

Reaction of R_3PSe with I_2 ; crystal structures of Ph_3PSeI_2 , $(Me_2N)_3PSeI_2$ and $(Et_2N)_3PSeI_2$, the first crystallographically characterised charge-transfer complexes of tertiary phosphine selenides with diiodine

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The compounds Ph_3PSeI_2 , $(Me_2N)_3PSeI_2$ and $(Et_2N)_3PSeI_2$ have been prepared and characterised by $^{31}P\{-H\}$ NMR and infrared spectroscopy. Their single crystal structures have also been determined. Interesting variations in $d(P-Se)$ and $d(I-I)$ are noted upon changing R (Ph, Me_2N , Et_2N). The variation in $d(P-Se)$ for R_3PSeI_2 compared to the parent tertiary phosphine selenide is also discussed with respect to the degree of retention of phosphorus selenium double-bond character upon co-ordination of I_2 . The variations in $d(P-Se)$ and $d(I-I)$ are reflected in the infrared and $^{31}P\{-H\}$ NMR spectra of the R_3PSeI_2 compounds when compared to R_3PSe (R = Ph, Me_2N or Et_2N). The P–Se–I geometries for all three compounds are bent [Ph_3PSeI_2 , 106.0(1), $(Me_2N)_3PSeI_2$, 100.4(2) (average); $(Et_2N)_3PSeI_2$, 106.4(1)°] whereas the Se–I–I linkages are all essentially linear [173.69(6), 174.98(8) (average); 178.04(5)°]. These results are interpreted as a donation of electron density from the selenium atom to the σ^* -antibonding orbital of the diiodine.

The nature of the compounds formed between tertiary phosphine sulfides and selenides and dihalogens has received only limited study. Spectroscopic studies by Zingaro and Meyers^{1,2} concerning the reaction of Ph_3PSe with diiodine or iodine monobromide and that of R_3PS (R = Ph or C_6H_{11}) with iodine monobromide or monochloride all point to the formation of a stable 1 : 1 adduct of general formula R_3PEX_2 (R = Ph or C_6H_{11} ; E = S, X_2 = IBr or ICl; R = Ph, E = Se, X_2 = I_2 or IBr). However, the stoichiometric reaction of diiodine with triphenylphosphine sulfide produces the unexpected compound $2Ph_3PS \cdot 3I_2$.³ All reactions were performed in carbon tetrachloride solution. An X-ray crystallographic study³ of this molecule, the only reported crystallographic study of a compound formed from the interaction of R_3PE (E = S or Se) with dihalogens, revealed an interesting dimeric structure where two Ph_3PSI_2 moieties are linked into pairs by an I_2 molecule. The $d(I-I)$ for the I_2 is significantly lengthened [2.85(1) Å] compared to $d(I-I)$ in solid I_2 (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 $d(I-I)$ between the terminal iodide atoms on the Ph_3PSI_2 moieties and the diiodine molecule is 3.57(1) Å, constituting long but significant I–I interaction when compared with the I_2 van der Waals radius (4.3 Å). From this observation, and the fact that lengthening of the $d(I-I)$ for the diiodine molecule is observed, it would appear that the donor power of Ph_3PS towards diiodine is not sufficiently strong to form a stable 1 : 1 adduct and that a further Ph_3PS moiety and a diiodine molecule are required to produce a stable adduct.

Zingaro and Meyers¹ also studied the reaction of some R_3AsS compounds (R = Me, Et, Ph or C_6H_{11}) with diiodine, also in carbon tetrachloride solution, and found that in no case a 1 : 1 R_3AsSI_2 adduct could be isolated. Instead, arsenic–sulfur bond cleavage occurs to produce iodoarsonium triiodides $[R_3AsI]I_3$. No sulfur-containing products were isolated from the reaction, but it was assumed that precipitation of elemental sulfur occurred. There are no reports concerning the reaction of R_3PE (E = S or Se) compounds with the lighter halogens (F, Cl or Br).

