons appeared, as expected, as a doublet of triplets centred at $\delta = 1.12$ ppm ($^3J_{\text{PH}} 21.7$, $^3J_{\text{HH}} 7.4$ Hz). For the methylene protons we would have expected a doublet of quartets, as observed for the $\text{Ph}_3\text{MS}(\text{S})\text{PEt}_2$ analogues, $\text{M} = \text{Sn}$,¹⁹ Pb .¹³ Surprisingly, in the case of the germanium derivative, the resonance signal for the methylene protons observed in the 1.6–2.0 ppm region, was much more complex. Its pattern corresponded to an ABXY_3 system, involving diastereotopic H_a and H_b protons of the $\text{P}-\text{CH}_2-\text{CH}_3$ group ($^2J_{\text{PH}} 10.9$, $^3J_{\text{HH}} 7.4$, $^2J_{\text{HH}} 14.6$ Hz). A variable-temperature ^1H NMR study was carried out both in C_6D_6 and $\text{DMSO}-d_6$. Heating the C_6D_6 sample up to 60°C did not result in the complete coalescence of the two doublet of doublets of quartets corresponding to H_a and H_b protons of the methylene groups, but a sharpening of the complex signal was noted. In $\text{DMSO}-d_6$ solution the pattern of the CH_2 resonance at room temperature was similar to that observed under the same conditions for the sample prepared in C_6D_6 , but at 65°C complete coalescence was achieved. Now the resonance corresponding to the methylene group protons had a doublet of quartets pattern ($^2J_{\text{PH}} 12.2$, $^3J_{\text{HH}} 7.7$ Hz), indicating equivalence of the CH_2 protons, as noted previously for tin and lead analogues at room temperature. At higher temperature (80°C) the appearance of new resonances indicated partial decomposition of the compound.

The solid state structures of $\text{Ph}_3\text{GeS}(\text{S})\text{PMe}_2$ (**1**) and $\text{Ph}_3\text{GeS}(\text{S})\text{PPh}_2$ (**3**) were determined by single crystal X-ray diffraction. Selected bond distances and angles are listed in Tables 2 and 3 for **1** and **3**, respectively. Figures 1 and 2 show the ORTEP-like

view of the molecular structures of **1** and **3**, with the atom numbering scheme.

For both compounds the lattice contains discrete molecules, without any *intermolecular* interactions. The 1,1-phosphenodithioato ligands are clearly monodentate, with phosphorus–sulphur bond distances characteristic for single $\text{P}-\text{S}$ (2.091(2) and 2.094(3) Å, for **1** and **3** and double $\text{P}=\text{S}$ (1.940(2) and 1.939(3) Å, for **1** and **3**) bonds (*cf* 2.077(1) and 1.954(1) Å in the free $\text{Ph}_2\text{P}(\text{S})\text{SH}$ acid²⁰). The tetrahedral geometry around phosphorus atoms in both ligands is distorted, with the $\text{S}-\text{P}-\text{S}$ angle ($117.5(1)$ and $116.8(1)^\circ$, for **1** and **3**) opened even more than in the free $\text{Ph}_2\text{P}(\text{S})\text{SH}$ acid ($\text{S}-\text{P}-\text{S}$ $108.16(2)^\circ$).²⁰

