



**DIPHENYLTELLURIUM(IV)  
BIS(DIORGANOPHOSPHINODITHIOATES). X-RAY  
CRYSTAL STRUCTURE OF  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2 \cdot 0.5\text{CHCl}_3$  AND A  
MULTINUCLEAR NMR STUDY OF THE DECOMPOSITION  
PROCESS OF  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$  TO  $\text{Ph}_2\text{Te}^{\text{II}}$  AND  $[\text{R}_2\text{P}(\text{S})\text{S}]_2$**

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**Abstract**—New diorganophosphinodithioato derivatives,  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$ , were formed in the reaction of  $\text{Ph}_2\text{TeCl}_2$  with  $\text{R}_2\text{PS}_2\text{M} \cdot x\text{H}_2\text{O}$  ( $\text{R} = \text{Me}, \text{Et}, \text{M} = \text{Na}, x = 2; \text{R} = \text{Ph}, \text{M} = \text{NH}_4, x = 0$ ) in a 1:2 molar ratio. In the case of alkyl derivatives, the expected  $\text{Te}^{\text{IV}}$  compounds decomposed rapidly to  $\text{Ph}_2\text{Te}^{\text{II}}$  and the corresponding disulphane,  $\text{R}_2\text{P}(\text{S})\text{-S-S}(\text{S})\text{PR}_2$ , as proved by multinuclear ( $^1\text{H}, ^{13}\text{C}, ^{31}\text{P}$ ) NMR studies. By contrast, for  $\text{R} = \text{Ph}$  the desired tellurium compound could be isolated as a pure sample and its crystal and molecular structure has been determined by single-crystal X-ray diffractometry. The 1,1-dithio ligands are coordinated to tellurium as anisobidentate groups, with single  $\text{P-S}$  [2.081(2), 2.057(2) Å] and double  $\text{P=S}$  [1.954(2), 1.966(2) Å] bonds coupled with primary  $\text{Te-S}$  [2.597(2), 2.658(2) Å] bonds and intramolecular  $\text{Te} \cdots \text{S}$  (3.316, 3.286 Å) secondary interactions, respectively. If only the primary covalent bonds are considered the coordination geometry about the central tellurium atom can be described as  $\psi$ -trigonal bipyramidal, with two sulphur atoms in axial positions [ $\text{S}(1)\text{-Te}(1)\text{-S}(3)$  174.1(1)°]. Two carbon atoms and the stereochemical active lone electron pair of tellurium occupy the equatorial sites. If the secondary interactions of tellurium with the S(2) and S(4) atoms which are placed above and below the  $\text{C}_2\text{Te}$  equatorial plane are taken into account the coordination number at tellurium is increased to 7 (including the lone pair).

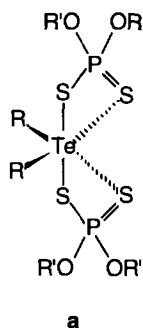
The continuous interest in tellurium compounds containing sulphur ligands is due to their broad structural variety.<sup>1</sup> In the case of 1,1-dithio ligands (i.e. dithiocarbamates, xanthates, phosphorodithioates, phosphinodithioates) this diversity is determined by the ability of these ligands to exhibit various coordination patterns, the tendency of tellurium to increase its coordination number,

and the possible stereochemical activity of lone electron pairs on tellurium.

Several studies on the chemistry of inorganic and organotellurium derivatives of phosphorodithioato ligands,  $(\text{R}'\text{O})_2\text{PS}_2^-$ , have been reported and the X-ray molecular structures of various compounds have been described.<sup>1</sup> In particular, for diorganotellurium(IV) bis(phosphorodithioates),  $\text{R}_2\text{Te}[\text{S}_2\text{P}(\text{OR}')_2]_2$ , the structure of  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{Me}$ ,<sup>2</sup>  $\text{Et}$ <sup>3</sup> and  $\text{R}_2 = \text{C}_8\text{H}_8$ ,  $\text{R}' = \text{Et}$ ,<sup>4</sup> are known. All these compounds exhibit a structure of type **a**, with the stereochemically active lone elec-

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tron pair of tellurium in an equatorial position. Although in solid state this type of compound is stable, in solution there is evidence concerning their decomposition to  $R_2Te^{II}$  and  $(R'O)_2P(S)-S-S-(S)P(OR')_2$ .<sup>5</sup> A significant increase in the stability could be achieved using phosphorodithioato ligands prepared from diols,<sup>6</sup>  $\overline{OR'OPS_2^-}$ . By contrast, no studies on diorganophosphino-dithioato derivatives,  $R_2Te(S_2PR'_2)_2$ , have been reported.



