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New aryltellurium(II) diorganophosphinodithioates. Crystal structure of red (294 K) and yellow (173 K) $^{1}_{\infty}$[PhTeS(S)PPh$_2$], a supramolecular polymer displaying an unusual coordination pattern of the phosphinodithioato ligand

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Abstract

Aryltellurium(II) diorganophosphinodithioates, ArTeS$_2$PR$_2$, were prepared by treating Ar$_2$Te$_2$ with R$_2$P(S)–S–S–P(S)R$_2$ (Ar = Ph, *p*-tolyl; R = Me, Et, Ph) (method (a)) or PhTeCl$_3$ with NaS$_2$PR$_2$ · 2H$_2$O (R = Me, Et) (method (b)). The compounds were characterized by IR, ^{1}H and ^{31}P NMR, and mass spectroscopy. The compound PhTeS(S)PPh$_2$ displays thermochromism; a yellow form is observed below −60°C and a red form at room temperature. The crystal structure of PhTeS(S)PPh$_2$ was investigated using X-ray diffraction, at both low and room temperature. In both cases the molecules are associated in polymeric chains through unusual monodentate biconnective phosphinodithioato bridges, in which the sulfur atom single bonded to phosphorus of the molecule units is involved in secondary bonding to the tellurium atoms of a symmetry related molecule (Te–S(–P) 2.406 Å, Te...S(–P) 3.383 Å at 173 K and, respectively, Te–S(–P) 2.401 Å, Te...S(–P) 3.422 Å at 294 K). The sulfur atoms doubly bonded to phosphorus are not involved in coordination to tellurium (non-bonding Te...S(=P) 3.989 Å at 173 K, and 3.964 Å at 294 K, respectively).

Key words: Tellurium; Polymer; Crystal structure; Supramolecular association; Phosphinodithioates

1. Introduction

The phosphino- and phosphoro-dithioic acids are versatile ligands, that can exhibit various coordination patterns [1] arising from the ability of the sulfur atoms to form both normal covalent bonds and secondary bonds to the metal centre. This often leads to dimers or polymers, generally through weak secondary M...S interactions [2–8]. Tellurium is a good candidate for forming such secondary interactions and many inorganic and organotellurium derivatives of 1,1-dithio ligands show interesting structures from increase the coordination number of the central atom [9]. Compounds containing antimony-antimony bonds, *i.e.* R$_2$Sb–SbR$_2$ or (RSb)$_x$ polymers, react with dichalcogenides of the type R′–E–E–R′ to give the corresponding rearrangement products containing metal-chalcogen bonds, *e.g.*

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TABLE 1. Preparation and physical properties of $ArTeS_2PR_2$

Method of synthesis	Starting materials		Product yield, g (%)	Analyses		Colour	m.p. (°C)
	Ar_2Te_2 $ArTeCl_3$ Ar, g (mmol)	$[R_2P(S)S]_2$ $NaS_2PR_2 \cdot 2H_2O$ R, g (mmol)		%C found (calcd)	%H found (calcd)		
	Ph	Me	$C_8H_{11}PS_2Te$	29.17	3.43	Orange	176–8
(i)	0.41(1.00)	0.25(1.0)	0.62(94)	(29.12)	(3.33)		
(ii)	0.78(2.50)	1.38(7.50)	0.71(86)				
	Ph	Et	$C_{10}H_{15}PS_2Te$	33.54	4.28	Yellow	157–8
(i)	0.51(1.25)	0.38(1.25)	0.87(97)	(33.65)	(4.19)		
(ii)	0.52(1.67)	1.06(5.00)	0.48(80)				
	Ph	Ph	$C_{18}H_{15}PS_2Te$	47.64	3.22	Red	90–2
(i)	0.41(1.00)	0.5(1.00)	0.81(89)	(47.62)	(3.30)		
	p – tolyl	Me	$C_9H_{13}PS_2Te$	31.77	3.74	Yellow	181–2
(i)	0.60(1.37)	0.36(1.37)	1.02(85)	(31.43)	(3.78)		
	p-tolyl	Et	$C_{11}H_{17}PS_2Te$	35.31	4.41	Yellow	105–7
(i)	0.60(1.37)	0.42(1.37)	0.81(79)	(35.52)	(4.57)		
	p-tolyl	Ph	$C_{19}H_{17}PS_2Te$	48.87	3.71	Red	86–8
(i)	0.62(1.25)	0.62(1.25)	0.62(73)	(48.76)	(3.63)		

