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The reaction of the tertiary phosphine sulfides R_3PS ($R = Ph$, Me_2N or C_6H_{11}) with X_2 ($X_2 = I_2$, Br_2, IBr or ICl); structural characterisation of the CT complexes $(Me_2N)_3PSI_2$ and $Ph_3PS(I_{0.89}Br_{0.11})Br$ and the ionic compound $[\{(Me_2N)_3PS\}_2S]^{2+}\ 2[Br_3]^-$

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The reactions of the tertiary phosphine sulfides R_3PS ($R = Ph$, Me_2N or C_6H_{11}) with X_2 (X = I or Br) and IX (X = Br or Cl) have been studied. Reaction of R_3PS with I_2 or IX results in quantitative isolation of the CT complexes R_3PSIX (X = I, Br or Cl), except for Ph_3PS with I_2 which produces the unusual compound $(Ph_3PSI_2)_2I_2$, which has been crystallographically characterised by earlier workers. The crystal structure of $(Me_2N)_3PSI_2$ has been determined and compared to Ph_3PSI_2, previously described. The greater *d*(I–I) for $(Me_2N)_3PSI_2$, 2.856(1) Å, compared to that of 2.823(1) Å for Ph_3PSI_2 clearly illustrates that *d*(I–I) in R_3PSI_2 compounds is sensitive to R, although this effect is less pronounced when compared to that of analogous R_3PSeI_2 compounds. The crystal structure of the product from the reaction of Ph_3PS with IBr has also been determined and represents the first example of a tertiary phosphine sulfide interhalogen CT complex. It has the formula $Ph_3PS(I_{0.89}Br_{0.11})Br$ and is isomorphous with Ph_3PSI_2. The reaction of R_3PS with Br_2 is complex. In the case of Ph_3PS, phosphorus–sulfur bond cleavage occurs quantitatively to produce Ph_3PBr_2 and elemental sulfur. Reaction of $(Me_2N)_3PS$ with Br_2 gives, as one product, $[\{(Me_2N)_3PS\}_2S][Br_3]_2$ in moderate (*ca.* 30%) yield. This unusual dication is compared to the previously reported $[(Bu^t_3PTe)_2Te][SbF_6]_2$. Tricyclohexylphosphine sulfide reacts with Br_2 in solvents of low relative permittivity (Et_2O) to produce the 1 : 1 addition complex $(C_6H_{11})_3PSBr_2$; however, dissolution of this material in solvents of higher relative permittivity results in phosphorus–sulfur bond cleavage to produce $(C_6H_{11})_3PBr_2$ and elemental sulfur.

Introduction

The ability of tertiary phosphine chalcogenides to form addition compounds with dihalogens and interhalogens was first recognised by Zingaro and co-workers[1–5] in the early 1960s. In the case of tertiary phosphine selenides, reaction with IX (X = Cl, Br or I) appeared to produce the CT compounds $R_3PSe–X–X$ where, in the case of the interhalogen complexes, the heavier halogen binds directly to the selenium atom, according to IR and UV/VIS spectroscopy.[1–5] Solution studies concerning trialkylphosphine sulfides indicated similar results, *i.e.* 1 : 1 CT complex formation upon reaction with IX (X = Cl, Br or I). However, in the case of the reaction of triphenylphosphine sulfide with diiodine, an unusual 2 : 3 ($Ph_3PS : I_2$) adduct was isolated.[6] The crystal structure of this adduct, the first reported for a tertiary phosphine sulfide–dihalogen complex, revealed two Ph_3PSI_2 units linked into pairs by a supporting I_2 molecule. The *d*(I–I) is significantly increased (2.85(1) Å) when compared to *d*(I–I) in solid diiodine (2.71 Å) indicating that electron density is being donated to the σ* antibonding orbitals of the I_2 by the two Ph_3PSI_2 moieties. The conclusion of these workers was that, despite the fact that a 1 : 1 triphenylphosphine sulfide–diiodine adduct, Ph_3PSI_2, could be identified in solution, it could not be isolated in the solid state. It was therefore reasoned that, due to the poor donor ability of triphenylphosphine sulfide towards diiodine, a 2 : 3 adduct formed consisting of two Ph_3PSI_2 moieties and a supporting diiodine molecule.