We wish to report here an investigation of the reaction of  $Ph_2TeCl_2$  with dialkyl- and diphenylphosphinodithioates, as well as the crystal and molecular structure of  $Ph_2Te(S_2PPh_2)_2$ . Multi-nuclear NMR studies emphasized the rapid decomposition of the related dimethyl- and diethylphosphinodithioato derivatives to  $Ph_2Te$  and  $[R_2PS(S)]_2$ , a behaviour which prevented any structural characterization.

## EXPERIMENTAL

The compounds used as starting materials in this study were prepared according to literature methods:  $Ph_2TeCl_2$  (from  $Ph_4Pb$  and  $TeCl_4$ ),<sup>7</sup>  $R_2PS_2Na \cdot 2H_2O$  ( $R = Me^8, Et^9$ ),  $Ph_2PS_2NH_4$ .<sup>10</sup> IR spectra were recorded in the range 4000–400  $cm^{-1}$  on Nujol mulls using a Bio-Rad-FTS7 instrument.  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR were obtained in  $CDCl_3$  solutions on a Bruker WH 360 instrument operating at 360.134, 145.785 and 90.554 MHz, respectively. Mass spectra were recorded using the EI method on a Varian CH7 (A) (MAT) spectrometer. Elemental analyses (carbon and hydrogen) were performed by Beller Mikroanalytisches Laboratorium (Göttingen).

### Reaction of $Ph_2TeCl_2$ with $Me_2PS_2Na \cdot 2H_2O$

$Me_2PS_2Na \cdot 2H_2O$  (0.74 g, 4.02 mmol) was added to a solution of  $Ph_2TeCl_2$  (0.71 g, 2.01 mmol) in chloroform (25  $cm^3$ ). The colour of the solution immediately became yellowish. The reaction mix-

ture was stirred at room temperature for 0.5 h, and then was filtered to remove the resulting sodium chloride. The clear filtrate was concentrated in a rotary evaporator until white crystals began to deposit. These were filtered off (yield: 0.16 g, 32% calculated for  $[Me_2P(S)S]_2$ ). Their  $^1H$  NMR spectrum indicated the presence of only methyl groups bound to phosphorus and the elemental analysis is in agreement with  $[Me_2P(S)S]_2$  (Found: C, 19.7, H, 4.6; Calc. for  $C_4H_{12}P_2S_2$ : C, 19.2, H, 4.8%). The remaining solution was evaporated in air, resulting in a yellow oil which was not further investigated.

### Reaction of $Ph_2TeCl_2$ with $Et_2PS_2Na \cdot 2H_2O$

The reaction of  $Et_2PS_2Na \cdot 2H_2O$  (0.85 g, 4.02 mmol) with  $Ph_2TeCl_2$  (0.71 g, 2.01 mmol) in chloroform (25  $cm^3$ ) was carried out in a similar way as described above for the methyl derivative. However, in this case no solid product could be isolated. The removal of the solvent to dryness led to a yellow oil product which could not be separated into components (see below Results and Discussion).

### Preparation of $Ph_2Te(S_2PPh_2)_2$

A mixture of  $Ph_2TeCl_2$  (0.5 g, 1.42 mmol) and  $Ph_2PS_2NH_4$  (0.76 g, 2.84 mmol) in chloroform (25  $cm^3$ ) was stirred at room temperature for 0.5 h. The resulting ammonium chloride was filtered off from the reaction mixture and the solvent was removed from the clear solution in a rotary evaporator. The solid product thus obtained was recrystallized from chloroform/petroleum ether (1:4 by volume), leading to yellowish crystals of the title compound.  $C_{36}H_{30}P_2S_4Te \cdot 0.5CHCl_3$  (840.06): Yield: 0.82 g (69%); m.p. 82–4°C. Found: C, 54.1; H, 3.8. Calc.: C, 53.6; H, 3.6%. IR (Nujol):  $\nu_{as}(PS_2)$  639s, 591s,  $\nu_s(PS_2)$  492m, 477s  $cm^{-1}$ . MS-EI (70 eV;  $m/z$ , (%)): 533(14)  $M^+ - Ph_2PS_2$ , 498(2)  $M^+ - Ph_2Te$ , 456(2)  $M^+ - Ph_2PS_2Ph$ , 284(15)  $M^+ - [Ph_2PS_2]_2$ , 249(41)  $Ph_2PS_2^+$ , 217(100)  $Ph_2PS^+$ , 207(6)  $PhTe^+$ , 185(13)  $Ph_2P^+$ , 154(31)  $Ph_2^+$ , 77(29)  $Ph^+$ .