$R_2Sb\text{-}SR'$ and $RSb(SR')_2$ [10–13]. The compound $Me_2Sb\text{-}SbMe_2$ also reacts with bis(diorganothiophosphinyl)disulfanes, to give dimethylantimony(III) phosphinodithioates [14]. Several of these compounds exhibit interesting thermochromic properties [15].

These facts prompted us to investigate the reaction between R–Te–Te–R derivatives and bis(diorganothiophosphinyl)disulfanes, with a view to obtaining new organotellurium(II) phosphinodithioates, $RTeS_2PR'_2$. So far, only two aryl-tellurium(II) phosphorodithioates,

TABLE 2. ^1H and $^{31}P\{^1H\}$ NMR data for $ArTeS_2PR_2$ [a]

Compound		^1H [b,c]	$\delta(^{31}P)$ [d]
Ar	R	Chemical shifts (ppm) and coupling constants (Hz)	
Ph	Me	2.11d (6H, P-CH_3), $^2J(PH) = 18$ 7.34m (3H-*meta* + *para*, Te-C_6H_5), 7.89 d(2H-*ortho*, Te-C_6H_5), $^3J(HH) = 7.7$	61.2
Ph	Et	0.91dt (6H, P-CH_2CH_3), $^3J(HH) = 7.6$, $^3J(PH) = 18$ 1.75dq (4H, P-CH_2CH_3), $^3J(HH) = 7.6$, $^2J(PH) = 10.4$ 6.84m (3H-*meta* + *para*, Te-C_6H_5) 7.66d (2H-*ortho*, Te-C_6H_5), $^3J(HH) = 7.2$	83.1
Ph	Ph	6.66t (2H-*meta*, Te-C_6H_5), $^3J(HH) = 7.3$ 6.91m (7H-*meta* + *para*, P-C_6H_5; *para*, Te-C_6H_5) 7.63d (2H-*ortho*, Te-C_6H_5), $^3J(HH) = 7.3$ 7.96 dm (4H-*ortho*, P-C_6H_5), $^3J(PH) = 10.9$	68.8
p-tolyl	Me	1.58d (6H, P-CH_3), $^2J(PH) = 14.4$ 1.98s (3H, Te-$C_6H_4CH_3$-*p*) 6.71d (2H-*meta*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$ 7.62 d (2H-*ortho*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$	59.3
p-tolyl	Et	0.93dt (6H, P-CH_2CH_3), $^3J(HH) = 7.6$, $^3J(PH) = 20.5$ 1.78dq (4H, P-CH_2CH_3), $^3J(HH) = 7.6$, $^2J(PH) = 10.4$ 1.98s (3H, Te-$C_6H_4CH_3$-*p*) 6.71d (2H-*meta*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$ 7.65d (2H-*ortho*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$	82.8
p-tolyl	Ph	2.33s (3H, Te-$C_6H_4CH_3$-*p*) 6.95d (2H-*meta*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$ 7.41m (6H*meta* + *para*, P-C_6H_5) 7.58d (2H-*ortho*, Te-$C_6H_4CH_3$-*p*), $^3J(HH) = 7.6$ 7.86 dm (4H-*ortho*, P-C_6H_5), $^3J(PH) = 14.4$	69.2

[a] In $CDCl_3$ solution (Ar = Ph, R = Me; Ar = *p*-tolyl, R = Ph), or in C_6D_6 solution (Ar = Ph, R = Et, Ph; Ar = *p*-tolyl, R = Me, Et); [b] Chemical shifts relative to TMS; [c] s - singlet, d - doublet, t - triplet, dt - doublet of triplets, dq - doublet of quartets, m - multiplet, dm - doublet of multiplets; [d] chemical shifts relative to H_3PO_4 85%.