The interaction of triphenylphosphine sulfide with diiodine has been independently re-examined by Sobczky and co-workers[7] and Kaur and Lobana.[8,9] Both groups reported the formation of a 1 : 1 CT complex, although it was noted by Kaur and Lobana[8] that Ph_3PS formed a 2 : 3 ($Ph_3PS : I_2$) complex in CCl_4 and a 1 : 1 complex in CH_2Cl_2, suggesting that the formation of the 1 : 1 complex is solvent dependent.

Very recently, the interaction of triphenylphosphine sulfide with diiodine has been studied by Bricklebank and co-workers[10] using ^{31}P-{^1H} NMR and UV/VIS spectroscopy. More significantly, the crystal structure of the 1 : 1 CT complex, Ph_3PSI_2, prepared from dichloromethane, was reported thus confirming the existence of the 1 : 1 CT adduct in the solid state. The *d*(P–S) for this compound, 1.998(2) Å, is rather short suggesting some retention of double bond character. However, *d*(I–I) for the complex, 2.823(1) Å, clearly illustrates lengthening of the I–I bond upon adduct formation when compared to that of free diiodine, as expected.

We are currently engaged in studying the interaction of a variety of tertiary phosphine chalcogenides with dihalogens and interhalogens and have found that, in the case of the reaction of R_3PSe with I_2 ($R = Ph$, Me_2N or Et_2N), 1 : 1 CT complexes result both in the solid state and in solution.[11] All three compounds have been studied crystallographically. The structural features of Ph_3PSeI_2 are generally very similar to those exhibited by Ph_3PSI_2. One notable difference however is *d*(I–I) for the two complexes, 2.823(1) and 2.881(3) Å for Ph_3PSI_2 and Ph_3PSeI_2, respectively. This greater lengthening of the diiodine bond in the tertiary phosphine selenide complex compared to the tertiary phosphine sulfide reflects the greater donor power of selenium compared to sulfur towards diiodine. The iodine–iodine bond length in the CT complexes R_3PSeI_2 is also sensitive to the nature of R. For example, as previously stated, *d*(I–I)

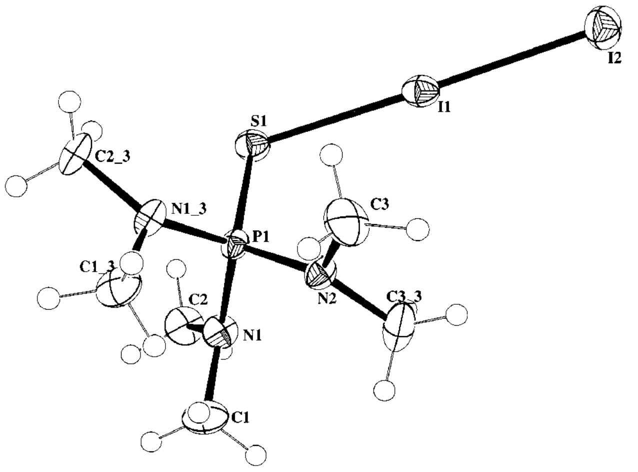

Fig. 1 The crystal structure of $(Me_2N)_3PSI_2$.

for Ph_3PSeI_2 is 2.881(3) Å whereas *d*(I–I) for the complex $(Et_2N)_3PSeI_2$ is 2.985(2) Å. This illustrates that the R groups on the parent tertiary phosphine significantly affect the donor power of the selenium atom towards diiodine, despite the fact that they are not directly bound to this atom. We have also investigated the reaction of dibromine with certain tertiary phosphine selenides. In the case of R_3PSe (R = Me_2N or C_6H_{11}), T-shaped 1 : 1 adducts result, R_3PSeBr_2.[12] However, in the case of Ph_3PSe, whilst reaction of this tertiary phosphine selenide with dibromine in diethyl ether produces the T-shaped Ph_3PSeBr_2, the reaction product proved to be solvent sensitive; the same reaction performed in dichloromethane produced the unusual ionic dinuclear compound $[Ph_3PSeBrSePPh_3]Br\cdot 2CH_2Cl_2$.[13] A further anomaly was noted for the reaction of $(Pr^n{}_2N)_3PSe$ with dibromine, which results in the isolation of equimolar quantities of $(Pr^n{}_2N)_3PSe_2Br_2$ and $(Pr^n{}_2N)_3PBr_2$. The former compound contains both bent and T-shaped geometries for the two selenium atoms, respectively.[13]