### X-Ray crystal structure of $Ph_2Te(S_2PPh_2)_2$

*Crystal data.*  $C_{36}H_{30}P_2S_4Te \cdot 0.5CHCl_3$ ,  $M = 840.06$ , monoclinic,  $a = 13.450(3)$  Å,  $b = 16.775(3)$  Å,  $c = 8.815(2)$  Å,  $\beta = 108.89(3)^\circ$ ,  $U = 1881.8(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.483$  g  $cm^{-3}$ ,  $F(000) = 842$ , space group  $Pc$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu(Mo-K_\alpha) = 1.229$  mm<sup>-1</sup>, crystal size 0.9 × 0.2 × 0.1 mm.

*Structure determination.* Data were collected at 173(2) K on a Siemens P4 four-circle diffractometer

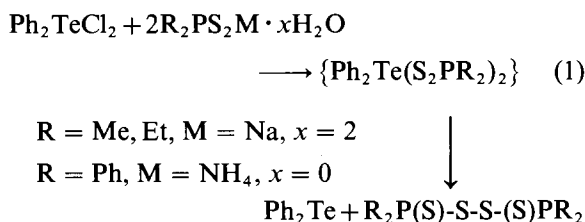
for 9233 reflections in the  $2\theta$ - $\omega$  scan mode ( $2\theta$  range from 5.0 to 55°), of which 8359 were independent reflections ( $R_{\text{int}} = 3.18\%$ ) and 8331 [ $I > 2\sigma(I)$ ] were used in the full-matrix least-squares refinement with the SHELXL-93 program.<sup>11</sup> Three standard reflections were measured after every 197 reflections. The structure was solved by direct methods with the SHELXTL PLUS (VMS) program system<sup>12</sup> for tellurium, difference Fourier synthesis for the positions for the other non-hydrogen atoms and has been refined anisotropically to a final  $R = \Sigma |F_o - F_c| / \Sigma |F_o| = 5.3\%$  and  $wR = [\Sigma w(|F_o - F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 13.2\%$ , with weights  $w^{-1} = \sigma^2(F) + 0.0008F^2$ . The goodness-of-fit (Goof) finished at 1.014. The residual electron density from a final difference-Fourier synthesis was in the range  $-0.804$  to  $1.643 \text{ e } \text{Å}^{-3}$ . Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Informations mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (Germany), on quoting the names of the authors and the journal citation.

## RESULTS AND DISCUSSION

The exchange reaction between  $\text{Ph}_2\text{TeCl}_2$  and sodium or ammonium salts of diorganophosphinodithioic acids (1:2 molar ratio) was carried out in chloroform. The colour of the reaction mixture turned yellow immediately after mixing of starting materials, thus indicating a fast reaction. In the case of dimethyl- and diethyl-phosphinodithioates, after the filtration of the resulting NaCl, all the attempts to obtain a pure sample of the expected  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$  ( $\text{R} = \text{Me}, \text{Et}$ ) have failed. For  $\text{R} = \text{Me}$  it was possible to separate from the clear filtrate a small amount of a white crystalline solid whose  $^1\text{H}$  NMR spectrum exhibited only a doublet resonance corresponding to methyl groups attached to phosphorus. Its elemental analysis (H, C) was consistent with  $[\text{Me}_2\text{P}(\text{S})\text{S}]_2$ . No other pure compound could be separated from the remaining yellowish oily product. In the case of  $\text{R} = \text{Et}$  again a yellowish oil was obtained after the removal of the solvent and the NMR spectra were consistent with a complex mixture. All attempts to isolate pure compounds have failed. However, NMR spectra of a freshly prepared reaction mixture indicated the presence of small amounts of the expected  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$  both in the case of  $\text{R} = \text{Me}$  and  $\text{Et}$ , respectively (see subsequent discussion). The reaction between  $\text{Ph}_2\text{TeCl}_2$  and  $\text{Ph}_2\text{PS}_2\text{NH}_4$  was carried out in a similar way to that for the alkyl derivatives, but in this case  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2$  was isolated as a pure, stable, solid compound and struc-

turally characterized (see below). However, in solution a decomposition process was also observed.