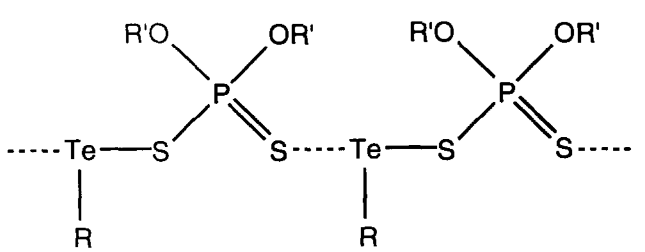

Fig. 1. Bimetallic biconnective coordination pattern of dithiophosphorus ligands to tellurium.

$ArTeS(S)P(OMe)_2$ ($Ar = 4\text{-}MeOC_6H_4$ [16], $4\text{-}EtOC_6H_4$ [17]) have been synthesized, by a redox reaction between $ArTeCl_3$ and the corresponding phosphorodithioic acids, and they were shown to exhibit supramolecular polymeric chains through normal bimetallic biconnective, dithiophosphorus bridges (Te–S(–P) *ca.* 2.05 Å, Te...S(=P) *ca.* 3.26–3.31 Å) (Fig. 1).

Recently [8], we reported on the low temperature crystal structure of $PhTeS(S)PPh_2$, a compound prepared by using the above type of rearrangement. This compound exhibits a unique coordination pattern for a dithiophosphosphorus ligand, being monodentate biconnective, with only the sulfur atom single bonded to phosphorus, involved in bridges between two tellurium atoms, thus leading to polymeric chains (see Section 2.2.4).

We describe below the synthesis and spectroscopic characterization of several related phenyl- and *p*-tolyltellurium derivatives, and the structure of $PhTeS(S)PPh_2$, determined for both the low and room temperature forms (yellow and red, respectively).

2. Results and discussion

2.1. Preparation

The title compounds were obtained, according to eq. (1), by refluxing stoichiometric amounts of the ditelluride, ArTe–TeAr, and the corresponding disulfane, $R_2P(S)\text{–}S\text{–}S\text{–}P(S)R_2$, in chloroform (R = Me, Et) or acetonitrile (R = Ph):

$$ArTe\text{–}TeAr + R_2P(S)\text{–}S\text{–}S\text{–}P(S)R_2 \rightarrow 2\,ArTeS_2PR_2 \quad (1)$$

Ar = Ph, p-tolyl R = Me, Et, Ph

The same compounds, *i.e.* $PhTeS_2PR_2$ (R = Me, Et), were also obtained according to eq. (2), *via* a redox reaction between $PhTeCl_3$ and the corresponding sodium phosphinodithioate:

$$PhTeCl_3 + 3NaS_2PR_2 \cdot 2H_2O \rightarrow PhTeS_2PR'_2 + [R_2P(S)S]_2 + 3\,NaCl + 6\,H_2O \quad (2)$$

R = Me, Et

This reaction was carried out in the hope of obtaining tellurium(IV) derivatives, $PhTe(S_2PR_2)_3$, in the way reported for the analogous phenyltellurium(IV) dithiocarbamates, $PhTe(S_2CNR_2)_3$ [18], but elemental analyses, ^1H and ^{31}P NMR spectra and the mass spectra of the resulting compounds (see Tables 1, 2 and 3) were identical with those recorded for the tellurium(II) derivatives, $PhTeS_2PR_2$. It can be assumed that a tellurium(IV) compound formed in the first stage (eq. (3)) rapidly undergoes a redox reaction with the formation of the tellurium(II) compound and disulfane (eq. (4)):

$$PhTeCl_3 + 3\,NaS_2PR_2 \cdot 2H_2O \rightarrow PhTe(S_2PR_2)_3 + 3\,NaCl + 6\,H_2O \quad (3)$$

$$PhTe[S(S)PR_2]_3 \rightarrow PhTeS_2PR_2 + [R_2P(S)S]_2 \quad (4)$$

The resulting products are yellow or red, crystalline solids, which can be recrystallized from acetonitrile, and regardless of the organic groups bound to tellurium or phosphorus, are red in the molten state. Preparative details, yields, elemental analyses, melting points and colours are listed in Table 1.