We now report the reaction of some tertiary phosphine sulfides with X_2 (X = I or Br) and IX (X = Br or Cl). Considering the variety and, in some cases, unexpected products obtained from the analogous reactions of the tertiary phosphine selenides, we felt the present study was certainly worthwhile.

Results and discussion

Analytical and spectroscopic data for the tertiary phosphine sulfides and the 1 : 1 addition compounds R_3PSX_2 ($X_2 = I_2$ or IBr) are displayed in Table 1. The tertiary phosphine sulfides were easily prepared from the direct reaction of the tertiary phosphine with elemental sulfur at room temperature (RT) in diethyl ether according to literature methods.[4,14] They were treated with X_2 ($X_2 = I_2$ or IBr) in a 1 : 1 stoichiometric ratio under anhydrous conditions according to eqn. (1). (R = Ph,

$$R_3PS + X_2 \xrightarrow[Et_2O,\ RT]{N_2,\ ca.\ 2\ d} R_3PSX_2 \qquad (1)$$

Me_2N or C_6H_{11}). All of the compounds were isolated in quantitative yield and proved to be air-stable.

In order to investigate the effects of the R groups on *d*(I–I) for a given R_3PSI_2 compound (we have previously reported the sensitivity of *d*(I–I) on R for analogous R_3PSeI_2 compounds[11]) we decided crystallographically to characterise $(Me_2N)_3PSI_2$ to compare with Ph_3PSI_2 which was recently reported by Bricklebank and co-workers.[10] Crystals of $(Me_2N)_3PSI_2$ were easily grown from diethyl ether–dichloromethane (1 : 1) solution at 50 °C on cooling to room temperature. From the large crop of dark red crystals one was chosen for analysis by single crystal X-ray diffraction. The structure of $(Me_2N)_3PSI_2$ is illustrated in Fig. 1 and selected bond lengths and angles are given in Table 2. In common with Ph_3PSI_2, $(Me_2N)_3PSI_2$ adopts the CT structure with an approximately linear S–I–I bond (177.98(6)°). The *d*(I–I), 2.856(1) Å, is significantly increased compared to that of solid diiodine, 2.71 Å, as expected since electron density is passed from the sulfur atom to the σ^* antibonding orbitals of the diiodine molecule. Significantly, it is also longer than that reported for Ph_3PSI_2 (2.823(1) Å), clearly illustrating that *d*(I–I) in R_3PSI_2 compounds is sensitive to R. However, the effect is less pronounced compared to that in the analogous R_3PSeI_2 (the difference in *d*(I–I) for $(Me_2N)_3PSI_2$ and Ph_3PSI_2 is 0.033(1) Å; the difference for $(Me_2N)_3PSeI_2$ and Ph_3PSeI_2 is 0.081(2) Å). In addition to the longer *d*(I–I) in $(Me_2N)_3PSI_2$ compared to Ph_3PSI_2, there is also a slight lengthening of the phosphorus–sulfur bond, 2.014(4) Å compared to 1.998(2) Å for Ph_3PSI_2.