The pathway of the decomposition process of  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$  can be described by eq. (1):



A similar decomposition process in solution was previously reported for diorganotellurium(IV) derivatives of other 1,1-dithiolato ligands, e.g. phosphorodithioates,  $\text{R}_2\text{Te}[\text{S}_2\text{P}(\text{OR})_2]_2$ ,<sup>5</sup> although they were stable enough in solid state to allow X-ray diffraction studies. This seems to be a common decomposition route of inorganic metal derivatives of 1,1-dithiophosphorus ligands, e.g.  $\text{Ti}(\text{S}_2\text{PR}_2)_3$  to  $\text{TiS}_2\text{PR}_2$  and  $[\text{R}_2\text{P}(\text{S})\text{S}]_2$ .<sup>13</sup> However, in the case of diphenyllead(IV) phosphinodithioates,  $\text{Ph}_2\text{Pb}(\text{S}_2\text{PR}_2)_2$ , a different decomposition pathway, resulting in  $\text{Ph}_3\text{PbS}_2\text{PR}_2$ , inorganic  $\text{Pb}(\text{S}_2\text{PR}_2)_2$  and  $\text{PhS}(\text{S})\text{PR}_2$  ester, was established.<sup>10</sup>

An NMR investigation was performed to elucidate the decomposition process. The results of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR monitoring of the reactions between  $\text{Ph}_2\text{TeCl}_2$  with sodium or ammonium diorganophosphinodithioates, carried out directly in an NMR tube, are presented in Tables 1, 2 and 3, and support the process described by eq. (1).

Thus, in all cases two  $^{31}\text{P}$  resonances were observed for the reaction mixture (Table 1): the low field signal is due to the corresponding disulphane,  $\text{R}_2\text{P}(\text{S})\text{-S-S-(S)PR}_2$ , formed during the decomposition, while the high field signal was assigned to the still undecomposed  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$ . Similar  $^{31}\text{P}$  chemical shifts have been reported for phosphinodithioato ligands in the related  $\text{Ph}_2\text{Pb}(\text{S}_2\text{PR}_2)_2$  derivatives (in  $\text{C}_6\text{D}_6$  solutions), i.e. 58.5, 79.1 and 61.0 ppm for  $\text{R} = \text{Me}, \text{Et}$  and  $\text{Ph}$ , respectively.<sup>10</sup>

For  $\text{R} = \text{Me}$  and  $\text{Et}$ , the  $^1\text{H}$  NMR spectra of the reaction mixtures exhibited two groups of signals in the aromatic region. One of them is due to the *ortho* (ca 8 ppm) and *meta+para* (ca 7.5 ppm) protons of the phenyl groups attached to tellurium in  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$ , and is in good intensity relation with resonances observed in the alkyl region for methyl and ethyl groups bound to phosphorus. The other signal was assigned to the decomposition product  $\text{Ph}_2\text{Te}$  (ca 7.7 ppm for *ortho* protons and ca 7.2 ppm for *meta+para* protons) by comparison with a pure sample of diphenyltellurium(II). It is

Table 1.  $^1\text{H}$  and  $^{31}\text{P}$  NMR data for  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$ 

	$^1\text{H}$ (chemical shifts in ppm, and coupling constants in Hz)				$^{31}\text{P}$	
	$\text{C}_6\text{H}_5$ protons	Alkyl protons				
$\text{Ph}_2\text{TeCl}_2 + 2\text{Me}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}^a$	8.06m <sup>b</sup> (4H-ortho)	7.69m (4H-ortho)	7.52m <sup>b</sup> (6H-meta + para)	7.24m (6H-meta + para)	1.85d <sup>b</sup> (12H- $\text{PCH}_3$ ) $^2J_{\text{PH}}13.5$	67.1
					2.15d ( $\text{PCH}_3$ ) $^2J_{\text{PH}}12.8$	54.5 <sup>b</sup>
$[\text{Me}_2\text{PS}_2]_2$					2.15d ( $\text{PCH}_3$ ) $^2J_{\text{PH}}12.5$	66.9
$\text{Ph}_2\text{TeCl}_2 + 2\text{Et}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}^a$	8.06m <sup>c</sup> (4H-ortho)	7.69m (4H-ortho)	7.48m <sup>c</sup> (6H-meta + para)	7.24m (6H-meta + para)	1.91dq <sup>c</sup> (8H- $\text{PCH}_2$ ) $^3J_{\text{HH}}7.7$ $^2J_{\text{PH}}8.4$	89.9
					2.21m (8H- $\text{PCH}_2$ )	75.8 <sup>c</sup>
$[\text{Et}_2\text{PS}_2]_2$					1.27dt (12H- $\text{PCH}_2\text{CH}_3$ ) $^3J_{\text{HH}}7.7$ $^3J_{\text{PH}}2.8$	89.7
$\text{Ph}_2\text{TeCl}_2 + 2\text{Ph}_3\text{PS}_2\text{NH}_2^a$ $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2^d$ $[\text{Ph}_2\text{PS}_2]_2$ $\text{Ph}_2\text{Te}$		7.69m (4H-ortho)		7.24m (6H-meta + para)	1.29dt (12H- $\text{PCH}_2\text{CH}_3$ ) $^3J_{\text{HH}}7.7$ $^3J_{\text{PH}}22.8$	89.7
					1.1dt <sup>e</sup> (12H- $\text{PCH}_2\text{CH}_3$ ) $^3J_{\text{HH}}7.7$ $^3J_{\text{PH}}22.8$	69.9
		7.78m, 7.32m <sup>e</sup> 7.78m, 7.32m <sup>e</sup>				56.7
						69.9