TABLE 3. 70 eV Monoisotopic mass spectra of $ArTeS_2PR_2$ (m/z, (%)) [a]

	Ar = Ph			Ar = *p* = tolyl		
	R = Me	R = Et	R = Ph	R = Me	R = Et	R = Ph
$ArTeS_2PR_2^{+\cdot}$	332(7)	360(20)	456(8)	346(33)	374(21)	470(7)
$TeS_2PR_2^+$	255(3)	283(1)	379(1)	255(1)	283(1)	379(1)
$ArTeS^+$	239(2)	239(2)	239(1)	253(1)	253(1)	253(1)
$TeSPR_2^+$	223(4)	251(8)	347(1)	223(4)	251(4)	347(2)
$ArTe^+$	207(37)	207(31)	207(34)	221(22)	221(10)	221(33)
$R_2PS_2^+$	125(24)	153(66)	249(7)	125(38)	153(43)	249(4)
R_2PS^+	93(88)	121(100)	217(95)	93(100)	121(100)	217(100)
$Ar^{+\cdot}$	77(100)	77(87)	77(100)	91(59)	91(49)	91(98)
R_2P^+	61(14)	89(9)	185(12)	61(15)	89(9)	185(3)

[a] The m/z values were computed with H = 1, C = 12, P = 31, S = 32, Te = 130.

TABLE 4. Infrared data for $ArTeS_2PR_2$ (cm^{-1}) [a]

Compound		$\nu_{as}(PS_2)$	$\nu_s(PS_2)$	$\Delta\nu$ [b]
Ar	R			
Ph	Me	566vs	484m	82
Ph	Et	552vs	480w	72
Ph	Ph	654vs	513s	141
p-tolyl	Me	561vs	484s	77
p-tolyl	Et	551vs	483m	68
p-tolyl	Ph	652vs	513vs	139

[a] vs - very strong, s - strong, m - medium, w -weak; [b] $\Delta\nu = \nu_{as}(PS_2)$-$\nu_s(PS_2)$.

2.2. *Spectra and structure*

All the compounds were characterized by infrared, ^1H NMR and ^{31}P NMR, and mass spectrometry. The crystal structure of $PhTeS(S)PPh_2$ was also determined by X-ray diffraction. Since this compound is thermochromic, *i.e.* yellow at *ca.* −60°C and red at room temperature, X-ray data were collected at both 173 K and at 294 K.

2.2.1. *Infrared spectra*

Comparison of the infrared spectra of these $ArTeS_2PR_2$ derivatives with those of the starting materials allows assignment of medium to strong absorption bands to the asymmetric and symmetric phosphorus-sulfur stretching vibrations (Table 4). The magnitude of the difference $\Delta\nu = \nu_{as}(PS_2) - \nu_s(PS_2)$ gives useful information on the coordination pattern of the phosphinodithioato ligands [19].

For the aryltellurium(II) diphenylphosphinodithioates the value of $\Delta\nu$ is *ca.* 140 cm^{-1} and is consistent with monodentate bonding of the dithio ligand; *i.e.* the sulfur atom doubly bonded to phosphorus is not involved in coordination to tellurium. By contrast, in the case of four dialkylphosphinodithioates, the difference $\Delta\nu$ is less than 90 cm^{-1}, suggesting a possible anisobidentate behavior of the ligand, and probably a chain polymeric structure similar to that of the phosphorodithioato analogues [16,17]. This suggestion should, however, be confirmed by an X-ray diffraction analysis and we are currently trying to obtain crystals of dialkylphosphinodithioates suitable for such an investigation.