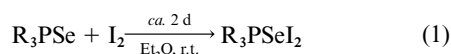
We are currently engaged in a study of the interaction of organo Group 15 and 16 donor atoms with dihalogens.^{4–11} We have found that the nature of the products formed is dependent

on three variables: the organo-substituents resident on the Group 15 or 16 donor atom, the donor atom itself, and the dihalogen employed. For example, triphenylarsine–diiodine is a molecular charge-transfer compound, $Ph_3As-I-I$, whereas triphenylarsine–dibromide is trigonal bipyramidal.⁸ On the other hand, trimethylarsine–dibromide also adopts the molecular four-co-ordinate charge-transfer structure $Me_3AsBr-Br$. Our studies on the analogous Group 16 systems, R_2SeX_2 , have shown that Me_2SeI_2 adopts a molecular three-co-ordinate charge-transfer structure, $Me_2Se-I-I$, whereas the adducts with the lighter halogens (Cl, Br) adopt a ψ -trigonal bipyramidal structure.¹¹ Finally, there is also evidence that the solvent of preparation for these compounds is of importance. We prepared a sample of Ph_3PI_2 and have shown, by $^{31}P\{-H\}$ solid-state magic angle spinning (MAS) NMR spectroscopy and single-crystal X-ray diffraction studies, that the compound exists as a molecular four-co-ordinate charge-transfer structure, Ph_3P-I-I .⁴ Conversely, Dillon and Waddington¹² prepared a sample of Ph_3PI_2 from the more polar nitrobenzene solution and showed, from solid-state $^{31}P\{-H\}$ NMR spectroscopy, that it possessed an ionic structure $[Ph_3P]I$, by comparison with $^{31}P\{-H\}$ NMR solution values in which the compound is known to adopt an ionic structure. Additionally, for the compounds R_3PI_2 , we have discovered a correlation between donor strength of the tertiary phosphine and iodine–iodine bond length, for example $d(I-I)$ for Ph_3PI_2 is 3.142(5) Å⁴ whereas with the more basic parent tertiary phosphine, $PhMe_2PI_2$, $d(I-I)$ is 3.408(2) Å.⁵ We were therefore interested structurally to characterise the products formed between tertiary phosphine selenides and diiodine for two reasons: first, possibly to verify the spectroscopic data of Zingaro and Meyers¹ and, secondly, to determine if changes in the R groups on a given R_3PSeI_2 compound appreciably affect $d(I-I)$, since, for these compounds, the R groups only have a secondary effect as they are not bound directly to the donor atom.

Results and Discussion

The three compounds R_3PSeI_2 (R = Ph, Me_2N or Et_2N) were prepared by the direct reaction at room temperature (r.t.) of the appropriate tertiary phosphine selenide with diiodine in diethyl

ether solution, equation (1). All compounds were isolated in



quantitative yield. In all cases, recrystallisation of the resultant red powders from diethyl ether–dichloromethane (1 : 1) solution at 50 °C produced a large quantity of dark red crystals on standing at room temperature for *ca.* 2 d. From these a crystal was chosen for analysis by single-crystal X-ray diffraction. The structures of Ph_3PSeI_2 , $(\text{Me}_2\text{N})_3\text{PSeI}_2$ and $(\text{Et}_2\text{N})_3\text{PSeI}_2$ are illustrated in Figs. 1, 2 and 3 respectively. Selected bond lengths and angles are given in Table 1. The compounds exist as a diiodine charge-transfer complex of the respective tertiary

Table 1 Selected bond lengths (Å) and angles (°) for R_3PSeI_2 (R = Ph, Me_2N or Et_2N)

Bond or angle	Ph_3PSeI_2	$(\text{Me}_2\text{N})_3\text{PSeI}_2^*$	$(\text{Et}_2\text{N})_3\text{PSeI}_2$
I–I	2.881(2)	2.959(2), 2.965(2)	2.985(2)
Se–I	2.803(3)	2.712(3), 2.724(2)	2.715(2)
Se–P	2.156(4)	2.185(7), 2.175(8)	2.203(3)
I–Se–P	106.0(1)	99.6(2), 101.2(2)	106.4(1)
I–I–Se	173.69(6)	177.33(8), 176.6(1)	178.04(5)
Se–P–C	113.6(5)	113.1(6), 111.9(9)	111.0(4)
or	113.4(4)	112.0(1), 109.4(7)	106.3(3)
Se–P–N	104.2(5)	107.4(1), 111.1(9)	111.8(4)