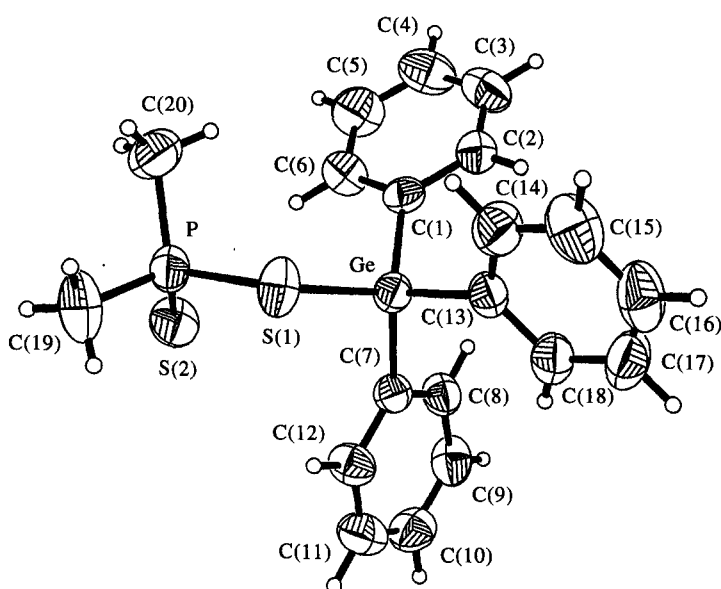
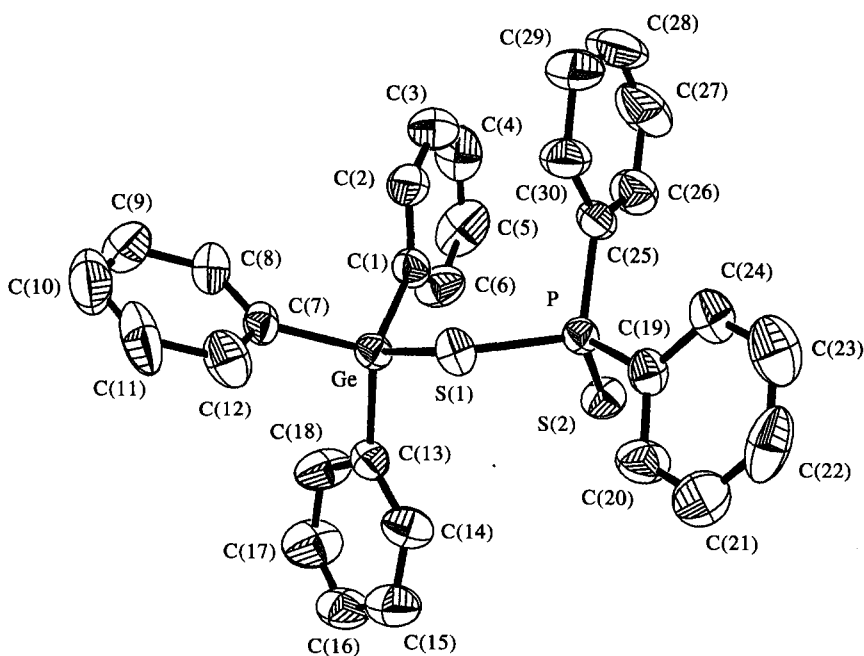
The magnitude of the $\text{Ge}-\text{S}(1)-\text{P}$ angle (107.8° in **1** and 103.8° in **3**) is comparable with that observed in the related $\text{Ph}_3\text{GeS}(\text{S})\text{P}(\text{OMe})_2$ (109.0°).² However, the relative position of the sulphur atom double bonded to phosphorus with respect to the germanium atom is completely different in the title phosphenodithioates in comparison with the related phosphorodithioate. Thus, in $\text{Ph}_3\text{GeS}(\text{S})\text{P}(\text{OMe})_2$ (Fig. 3(c)) the non-bonded sulphur atom is twisted as far as possible from the germanium atom ($\text{Ge}\cdots\text{S}(2)$ 5.253 Å).² A similar situation was described for $\text{Ph}_3\text{SnS}(\text{S})\text{P}(\text{OEt})_2$ ($\text{Sn}\cdots\text{S}(\text{P})$ 5.326 Å)³ and $\text{Ph}_3\text{PbS}(\text{S})\text{P}(\text{OEt})_2$ ($\text{Pb}\cdots\text{S}(\text{P})$ 5.435 Å),⁴ respectively. By contrast, in the title compounds **1** and **3** (Figs 3(a) and (b)) the 1,1-dithio ligand group is twisted to bring the non-bonded $\text{S}(2)$ atom much closer to the germanium atom (i.e. $\text{Ge}\cdots\text{S}(2)$ 3.879 and 3.803 Å, respectively), thus leading to *syn* conformation of the $\text{Ge}-\text{S}-\text{P}=\text{S}$ fragment. However, these values are in the range of van der Waals distances and

Table 2. Interatomic distances (Å) and angles ($^\circ$) in $\text{Ph}_3\text{GeS}(\text{S})\text{PMe}_2$ (**1**)