2.2.2. *NMR spectra*

^1H and $^{31}P\{^1H\}$ NMR parameters are listed in Table 2. As expected, the proton resonances corresponding to the organic groups in the ligand are split into two components of equal intensity owing to proton–phosphorus coupling. All the compounds exhibit only one singlet phosphorus resonance, suggesting that the compound is present in monomeric form in solution.

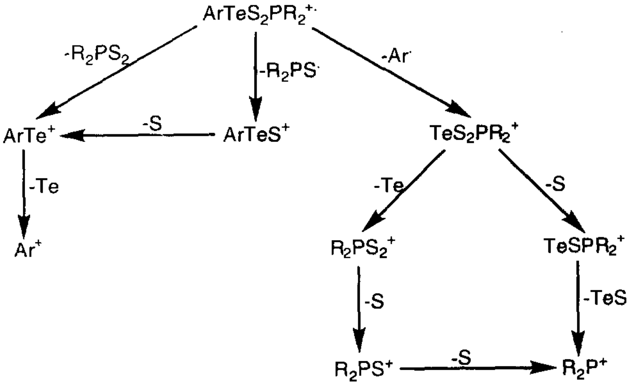

Fig. 2. Fragmentation pattern of $ArTeS_2PR_2$.

2.2.3. *Mass spectra*

The main monoisotopic peaks in the mass spectra of the title compounds are listed in Table 3, and a tentative fragmentation pattern is shown in Fig. 2. In addition to the expected ions of the initial fragmentation, *i.e.* $ArTe^+$ and $TeS_2PR_2^+$, which are the result of Te–S and Te–C bond cleavages, several other fragments formed by cleavage of a phosphorus–sulfur bond are also observed. A parent ion, of variable intensity, was observed for each compound and the primary fragmentation is clearly cleavage of a Te–S bond (to give $ArTe^+$) rather than phenyl group loss (to give $TeS_2PR_2^+$). Other ions of high intensity are associated with ligand fragments, though low intensity peaks are observed for the $ArTeS^+$ and $TeSPR_2^+$ ions.

2.2.4. *Crystal and molecular structure of phenyltellurium(II) diphenylphosphinodithioate, $PhTeS(S)PPh_2$*

The crystal structure of phenyltellurium(II) diphenylphosphinodithioate, $PhTeS(S)PPh_2$, has been determined by X-ray diffraction. A new coordination pattern has been found in which the ligand acts as a

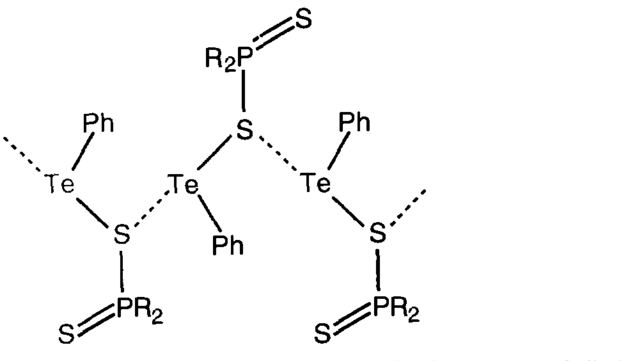

Fig. 3. Monodentate biconnective coordination pattern of dithiophosphorus ligands to tellurium.

monodentate biconnective moiety. As a result, the tellurium atoms are bridged in an unexpected and unique supramolecular structure in which only one sulfur atom from the phosphinodithioic ligand is involved in bonding to tellurium (Fig. 3).

Because of the thermochromism of this compound, the reflection data were collected at both 173 K and room temperature (294 K). The polymeric chain at room temperature is shown in Fig. 4 and important bond lengths and angles, at low and room temperature, are listed in Table 5. As can be observed, there are no significant structural differences between the data collected at the two temperatures, except in respect of the weak intermolecular Te(1a)...S(1c) interaction, for which a significant difference of *ca.* 0.03 Å was found.