* Two molecules are present in the asymmetric unit, see Fig. 2

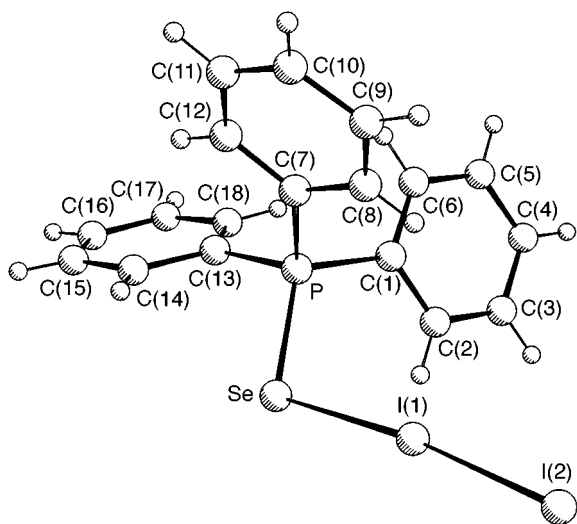


Fig. 1 Crystal structure of Ph_3PSeI_2

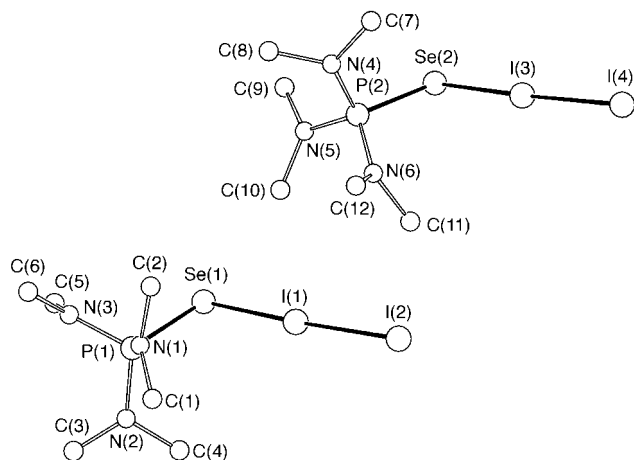


Fig. 2 Crystal structure of $(\text{Me}_2\text{N})_3\text{PSeI}_2$ (hydrogen atoms are omitted for clarity). There are two independent molecules in the asymmetric unit

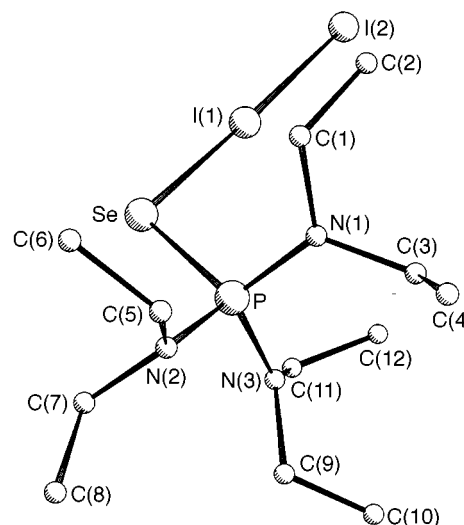


Fig. 3 Crystal structure of $(\text{Et}_2\text{N})_3\text{PSeI}_2$ (hydrogen atoms are omitted for clarity)