$\text{Ge}-\text{C}(1)$	1.954(4)	$\text{C}(1)-\text{Ge}-\text{C}(7)$	111.6(2)
$\text{Ge}-\text{C}(7)$	1.942(4)	$\text{C}(1)-\text{Ge}-\text{C}(13)$	109.1(2)
$\text{Ge}-\text{C}(13)$	1.951(4)	$\text{C}(7)-\text{Ge}-\text{C}(13)$	109.7(2)
$\text{Ge}-\text{S}(1)$	2.255(1)	$\text{S}(1)-\text{Ge}-\text{C}(1)$	115.0(1)
		$\text{S}(1)-\text{Ge}-\text{C}(7)$	111.9(1)
		$\text{S}(1)-\text{Ge}-\text{C}(13)$	98.6(1)
$\text{P}-\text{S}(1)$	2.091(2)	$\text{S}(1)-\text{P}-\text{S}(2)$	117.5(1)
$\text{P}-\text{S}(2)$	1.940(2)	$\text{S}(1)-\text{P}-\text{C}(19)$	100.3(2)
$\text{P}-\text{C}(19)$	1.797(7)	$\text{S}(1)-\text{P}-\text{C}(20)$	105.0(2)
$\text{P}-\text{C}(20)$	1.797(6)	$\text{S}(2)-\text{P}-\text{C}(19)$	114.1(2)
		$\text{S}(2)-\text{P}-\text{C}(20)$	113.7(2)
		$\text{C}(19)-\text{P}-\text{C}(20)$	104.6(3)
		$\text{Ge}-\text{S}(1)-\text{P}$	107.8(1)

Table 3. Interatomic distances (Å) and angles (°) in $\text{Ph}_3\text{GeS}(\text{S})\text{PPh}_2$ (3)

Ge—C(1)	1.927(8)	C(1)—Ge—C(7)	111.0(4)
Ge—C(7)	1.951(7)	C(1)—Ge—C(13)	116.2(4)
Ge—C(13)	1.939(7)	C(7)—Ge—C(13)	108.4(3)
Ge—S(1)	2.263(2)	S(1)—Ge—C(1)	110.6(3)
		S(1)—Ge—C(7)	100.0(3)
		S(1)—Ge—C(13)	109.4(3)
P—S(1)	2.094(3)	S(1)—P—S(2)	116.8(1)
P—S(2)	1.939(3)	S(1)—P—C(19)	98.5(3)
P—C(19)	1.816(8)	S(1)—P—C(26)	106.3(3)
P—C(25)	1.816(8)	S(2)—P—C(19)	113.0(3)
		S(2)—P—C(25)	113.5(3)
		C(19)—P—C(25)	107.4(4)
		Ge—S(1)—P	103.8(1)


 Fig. 1. ORTEP-like view of the $\text{Ph}_3\text{GeS}(\text{S})\text{PMe}_2$ (1) molecule.

 Fig. 2. ORTEP-like view of the $\text{Ph}_3\text{GeS}(\text{S})\text{PPh}_2$ (3) molecule.