As can be seen from Fig. 4, the structure consists of PhTeS(S)PPh$_2$ units linked together by weak intermolecular tellurium–sulfur interactions, leading to polymeric chains. If only primary bonds are considered, the phosphinodithioato ligand may be described as essentially monodentate, with single P–S (2.118(2) Å) and double P=S (1.934(2) Å) bonds, comparable with those observed in the free acid, Ph$_2$P(S)SH, *i.e.* 2.077(1) and 1.954(1) Å, respectively [20], although the P–S distance is somewhat longer.

Each tellurium atom has a semibonding contact (3.422(2) Å at 294 K and 3.383(2) Å at 173 K) with a sulfur atom of a neighbouring molecule (cf. the sum of van der Waals radii, Σ(Te, S) = 3.9 Å [21]). If these weak interactions are considered, the result is a T-shaped environment around the three-coordinated tellurium atom (*e.g.* S(1a)–Te(1a)... S(1c) 173.5(1)°, C(1a)–Te(1a)–S(1a) 99.2(1)°, C(1a)–Te(1a)... S(1c) 87.1°, at 294 K). The sulfur atom single bonded to phosphorus, i.e. S(1a), is involved in semibonding interactions, while the doubly bonded sulfur, *i.e.* S(2a), is not involved in any inter- or intramolecular interactions with tellurium atoms. The result is a $^1_\infty$[PhTeS(S)PPh$_2$] polymer with units bridged *via* monodentate biconnective phosphinodithioato groups. This unexpected coordination pattern may be the cause of the fact that the P–S distance is slightly longer in this phenyltellurium(II) derivative, than in the free acid (2.121 Å *vs.* 2.077 Å).

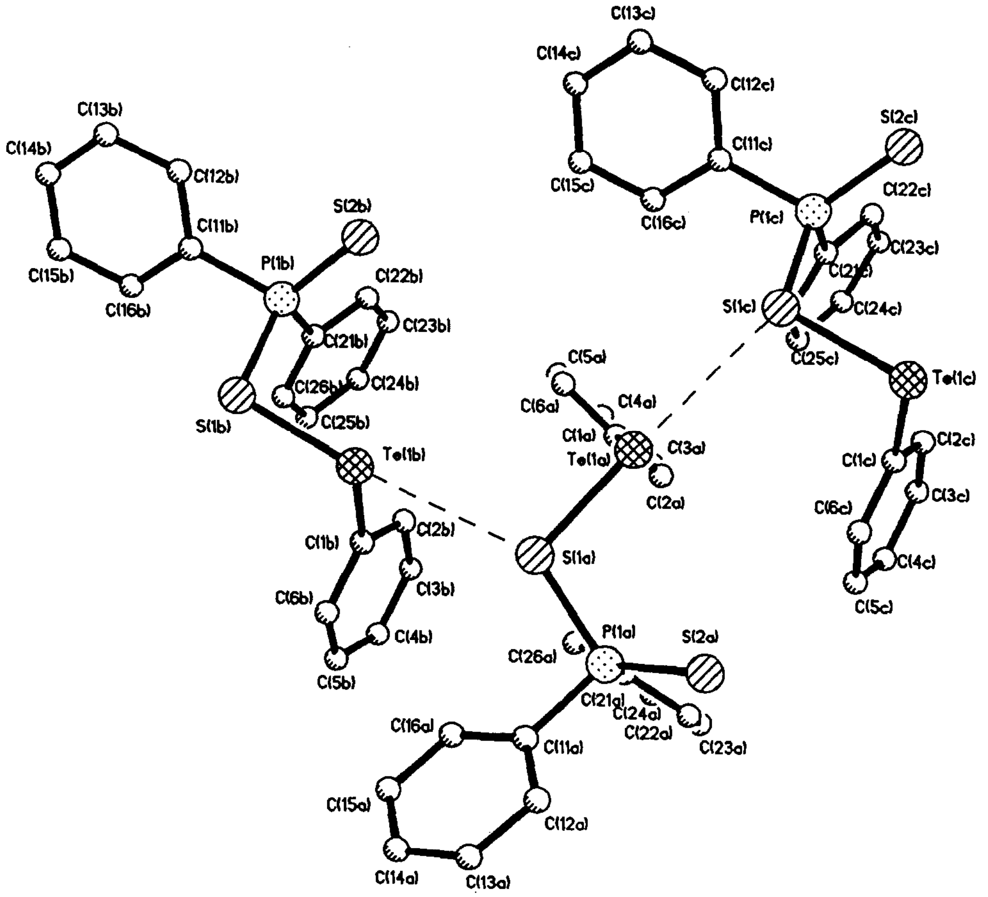

Fig. 4. View of the polymeric chain in $^1_\infty$[PhTeS(S)PPh$_2$] (at 294 K).