<sup>a</sup>NMR spectra obtained in  $\text{CHCl}_3$  solution directly in an NMR tube for a 1 : 2 molar ratio reaction mixture of  $\text{Ph}_2\text{TeCl}_2$  (0.0333 g)/ $\text{Me}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$  (0.0340 g),  $\text{Ph}_2\text{TeCl}_2$  (0.0340 g)/ $\text{Et}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}$  (0.0530 g), and  $\text{Ph}_2\text{TeCl}_2$  (0.0246 g)/ $\text{Ph}_2\text{PS}_2\text{NH}_2$  (0.0490 g), respectively, immediately after mixing the reactants.

<sup>b</sup>Signal assigned to  $\text{Ph}_2\text{Te}(\text{S}_2\text{PMe}_2)_2$ .

<sup>c</sup>Signal assigned to  $\text{Ph}_2\text{Te}(\text{S}_2\text{PEt}_2)_2$ .

<sup>d</sup>NMR data for the  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2$ , isolated as pure solid sample.

<sup>e</sup>Very complex signals.

Table 2.  $^{13}\text{C}$  NMR data for  $\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$ , R = Me, Et (chemical shifts in ppm, and coupling constants in Hz)

	$\text{Ph}_2\text{Te}(\text{S}_2\text{PR}_2)_2$													
	$\text{C}_6\text{H}_5\text{-Te}$				Alkyl-P				$\text{Ph}_2\text{Te}$				$[\text{R}_2\text{PS}_2]_2$	
	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{PCH}_3$	$\text{PCH}_2$	$\text{PCH}_2\text{CH}_3$	$\text{C}_o^a$	$\text{C}_m^a$	$\text{C}_p$	$\text{C}_i$	$\text{PCH}_3$	$\text{PCH}_2$	$\text{PCH}_2\text{CH}_3$
$\text{Ph}_2\text{TeCl}_2 + 2\text{Me}_3\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}^b$	135.00	133.71	131.74	130.05	29.55d $^1J_{\text{PC}}$ 55.4			137.88	129.46	127.83	114.61	25.51d $^1J_{\text{PC}}$ 53.0		
$[\text{Me}_2\text{PS}_2]_2$												25.32d $^1J_{\text{PC}}$ 52.7		
$\text{Ph}_2\text{TeCl}_2 + 2\text{Et}_2\text{PS}_2\text{Na} \cdot 2\text{H}_2\text{O}^b$	136.2	134.9	130.9	129.8		33.21d $^1J_{\text{PC}}$ 56.14	6.43d $^2J_{\text{PC}}$ 17.2	137.79	129.45	127.78	114.59	27.8d $^1J_{\text{PC}}$ 48.9	6.91d $^2J_{\text{PC}}$ 5.4	
$[\text{Et}_2\text{PS}_2]_2$												28.1d $^1J_{\text{PC}}$ 45.0	7.1s <sup>c</sup>	
$\text{Ph}_2\text{Te}$							137.95	129.46	127.80	114.64				

<sup>a</sup>The assignments for *ortho* and *meta* carbons of the phenyl groups in  $\text{Ph}_2\text{Te}$  are not unambiguous.<sup>b</sup>NMR data for the reaction mixture obtained directly in an NMR tube as described in the footnote of Table 1.<sup>c</sup>Unresolved doublet.