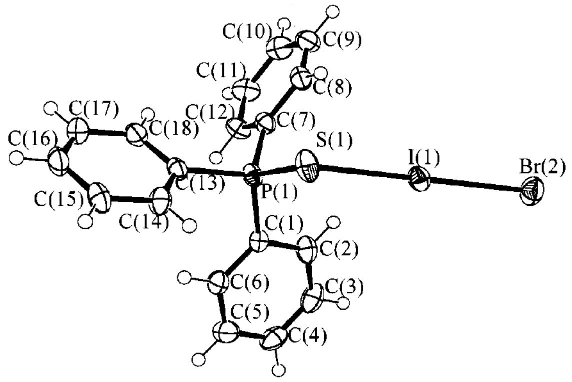

Fig. 2 The crystal structure of $Ph_3PS(I_{0.89}Br_{0.11})Br$.

Although the ability of Ph_3PS to form a stable 1 : 1 adduct with iodine monobromide was reported by Zingaro and Meyers,[3] no compound of this stoichiometry has been crystallographically characterised. We therefore decided to prepare crystals of Ph_3PSIBr with a view to comparing the resultant crystal structure with that recently reported for Ph_3PSI_2. Crystals of Ph_3PSIBr were prepared from diethyl ether–dichloromethane solution (1 : 1) by dissolution of the orange powder in the solvent at *ca.* 50 °C and subsequently allowing the solution to cool slowly to RT. After *ca.* 3 d, large orange crystals formed in the reaction vessel, one of which was selected for analysis by single crystal X-ray diffraction. The crystal structure of the resultant complex is illustrated in Fig. 2. Selected bond lengths and angles are displayed in Table 3. In fact the compound has the formula $Ph_3PS(I_{0.89}Br_{0.11})Br$ and is isomorphous with the previously reported Ph_3PSI_2. The *d*(I–Br), 2.6832(6) Å, is increased with respect to that of solid IBr (2.52 Å) as expected with the formation of a CT complex. Unlike $Ph_3PI_{1.27}Br_{0.73}$, which shows dual occupancy of the halogen sites and is rich in diiodine,[15] Ph_3PSIBr exists as $Ph_3PS(I_{0.89}Br_{0.11})Br$, *i.e.* although predominantly the heavier halogen is bound to the sulfur atom, the molecule overall is rich in bromine with respect to iodine. The *d*(S–I) for Ph_3PSIBr is 2.656(1) Å, less than that observed in Ph_3PSI_2, 2.753(2) Å. The *d*(P–S) 2.007(1) Å, is greater than that observed for Ph_3PSI_2, 1.998(2) Å, although clearly this difference is very slight. Thus Ph_3PSIBr represents the first crystallographically characterised R_3PSIBr compound and verifies the spectroscopic data reported by earlier workers.[3]

The reaction of R_3PS with Br_2

Unlike the reaction of R_3PS with X_2 ($X_2 = I_2$ or IBr), which produce the 1 : 1 addition compounds R_3PSX_2 in quantitative yield, the reaction of R_3PS with dibromine is complex. In the case of the reaction of triphenylphosphine sulfide with dibromine two reaction products appear to be formed. Addition of the two reactants in diethyl ether produces after *ca.* 2 d a large quantity of a white solid. The ^{31}P-$\{^1H\}$ NMR spectrum of this material, recorded in $CDCl_3$, showed a single resonance at δ 51.8, very similar to that previously recorded for Ph_3PBr_2,

Table 1 The reaction of R_3P with S and R_3PS with X_2 (R = Ph, Me_2N or C_6H_{11}; X_2 = I_2, IBr, ICl or Br_2); analytical and spectroscopic data for the products formed