3. Experimental details

The diarylditellurides, Ar_2Te_2 (Ar = Ph, *p*-tolyl), were prepared by treating the corresponding Grignard reagent with elemental tellurium, as described previously [22,23]. Bis(diorganothiophosphinyl) disulfanes, $R_2P(S)–S–S–P(S)R_2$ (R = Me, Et, Ph), were obtained by published procedures [24,25], involving redox reactions between sodium or ammonium diorganophosphinodithioates and aqueous I_2/KI solutions.

Infrared spectra were obtained in the range 4000–400 cm^{-1}, as Nujol mulls, on a BIO-RAD-FTS7 spectrometer. ^1H and ^{31}P spectra were recorded with C_6D_6 or $CDCl_3$ solutions on a BRUKER WH 360 instrument, operating at 360 and 145.8 MHz, respectively. The ^1H and ^{31}P chemical shifts are reported in ppm relative to TMS and 85% H_3PO_4 respectively. The EI mass spectra were recorded on a CH7 (A) (MAT) apparatus.

3.1. General procedure for the preparation of $ArTeS_2PR_2$

The preparations of all new compounds involved the general procedures described below. Experimental details are given in Table 1.

(i) A colorless solution of $R_2P(S)–S–S–P(S)R_2$ in chloroform was added to a red solution of Ar_2Te_2 (1:1 molar ratio) in the same solvent (except for Ar = R = Ph acetonitrile was used as solvent). The mixture was stirred at room temperature for 12 h, or refluxed for 6 h (Ar = R = Ph). For Ar = Ph, R = Me, Et, and Ar = *p* = tolyl, R = Me, the reaction mixture immediately turned orange, and the title compounds separated as yellow-orange solids, which were filtered off. For the other compounds, a clear, red solution was obtained, which, after the partial removal of the solvent in vacuum, deposited the desired product as yellow (R = Et) or red (R = Ph) crystals. All compounds were recrystallized from acetonitrile.

TABLE 5. Important bond lengths (Å) and angles (°) for $PhTeS(S)PPh_2$

	174 K (yellow form) [a]	294 K (red form) [b]
Intramolecular		
Te(1a)–S(1a)	2.406(2)	2.401(2)
Te(1a)–C(1a)	2.112(5)	2.113(5)
Te(1a)...S(2a) (nonbonding)	3.989(2)	3.964(2)
P(1a)–S(1a)	2.121(2)	2.118(2)
P(1a)–S(2a)	1.944(2)	1.934(2)
P(1a)–C(11a)	1.809(6)	1.813(5)
P(1a)–C(21a)	1.817(5)	1.813(4)
C(1a)–Te(1a)–S(1a)	98.9(2)	99.2(1)
S(1a)–P(1a)–S(2a)	115.2(1)	115.0(1)
S(1a)–P(1a)–C(11a)	98.4(2)	98.7(2)
S(1a)–P)1a)–C(21a)	106.5(2)	106.8(2)
S(2a)–P(1a)–C(11a)	115.0(2)	114.6(2)
S(2a)–P(1a)–C(21a)	113.3(2)	113.5(2)
C(11a)–P(1a)–C(21a)	107.1(2)	106.8(2)
Te(1a)–S(1a)–P(1a)	103.7(1)	103.7(1)
Intermolecular		
Te(1a)...S(1c)	3.383(2)	3.422(2)
S(1a)–Te(1a)...S(1c)	173.1(1)	173.5(1)
S(1c)...Te(1a)–C(1a)	87.9(2)	87.1(1)

[a] Ref. 8; [b] This work.