Table 3.  $^{13}\text{C}$  NMR data for  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2$  (chemical shifts in ppm, and coupling constants in Hz)

	$\text{C}_6\text{H}_5\text{-Te}$						$\text{C}_6\text{H}_5\text{-P}$						$\text{Ph}_2\text{Te}$						$[\text{Ph}_3\text{PS}]_2$							
	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$	$\text{C}_i$	$\text{C}_o$	$\text{C}_p$	$\text{C}_m$		
$\text{Ph}_2\text{TeCl}_2 + 2\text{Ph}_2\text{PS}_2\text{NH}_4^b$	136.03	132.46	130.27	129.80	137.68d	130.67d	$\epsilon$	128.01d	137.88	129.45	127.76	114.58	133.13 <sup>d</sup>	132.11d	131.87	128.45d										
$[\text{Ph}_2\text{PS}]_2$					$^1J_{\text{PC}}$ 84.2	$^2J_{\text{PC}}$ 11.8		$^3J_{\text{PC}}$ 13.6										133.4 <sup>d</sup>	132.17d	131.92	128.51d					
$[\text{Ph}_2\text{PS}]_2^c$													133.90d	132.32d	132.12	128.62d										
$\text{Ph}_2\text{Te}$									137.95	129.46	127.80	114.64						83.1	11.6							

<sup>a</sup>The assignments for *ortho* and *meta* carbons of the phenyl groups in  $\text{Ph}_2\text{Te}$  are not unambiguous.<sup>b</sup>NMR data for the reaction mixture obtained directly in an NMR tube as described in the footnote of Table 1.<sup>c</sup>Resonance obscured by the doublet signal of *ortho* carbons of the same group.<sup>d</sup>The second branch of the corresponding doublet is masked by the signal of *ortho* carbons of the same group.<sup>e</sup>In  $\text{C}_6\text{D}_6$  solution.

worth mentioning that for  $R = Et$  the relative intensity of the resonances corresponding to  $Ph_2Te(S_2PR_2)_2$  and  $Ph_2Te$  is 1:5, thus suggesting a fast decomposition as noted for the lead(IV) analogue.<sup>14</sup> Additionally, both for  $R = Me$  and  $Et$ , the  $^1H$  NMR spectra exhibited resonances for the corresponding disulphanes, with a characteristic splitting pattern due to proton-proton and phosphorus-proton couplings.

The  $^{13}C$  NMR data (Tables 2 and 3) are also consistent with the presence of  $Ph_2Te(S_2PR_2)_2$ , as well as decomposition products  $Ph_2Te$  and  $R_2P(S)-S-S(S)PR_2$ , in all three reaction mixtures, thus providing further proof in support of the decomposition pathway described by eq. (1).

Although  $Ph_2Te(S_2PPh_2)_2$  was also found to undergo a similar decomposition process in solution, its successful isolation as yellowish crystals allowed characterization by IR and mass spectroscopy, as well as by an X-ray diffraction study. In the infrared spectrum strong bands in the 650–450  $cm^{-1}$  region were assigned to P—S stretching vibrations. Their splitting into two components is frequently observed in other metal diphenylphosphinodithioates.<sup>14</sup> The difference  $\Delta = \nu_{as}(PS_2) - \nu_s(PS_2) = 147, 114 cm^{-1}$  suggests a monodentate coordination of the 1,1-dithio ligands to the tellurium atom,<sup>15</sup> but secondary interactions between sulphur atoms doubly bonded to phosphorus and tellurium cannot be definitely ruled out

only on this basis. The EI-MS spectrum does not show the molecular ion, but an ion corresponding to the first fragmentation, i.e.  $Ph_2TeS_2PPh_2^+$  ( $m/z$  533, 14%) resulting from the cleavage of a Te—S bond, can be observed. The base peak was a tellurium-free ion,  $Ph_2PS^+$  ( $m/z$  217). Fragments containing both phosphinodithioato groups bound to tellurium are not present.

*X-Ray crystal structure of  $Ph_2Te(S_2PPh_2)_2 \cdot 0.5CHCl_3$*

The crystal structure of the title compound was determined by X-ray diffraction. Important interatomic distances and angles are listed in Table 4, and an ORTEP diagram of the complex structure with the numbering scheme is shown in Fig. 1.