				Analysis (%), found (calculated)								
Reactants	Product(s)	Colour	Mp/°C	C	H	N	S	I	Br	Cl	$^{31}P-\{^1H\}$ NMR, δ[a]	$\tilde{\nu}$(P–S)/cm^{-1}
$Ph_3PS + I_2$	$(Ph_3PSI_2)_2I_2 + Ph_3PS$	Red	140 (decomp.)	32.0 (32.0)	2.5 (2.2)	—	4.7 (4.7)	55.2 (56.4)	—	—	42.3, 44.0	592, 638
Ph_3PS + IBr	Ph_3PSIBr	Yellow	145 (decomp.)	43.0 (43.1)	3.4 (3.0)	—	6.0 (6.4)	23.8 (25.3)	18.9 (16.0)	—	42.0	588
Ph_3PS + ICl	Ph_3PSICl	Yellow	138–139	47.1 (47.3)	3.0 (3.3)	—	6.7 (7.0)	27.8 (27.8)	—	7.7 (7.8)	42.7	586
$Ph_3PS + Br_2$	$Ph_3PBr_2 + S_8$	White		51.5 (51.2)	3.7 (3.6)	—	—	—	37.8 (37.9)	—	51.8	—
$(Me_2N)_3P$ + S	$(Me_2N)_3PS$	White	30–31	36.1 (36.9)	10.0 (9.2)	20.9 (21.5)	15.3 (16.4)	—	—	—	82.4	565
$(Me_2N)_3PS + I_2$	$(Me_2N)_3PSI_2$	Red	49–50	16.3 (16.0)	4.3 (4.0)	9.5 (9.4)	8.0 (7.1)	55.4 (56.6)	—	—	73.8	544
$(Me_2N)_3PS$ + IBr	$(Me_2N)_3PSIBr$	Yellow	99–100	18.3 (17.9)	4.8 (4.5)	10.6 (10.4)	8.6 (8.0)	30.9 (31.6)	20.6 (19.9)	—	70.1	538
$(Me_2N)_3PS$ + ICl	$(Me_2N)_3PSICl$	Yellow	90–91	20.9 (20.1)	5.3 (5.0)	11.9 (11.7)	9.1 (9.0)	34.8 (35.5)	—	9.5 (9.9)	69.6	540
$(Me_2N)_3PS + Br_2$	$[\{(Me_2N)_3PS\}_2S]^{2+}\ 2[Br_3]^-$	Yellow	66–68	16.4 (16.0)	4.2 (4.0)	9.3 (9.3)	10.0 (10.6)	—	50.0 (53.4)	—	Insoluble	
$(C_6H_{11})_3P$ + S	$(C_6H_{11})_3PS$	White	183–184	70.0 (69.2)	10.7 (10.6)	—	9.9 (10.3)	—	—	—	62.7	629
$(C_6H_{11})_3PS + I_2$	$(C_6H_{11})_3PSI_2$	Dark Red	173–174	38.1 (38.2)	6.1 (5.8)	—	5.6 (5.7)	44.8 (44.9)	—	—	58.4	583
$(C_6H_{11})_3PS + Br_2$	$(C_6H_{11})_3PSBr_2$	Yellow	121–122	44.2 (45.8)	7.0 (7.0)	—	5.7 (6.8)	33.6 (33.9)	—	—	103.9[b]	573

[a] Shifts recorded in $CDCl_3$ relative to concentrated phosphoric acid as standard. [b] NMR resonance due to $(C_6H_{11})_3PBr_2$, see text.

Table 2 Selected bond lengths (Å) and angles (°) for $(Me_2N)_3PSI_2$

I(1)–I(2)	2.856(1)	P(1)–S(1)	2.014(4)
I(1)–S(1)	2.705(3)		
S(1)–I(1)–I(2)	177.98(6)	N(2)–P(1)–S(1)	118.4(4)
N(2)–P(1)–N(1)	102.6(3)		

Table 3 Selected bond lengths (Å) and angles (°) for $Ph_3PS(I_{0.89}Br_{0.11})Br$

S(1)–I(1)	2.656(1)	P(1)–S(1)	2.007(1)
I(1)–Br(2)	2.6832(6)		
S(1)–I(1)–Br(2)	175.13(2)	P(1)–S(1)–I(1)	107.63(5)

δ 49.2.[16] Elemental analysis of this solid confirms its identity as Ph_3PBr_2 [Found (Calc.): C, 51.5 (51.2); H, 3.7 (3.6); Br, 37.8 (37.9)%]. Concentration of the resultant filtrate produced some pale yellow crystals, one of which was selected for analysis by single crystal X-ray diffraction. A unit cell determination of this material revealed it to be S_8. Clearly, reaction of Ph_3PS with dibromine results in the cleavage of the phosphorus–sulfur bond, eqn. (2).