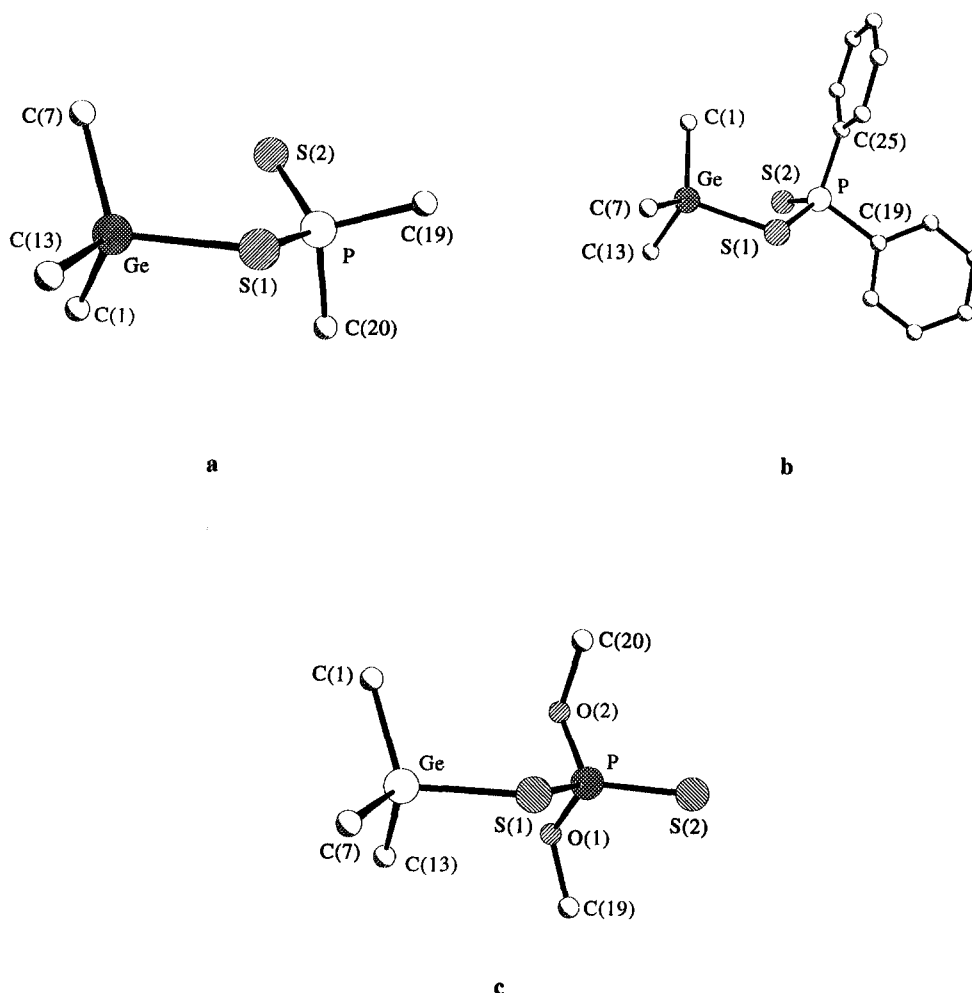


Fig. 3. Comparative orientation of the 1,1-dithiophosphorus ligand in: (a) $\text{Ph}_3\text{GeS}(\text{S})\text{PMe}_2$; (b) $\text{Ph}_3\text{GeS}(\text{S})\text{PPh}_2$ (this work); and (c) $\text{Ph}_3\text{GeS}(\text{S})\text{P}(\text{OMe})_2$ (redrawn from the atomic coordinates given in ref. 2). Only *ipso*-carbons of the phenyl groups attached to germanium are shown, the others being omitted for clarity.

are too large to suggest any significant secondary interaction between S(2) and the germanium atom.

The coordination polyhedron around the germanium atom is a slightly distorted tetrahedron, with C—Ge—C and C—Ge—S angles in the range 109.1 – 111.6° and 98.6 – 115.0° for **1** and 108.4 – 116.2° and 100.0 – 110.6° for **3**. Due to the spatial requirement of the non-bonded S(2) atom the S(1)—Ge—C(13) (98.6°) in **1** and S(1)—Ge—C(7) (100.0°) in **3**, respectively, are significantly diminished by comparison to the other S(1)—Ge—C angles.

The Ge—S, P—S and P=S bond lengths in our phosphinodithioates (Tables 2 and 3) are comparable with those found in the phosphorodithioate $\text{Ph}_3\text{GeS}(\text{S})\text{P}(\text{OMe})_2$, although somewhat different: Ge—S is slightly shorter in phosphinodithioates than in the phosphorodithioate (Ge—S $2.285(1)$

$\text{\AA}$),² and the phosphorus—sulphur bonds are shorter in the phosphorodithioate (P—S $2.060(2)$, P=S $1.923(2)$ $\text{\AA}$)² than in the phosphinodithioates.

It is interesting to compare the molecular dimensions in our compounds with those in the germanium(II) derivative, $\text{Ge}(\text{S}_2\text{PMe}_2)_2$.⁷ In the latter, the coordination geometry is ψ -trigonal bipyramidal and, thus, the Ge—S bonds are different: axial ($2.693(1)$ and $2.751(1)$ $\text{\AA}$) and equatorial ($2.421(1)$ and $2.408(1)$ $\text{\AA}$), both significantly longer than in $\text{Ph}_3\text{GeS}(\text{S})\text{PR}_2$ (R = Me, Ph). The phosphinodithioato ligand in $\text{Ge}(\text{S}_2\text{PMe}_2)_2$ displays a different coordination pattern: P—S bond lengths (1.994 – $2.033(1)$ $\text{\AA}$) clearly indicate basically isobidentate coordination.⁷ This is a dramatic example of the geometric effects produced by changing the hybridization (and oxidation) state of the central atom in phosphorus-1,1-dithiolato complexes.

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