The crystal consists of monomeric  $Ph_2Te(S_2PPh_2)_2$  units and contains  $CHCl_3$  molecules, as crystallization solvent, in a 2:1 ratio (Fig. 2). The P—S distances in the phosphinodithioato units are characteristic for single P—S (2.081(2) and 2.057(2) Å) and double P=S (1.954(2) and 1.966(2) Å) bonds (*cf.* 2.077(1) and 1.954(1) Å in the free  $Ph_2P(S)SH$  acid),<sup>16</sup> suggesting a monodentate coordination. However, both sulphur atoms doubly bonded to phosphorus exhibit intramolecular secondary interactions with the tellurium atom, i.e.  $Te(1) \cdots S(2)$  3.316 Å and  $Te(1) \cdots S(4)$  3.286 Å. If only the primary covalent bonds at tellurium are

Table 4. Selected interatomic distances (Å) and angles (°) in  $Ph_2Te(S_2PPh_2)_2$

Te(1)—C(1)	2.131(6)	C(1)—Te(1)—C(10)	96.3(2)
Te(1)—C(10)	2.128(6)	C(1)—Te(1)—S(1)	87.7(2)
Te(1)—S(1)	2.597(2)	C(1)—Te(1)—S(3)	92.7(3)
Te(1) $\cdots$ S(2)	3.316	C(10)—Te(1)—S(1)	88.3(2)
Te(1)—S(3)	2.658(2)	C(10)—Te(1)—S(3)	85.8(2)
Te(1) $\cdots$ S(4)	3.286	S(1)—Te(1)—S(3)	174.1(1)
P(1)—S(1)	2.081(2)	C(1)—Te(1) $\cdots$ S(2)	154.0
P(1)—S(2)	1.954(2)	C(1)—Te(1) $\cdots$ S(4)	83.2
P(1)—C(20)	1.814(7)	C(10)—Te(1) $\cdots$ S(2)	95.0
P(1)—C(30)	1.817(6)	C(10)—Te(1) $\cdots$ S(4)	154.2
P(2)—S(3)	2.057(2)	S(1)—Te(1) $\cdots$ S(2)	69.3
P(2)—S(4)	1.966(2)	S(1)—Te(1) $\cdots$ S(4)	117.4
P(2)—C(40)	1.816(7)	S(3)—Te(1) $\cdots$ S(2)	111.4
P(2)—C(50)	1.804(7)	S(3)—Te(1) $\cdots$ S(4)	68.6
		S(2) $\cdots$ Te(1) $\cdots$ S(4)	96.3
		Te(1)—S(1)—P(1)	96.1(1)
		Te(1) $\cdots$ S(2)—P(1)	78.4
		Te(1)—S(3)—P(2)	93.9(1)
		Te(1) $\cdots$ S(4)—P(1)	78.3
		S(1)—P(1)—S(2)	115.7(1)
		S(3)—P(2)—S(4)	114.7(1)

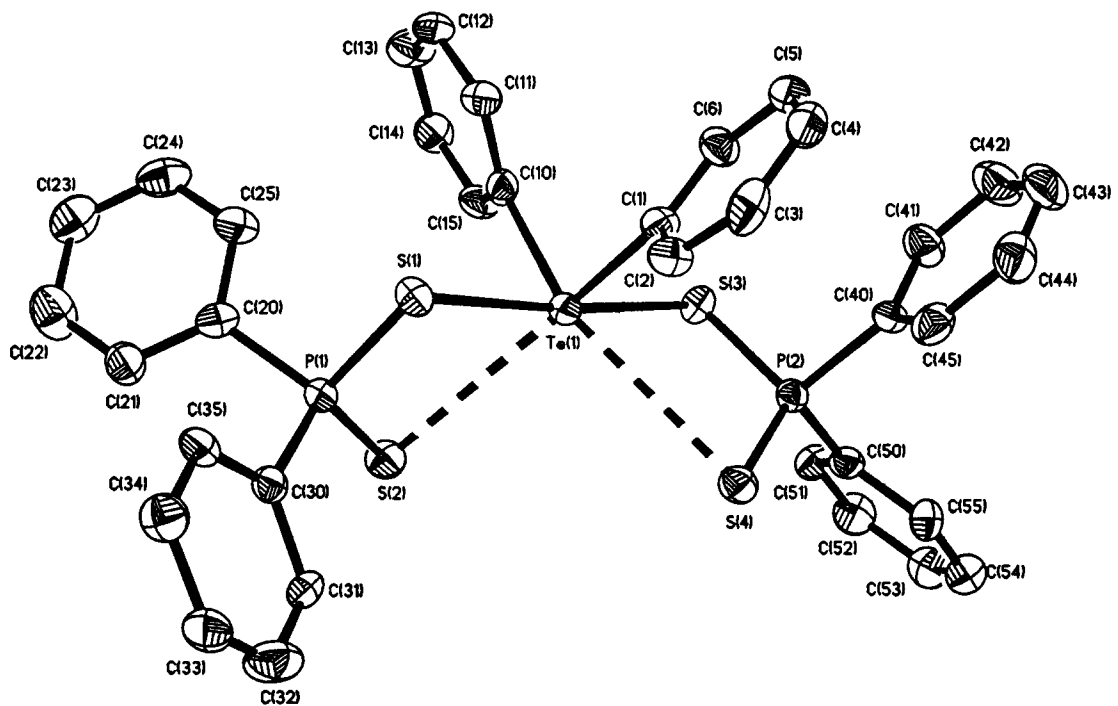


Fig. 1. ORTEP drawing of the  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2$  molecule (hydrogen atoms and the chloroform molecule present in the lattice were omitted for clarity).