$$8\ Ph_3PS + 8\ Br_2 \xrightarrow[\text{Et}_2\text{O, RT}]{\text{N}_2,\ ca.\ 2\ \text{d}} 8\ Ph_3PBr_2 + S_8 \qquad (2)$$

This result is in direct contrast to the analogous reaction of triphenylphosphine selenide with dibromine[13] which, in solvents of low relative permittivity, produces the T-shaped adduct Ph_3PSeBr_2, analogous to $(Me_2N)_3PSeBr_2$ and $(C_6H_{11})_3PSeBr_2$ previously described. However, reaction of Ph_3PSe with Br_2 in solvents of higher relative permittivity, *e.g.* CH_2Cl_2, produces the unusual dinuclear complex $[Ph_3PSeBrSePPh_3]Br{\cdot}2CH_2Cl_2$, thus illustrating that the phosphorus–sulfur bond is more susceptible to cleavage upon reaction with dihalogens than the phosphorus–selenide bond.

In order to gain further information concerning the reaction of R_3PS with dibromine, we also investigated the reaction of $(C_6H_{11})_3PS$ with dibromine in diethyl ether solution. Reaction of dibromine with this triorganophosphine sulfide appeared to proceed in a different way than the analogous reaction with Ph_3PS, described above. Tricyclohexylphosphine sulfide reacts with dibromine over *ca.* 2 d to produce a yellow solid. Elemental analysis of this material suggests the formation of a 1 : 1 adduct, $(C_6H_{11})_3PSBr_2$, Table 1. Further evidence for this adduct formation may be inferred from its IR spectrum, clearly illustrating a band due to the phosphorus–sulfur stretch, thus confirming that, in contrast to the reaction of Ph_3PS with Br_2, which results in cleavage of the P–S bond to produce Ph_3PBr_2, reaction of $(C_6H_{11})_3PS$ does not result in cleavage of the P–S bond. Moreover, ν(P–S) for $(C_6H_{11})_3PSBr_2$, 573 cm^{-1}, is shifted downfield compared to ν(P–S) for the parent tricyclohexylphosphine sulfide, 629 cm^{-1}. Both we[11–13] and other workers[3,10] have previously noted both in the present and previous studies that this is a good indication of adduct formation since ν(P–S) shifts to lower frequency upon co-ordination of a halogen atom to the sulfur donor, as expected. Final confirmation of the formation of $(C_6H_{11})_3PSBr_2$ should be provided by its $^{31}P\text{-}\{^1H\}$ NMR spectrum, which would be expected to exhibit a single peak, shifted from that observed from the parent tertiary phosphine selenide. Unfortunately, $(C_6H_{11})_3PSBr_2$ is insoluble in non-polar solvents. Dissolution of the material in polar solvents such as $CDCl_3$ results in cleavage of the P–S bond to produce $(C_6H_{11})_3PBr_2$ and, presumably, elemental sulfur, since a single resonance at δ 103.9 is observed which is very close to the reported value for tricyclohexylphosphine dibromide.[16] This behaviour mirrors the triphenylphosphine sulfide–dibromine system, although in this case P–S bond cleavage occurs regardless of the relative permittivity of the solvent.

Table 4 Selected bond lengths (Å) and angles (°) for $[\{(Me_2N)_3PS\}_2S]^{2+}\ 2[Br_3]^-$

Br(1)–Br(2)	2.506(1)	S(1)–S(2)	2.032(3)
Br(2)–Br(3)	2.538(1)	S(1)–P(1)	2.119(3)
Br(4)–Br(5)	2.550(1)	S(2)–S(3)	2.053(3)
Br(5)–Br(6)	2.521(1)	S(3)–P(2)	2.079(3)
Br(1)–Br(2)–Br(3)	176.51(5)	S(1)–S(2)–S(3)	104.7(1)
Br(6)–Br(5)–Br(4)	177.38(5)	S(2)–S(3)–P(2)	100.7(1)
S(2)–S(1)–P(1)	104.2(1)		