phosphine selenide and represent a further example of molecular ‘spoke’ structures first established by our group for triphenylphosphine–diiodine.⁴ The $d(\text{I}–\text{I})$ for R_3PSeI_2 are 2.881(2) (R = Ph), 2.959(2), 2.965(2) (R = Me_2N), 2.985(2) (R = Et_2N), significantly lengthened with respect to molecular iodine (2.71 Å) but considerably shorter than Ph_3PI_2 , 3.142(5) Å.⁴ These values are more similar to those of the analogous Group 16 compound $\text{Me}_2\text{SeI}–\text{I}$, 2.916(3) Å.¹¹ The P–Se–I bond angles are 106.0(1) (R = Ph), 99.6(2), 101.1(2) (R = Me_2N) and 106.4(1)° (R = Et_2N). The complexes R_3PSeI_2 may therefore be considered as donation of electron density from the selenium atoms to the σ^* -antibonding orbital of the respective diiodine molecules, illustrating approximately tetrahedral angles around the selenium atoms. The fact that the angles are rather less than the ideal tetrahedral angles is probably due to two factors, first the degree of retention of P–Se double-bond character, and secondly the fact that lone pairs on larger atoms tend to cause the angles between bonds to be appreciably smaller than the tetrahedral angle [valence shell electron pair repulsion (VESPR) model]. The Se–I–I linkages are essentially linear, 173.69(6) (R = Ph), 177.33(8), 176.6(1) (R = Me_2N), and 178.04(5) (R = Et_2N), in common with all crystallographically characterised charge-transfer complexes of diiodine. The P–Se bond in Ph_3PSeI_2 , 2.156(4) Å, is considerably lengthened with respect to free triphenylphosphine selenide [2.112(1) Å],¹³ as expected upon co-ordination of diiodine. However, it is interesting that it is intermediate between those of free Ph_3PSe and a typical P–Se single bond, *e.g.* as in P_4Se_3 [2.24(1) Å].¹⁴ Clearly the P–Se bond in Ph_3PSeI_2 retains considerable double-bond character. This phenomenon has previously been observed in the complex $\text{Ph}_3\text{PSe}·\text{AlCl}_3$ by Burford *et al.*¹⁵ which exhibits $d(\text{P}–\text{Se})$ of 2.181(2) Å. This is reflected in the infrared stretching frequency of the P=Se bond. The $\nu(\text{P}=\text{Se})$ for Ph_3PSe is 560 cm^{-1} , and falls to 540 cm^{-1} for the adduct Ph_3PSeI_2 , Table 2. A similar shift was observed by previous workers² for the compounds Ph_3PSe (560 cm^{-1}) and Ph_3PSeIBr (535 cm^{-1}). A comparison of the $^{31}\text{P}\{-\text{H}\}$ NMR spectra of free Ph_3PSe (δ 35.8) and Ph_3PSeI_2 (δ 31.1), reveals only a slight shift (4.7 ppm). This again supports the assertion that the charge-transfer complex Ph_3PSeI_2 contains significant P–Se double-bond character since the perturbation of the phosphorus atom in Ph_3PSe is relatively small upon co-ordination of diiodine. The crystal structure of Ph_3PSeI_2 therefore verifies the spectroscopic data of Zingaro and Meyers¹ and illustrates the greater donor power of Ph_3PSe towards diiodine compared to Ph_3PS , namely Ph_3PSe forms a stable 1 : 1 adduct with diiodine, whereas, for Ph_3PS , a stable adduct can only be formed with two triphenylphosphine sulfide–diiodine moieties and a supporting diiodine molecule.³

Table 2 Analytical and spectroscopic data for the compounds R₃PSe and R₃PSeI₂ (R = Ph, Me₂N or Et₂N)

Compound	Colour	M.p./°C	Analysis [Found (Calc.)] (%)				δ (³¹ P-{H}) ^a	ν (P=Se)/cm ⁻¹
			C	H	N	I		
Ph ₃ PSe ^b	White	188–189	—	—	—	—	35.8	560
Ph ₃ PSeI ₂	Red	139–141	36.1 (36.3)	2.6 (2.5)	—	—	42.3 (42.6)	31.1
(Me ₂ N) ₃ PSe	White	51–52	29.6 (29.8)	7.4 (7.4)	17.2 (17.4)	—	—	83.2
(Me ₂ N) ₃ PSeI ₂	Dark red	94–95 (decomp.)	14.5 (14.5)	3.6 (3.6)	8.4 (8.5)	51.2 (51.2)	—	66.7
(Et ₂ N) ₃ PSe	White	45–46	43.8 (44.1)	9.4 (9.2)	12.8 (12.9)	—	—	77.1 ^c
(Et ₂ N) ₃ PSeI ₂	Dark red	86–87 (decomp.)	24.6 (24.8)	4.9 (5.2)	7.0 (7.2)	43.9 (43.8)	—	60.1 ^d

^a All shifts were recorded relative to 85% concentrated phosphoric acid standard. ^b Commercially obtained product, used as received. ^c Peaks were also observed at δ 72.3 and 81.9 due to P–Se coupling, see text. ^d Peaks were also observed at δ 56.2 and 64.0 due to P–Se coupling, see text.