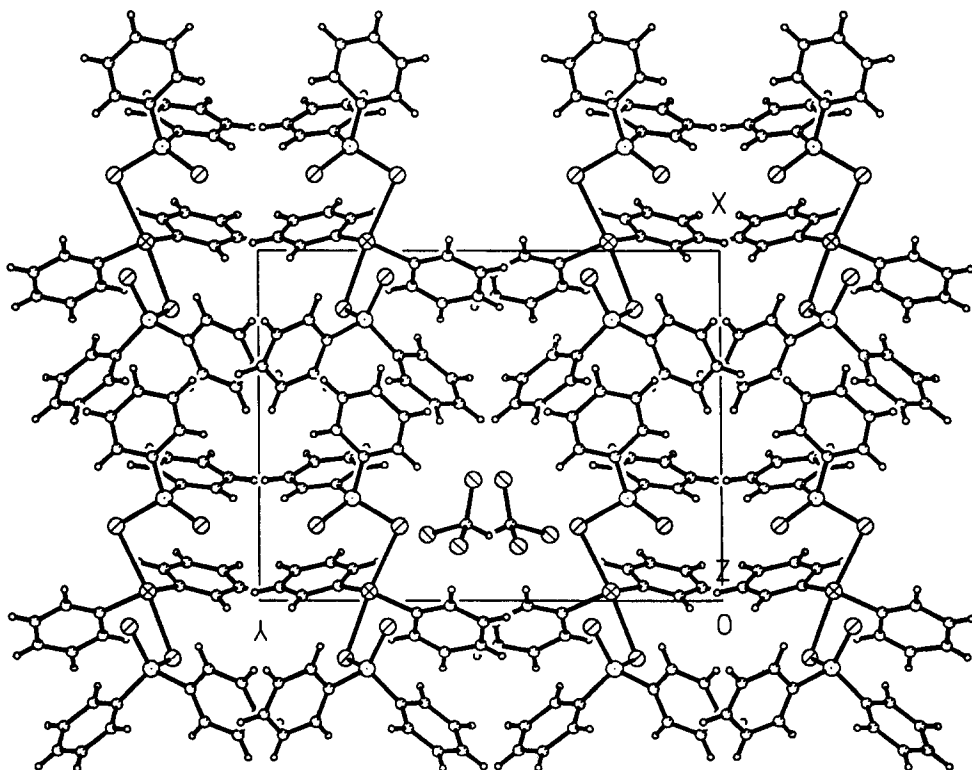


Fig. 2. View of the unit cell of  $\text{Ph}_2\text{Te}(\text{S}_2\text{PPh}_2)_2$  (including the  $\text{CHCl}_3$  molecules).



considered, the coordination polyhedron can be described as a distorted  $\psi$ -trigonal bipyramid, with S(1) and S(3) atoms in axial positions [S(1)—Te(1)—S(3) 174.1(1)°]. Two of the equatorial sites are occupied by the C(1) and C(10) atoms of the phenyl groups attached to tellurium. The lone electron pair of tellurium is stereochemically active, occupying the third equatorial position. This is supported by the C(1)—Te(1)—C(10) angle significantly smaller [96.3(2)°] than the normal 120° value.

The S(2) and S(4) atoms, exhibiting the secondary interactions with tellurium atom, are placed above and below the equatorial C(1)Te(1)C(10) plane at  $-1.313$  and  $1.427$  Å, respectively. This can be due to the small bite of the ligands, but can be also interpreted as being a result of the tendency of these sulphur atoms to avoid the lone pair of electrons at tellurium.

Similar structures have been established for diorganotellurium(IV) bis(dithiocarbamates),  $R_2Te(S_2CNR'_2)_2$ ,<sup>17-19</sup> and diorganotellurium(IV) bis(phosphorodithioates),  $R_2Te[S_2P(OR')_2]_2$ .<sup>2-4</sup>

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