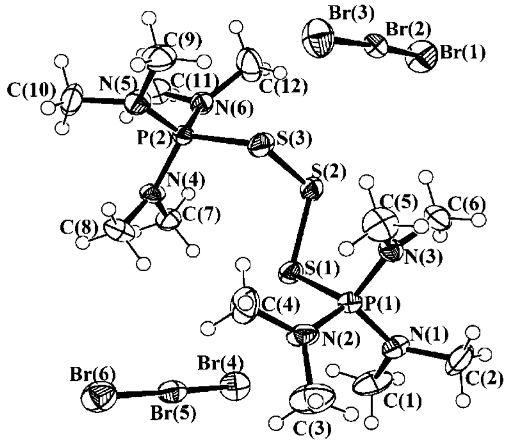

Fig. 3 The crystal structure of $[\{(Me_2N)_3PS\}_2S][Br_3]_2$.

In a final attempt crystallographically to characterise the elusive R_3PSBr_2, we decided to treat $(Me_2N)_3PS$ with Br_2 in diethyl ether solution. This tertiary phosphine sulfide was chosen since it contains a very basic parent tertiary phosphine and we have previously reported that the analogous compound, $(Me_2N)_3PSe$, reacts with dibromine to produce $(Me_2N)_3PSeBr_2$ quantitatively.[12] In the reaction of $(Me_2N)_3PS$ with Br_2, after *ca.* 2 d a large quantity of yellow powder was produced which was isolated by standard Schlenk techniques. Recrystallisation of the product from diethyl ether solution (dichloromethane was avoided since the use of this solvent may have resulted in cleavage of the phosphorus–sulfur bond) at 50 °C produced, on standing at room temperature for *ca.* 5 d, a small crop of yellow-orange crystals which we assumed to be $(Me_2N)_3PSBr_2$. The crystals were plunged into an inert oil under anaerobic conditions and examined under the microscope. From these, one was chosen for analysis by single crystal X-ray diffraction. Surprisingly, the material proved to be the unusual ionic compound $[\{(Me_2N)_3PS\}_2S]^{2+}\ 2[Br_3]^-$, Fig. 3, and not the expected 1 : 1 addition compound $(Me_2N)_3PSBr_2$. Selected bond lengths and angles are in Table 4. Clearly, this material cannot be considered as representative of the only bulk product from the reaction of $(Me_2N)_3PS$ with Br_2, but it is nevertheless isolated in significant yield (*ca.* 30%) and provides an interesting insight into the complex reaction of certain R_3PS compounds with dibromine. One possible other product is the free phosphine $(Me_2N)_3P$, although this was not observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the bulk material. It is possible to speculate that during the reaction phosphorus–sulfur bond cleavage has again occurred, but only for some of the $(Me_2N)_3PS$ molecules. The free elemental sulfur thus produced may then react with dibromine to produce transient dications (*e.g.* SBr_2) which then react with other $(Me_2N)_3PS$ moieties producing the dipositive cation $[\{(Me_2N)_3PS\}_2S]^{2+}$, the charge being balanced by tribromide anions. Again, no evidence for a sulfur–bromine bond is observed. No cation of the formula $[(R_3PS)_2S]^{2+}$ has previously been crystallographically characterised; however, the analogous tellurium containing cation, $[(Bu^t{}_3PTe)_2Te]^{2+}$, has been described by Kuhn *et al.*[17] This cation may be considered as a tellurophosphorane Te^{2+} complex or as a phosphine stabil-

Table 5 Crystal data and details of refinement for $Ph_3PS(I_{0.89}Br_{0.11})Br$, R_3PSI_2 and $[(R_3PS)_2S][Br_3]_2$ (R = Me_2N)