TABLE 6. Summary of crystal data for phenyltellurium(II) diphenylphosphinodithioate, $PhTeS(S)PPh_2$

	173 K (yellow form)	294 K (red form)
Formula	$C_{18}H_{15}PS_2Te$	$C_{18}H_{15}PS_2Te$
Fw	454.0	454.0
Space group	$P2_1/c$ Monoclinic	$P2_1/c$ Monoclinic
a (Å)	8.658(3)	8.739(3)
b (Å)	24.270(9)	24.597(7)
c (Å)	9.237(3)	9.243(3)
β (°)	112.28(2)	112.64(2)
V (Å³)	1796.3(11)	1833.6(10)
Z	4	4
Density (calcd.)	1.679 mg m	1.645 mg m
μ (mm^{-1})	1.971	1.931
λ(MoK_α)	0.71073	0.71073

TABLE 7. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$)

	x	*y*	*z*	U_{eq} [a]
Te(1)	2187(1)	2593(1)	4998(1)	55(1)
C(1)	−181(6)	2258(2)	3733(6)	50(2)
C(2)	−1560(8)	2477(3)	3877(8)	69(3)
C(3)	−3109(8)	2246(3)	3114(10)	91(3)
C(4)	−3268(11)	1802(4)	2220(9)	108(4)
C(5)	−1908(12)	1571(3)	2066(8)	100(4)
C(6)	−329(9)	1804(2)	2830(6)	72(3)
S(1)	2340(1)	3217(1)	3060(1)	42(1)
S(2)	2557(2)	4180(1)	5801(2)	70(1)
P(1)	1480(1)	3959(1)	3634(1)	40(1)
C(11)	1884(5)	4398(2)	2245(6)	42(2)
C(12)	2889(6)	4851(2)	2764(7)	61(2)
C(13)	3231(8)	5171(3)	1670(11)	86(4)
C(14)	2628(8)	5034(3)	150(10)	82(3)
C(15)	1612(7)	4591(3)	−407(8)	70(3)
C(16)	1240(6)	4271(2)	667(6)	54(2)
C(21)	−753(5)	3902(2)	2983(5)	40(2)
C(22)	−1550(7)	4219(2)	3719(6)	63(2)
C(23)	−3250(7)	4203(3)	3216(8)	75(3)
C(24)	−4168(6)	3884(3)	1990(7)	68(3)
C(25)	−3403(6)	3566(2)	1247(7)	60(2)
C(26)	−1695(6)	3580(2)	1732(6)	50(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

(ii) A mixture of $PhTeCl_3$ and $NaS_2PR_2 \cdot 2H_2O$ (1:3 molar ratio) in toluene (R = Me) or acetonitrile (R = Et), was stirred under reflux for 3 h, immediately turning to orange. The deposited NaCl was filtered off and the clear filtrate, after partial removal of the solvent in vacuum deposited an orange (R = Me) or a yellow (R = Et) crystalline product. The compounds were purified by recrystallization from chloroform.

3.2. *Crystal structure determination of $PhTeS(S)PPh_2$ (at 294 K)*

Crystal data are given in Table 6 and atomic coordinates in Table 7. Data were collected on a Siemens P4 four-circle diffractometer for 4565 reflections in the ω-2θ mode of which were 4237 independent reflections (R_{int} = 1.20%) and 2933 ($F > 4.0\sigma(F)$) were used in the full matrix least squares refinement with the SHELXTL PLUS (VMS) program system. The position of the tellurium atom was obtained by direct methods after which a series of least-square refinements and difference Fourier syntheses revealed positions for the other non-hydrogen atoms. The structure was refined with anisotropic thermal parameters for all non-hydrogen atoms to a final R value of 4.07% (R_W = 4.89%). Further details of the crystal structure of $PhTeS(S)PPh_2$ (at 294 K) are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informations mbH, D-76344 Eggenstein-Leopoldshafen 2 (FRG), on quoting the deposit number CSD-, the names of the authors, and the journal citation.

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