	$Ph_3PS(I_{0.89}Br_{0.11})Br$	$(Me_2N)_3PSI_2$	$[\{(Me_2N)_3PS\}_2S][Br_3]_2$
Formula	$C_{18}H_{15}BrIPS$	$C_6H_{18}I_2N_3PS$	$C_{12}H_{36}Br_6N_6P_2S_3$
M	501.14	449.06	902.04
T/K	203(2)	203(2)	203(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$Cmc2_1$	$P\bar{1}$
a/Å	12.352(2)	10.878(1)	8.429(2)
b/Å	9.386(1)	9.0848(9)	9.972(2)
c/Å	15.298(2)	14.213(2)	19.282(4)
α/°	—	—	80.66(2)
β/°	95.47(2)	—	81.18(2)
γ/°	—	—	74.33(2)
U/Å^3	1765.5(4)	1404.6(3)	1529.5(6)
Z	4	4	4
μ/cm^{-1}	42.80	47.10	81.98
Reflections collected	3249	688	5871
Observed reflections	3249	688	5361
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0295, 0.0724	0.0323, 0.0827	0.0544, 0.1176
(all data)	0.0410, 0.0779	0.0326, 0.0830	0.1048, 0.1386

ised Te_3 dication. This description is equally valid for $[\{(Me_2N)_3PS\}_2S]^{2+}$ described here, which could be considered as either a tertiary phosphine sulfide S^{2+} complex or as a phosphine stabilised S_3 dication. The sulfur–sulfur bond distances, 2.032(3) and 2.053(3) Å, are fairly typical for a single bond, 2.05 Å, thus indicating that little or no S–S double bond character is observed in this dication. A similar situation is observed for the tellurium analogue $[(Bu^t{}_3PTe)_2Te]^{2+}$, d(Te–Te) = 2.713(1), 2.715(2) Å; d(Te–Te) for organic ditellurides = 2.70 Å.

Experimental

The compounds R_3PS were either obtained commercially (R = Ph) (Lancaster) or easily prepared from the direct reaction of the appropriate tertiary phosphine with elemental sulfur, according to literature methods.[14] Reaction time was approximately 1 d. Reaction of the tertiary phosphine sulfides with dihalogens or interhalogens was carried out under anaerobic and anhydrous conditions, although it was later noted that the complexes R_3PSI_2 and R_3PSIBr are moisture-stable. All manipulations of the compounds were performed inside a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d, refluxed over CaH_2 in an inert atmosphere (N_2) and distilled directly into the reaction vessel. Anhydrous CH_2Cl_2 was obtained commercially and used as received, as were the dihalogens (I_2, Br_2) and iodine monobromide (Aldrich).

The R_3PSX_2 compounds ($X_2 = I_2$ or IBr) were synthesized in the same way, that of Ph_3PSIBr being typical. Triphenylphosphine sulfide (2.00 g, 6.80 mmol) was suspended in Et_2O (*ca.* 75 cm^3) and subsequently iodine monobromide (1.41 g, 6.80 mmol) added. After *ca.* 2 d the resultant dark red (R_3PSI_2) or orange (R_3PSIBr) solid was isolated using standard Schlenk techniques. The solids were then transferred to pre-dried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department. The ^{31}P-$\{^1H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Brüker AC200 high resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard, IR spectra on a Nicolet 5PC FT spectrometer.

Crystallography

Crystals of all three compounds were independently submerged in an inert oil under anaerobic conditions and suitable ones were chosen by examination under a microscope. The crystals, with their protective coating of oil, were then independently mounted on glass fibres and transferred to the diffractometer and cooled to 203(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a Nonius MAC 3 CAD 4 diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and ω–2θ scans. The structures were solved by direct methods. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 5. During refinement of Ph_3PSIBr it was noticed that the iodine vibrational ellipsoid was significantly larger than those of the surrounding atoms. The iodine site was therefore refined as a mixture of I and Br atoms, which converged to give a crystal composition of 89% Ph_3PSIBr and 11% $Ph_3PSBrBr$. A similar treatment of the terminal Br indicated that it should remain a purely Br site. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 18, anomalous dispersion effects from ref. 19. The structure determinations were performed using SHELXS 86 and refinement based on F^2 by using SHELXL 93 crystallographic software packages.[20,21]

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See http://www.rsc.org/suppdata/dt/1999/2225/ for crystallographic files in .cif format.

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