The d (I–I) for (Me₂N)₃PSeI₂, 2.959(2) and 2.965(2) Å (there are two molecules in the asymmetric unit), is significantly longer than that observed for Ph₃PSeI₂ (0.084 Å) thus illustrating that changing the R groups on R₃PSeI₂ compounds does affect the d (I–I), but the effect is more subtle when compared to R₃PI₂ compounds [d (I–I) for Ph₃PI₂ is 3.142(5)⁴ compared to 3.408(2) Å for PhMe₂PI₂,⁵ a difference of 0.266 Å]. This is as expected, since for R₃PSeI₂ compounds the R groups are not directly bound to the donor selenium atom and thus do not affect the donor power of the atom directly, but nevertheless illustrate a secondary effect. The P–Se bond lengths in (Me₂N)₃PSeI₂ are 2.185(7) and 2.175(8) Å, significantly lengthened when compared to the parent (Me₂N)₃PSe, 2.120(1) Å,¹⁵ as expected upon co-ordination of diiodine. The P–Se bond lengthening in (Me₂N)₃PSeI₂, 0.060(8) Å, is greater than that observed for Ph₃PSeI₂, 0.044(5) Å, suggesting greater perturbation on the P–Se double bond. Nevertheless, significant double-bond character is still retained in (Me₂N)₃PSeI₂ when d (P–Se) for this compound, 2.180(7) Å, is compared to a typical P–Se single bond [2.24(1) Å]. This is again reflected in the infrared stretching frequency of the P=Se bond. The ν (P=Se) for (Me₂N)₃PSe is 530 cm⁻¹ which falls to 507 cm⁻¹ for the adduct (Me₂N)₃PSeI₂, Table 2. There is greater variation in the ³¹P-{H} NMR spectra of the compounds (Me₂N)₃PSe (δ 83.2) and (Me₂N)₃PSeI₂ (δ 66.7), again suggesting that the perturbation of the phosphorus atom in (Me₂N)₃PSe upon co-ordination of diiodine is greater for (Me₂N)₃PSeI₂ than observed for Ph₃PSeI₂. Consequently, from X-ray crystallographic data and ³¹P-{H} NMR studies, greater P–Se double-bond character is observed for Ph₃PSeI₂ than for (Me₂N)₃PSeI₂. As a consequence, different d (I–I) are observed [2.881(2) and 2.962(2) Å (average), respectively].

As expected, (Et₂N)₃PSeI₂ also adopts the molecular ‘spoke’ structure (Et₂N)₃PSeI–I; d (I–I) is 2.985(2) Å, which does illustrate a slight but nevertheless significant lengthening of the I–I bond compared to (Me₂N)₃PSeI₂ [d (I–I) 2.959(2) and 2.965(2) Å]. Therefore, an average increase in d (I–I) of 0.023(2) Å is observed when changing the R groups in R₃PSeI₂ from Me₂N to Et₂N. Although this increase is small, as expected, it illustrates the sensitivity of the d (I–I) to even small changes in R for the compounds R₃PSeI₂. The d (P–Se) for (Et₂N)₃PSeI₂, 2.203(3) Å, is similar to that of (Me₂N)₃PSeI₂ [2.180(8) Å (average)] but cannot be compared to that of the parent tertiary phosphine selenide (Et₂N)₃PSe since this compound has not been crystallographically characterised. Again, a similar shift in the ν (P=Se) in the infrared spectrum is observed for (Et₂N)₃PSe (553 cm⁻¹) upon co-ordination of diiodine (530 cm⁻¹), Table 2. Shifts in the ³¹P-{H} NMR spectrum for (Et₂N)₃PSe and (Et₂N)₃PSeI₂ (δ 77.1 and 60.1, respectively) and (Me₂N)₃PSe and (Me₂N)₃PSeI₂ (δ 83.2 and 66.7, respectively) are very similar (shifts of 17.0 and 16.5 ppm, respectively, upon diiodine co-ordination), Table 2. The ³¹P-{H} NMR spectra of (Et₂N)₃PSe and (Et₂N)₃PSeI₂ also exhibit peaks due to P–Se coupling, which are rather difficult unequivocally to assign for the corresponding methyl derivatives which are rather less soluble in CDCl₃. The com-

pound (Et₂N)₃PSe exhibits two small peaks (*ca.* 4% compared to the central phosphorus resonance) at δ 72.3 and 81.9, giving a coupling constant J (⁷⁷Se–P) of 794 Hz. This coupling constant shifts to a lower value upon co-ordination of diiodine [(Et₂N)₃PSeI₂ exhibits two small peaks at δ 56.2 and 64.0, J (⁷⁷Se–P) = 632 Hz].

Conclusion

A single-crystal determination of Ph₃PSeI₂ illustrates a molecular charge-transfer structure, Ph₃PSeI–I, and thus confirms the conclusions of Zingaro and Meyers,¹ from their earlier spectroscopic studies. The compounds R₃PSeI₂ (R = Me₂N or Et₂N) have not previously been reported, but, in agreement with Ph₃PSeI₂, they also adopt a molecular charge-transfer structure. There is significant variation in d (I–I) upon variation in R, that for Ph₃PSeI₂, 2.881(2) Å, being significantly shorter than for (Me₂N)₃PSeI₂, 2.962(2) Å (average), illustrating that the donor power of the selenium atom towards diiodine for R₃PSeI₂ compounds is sensitive to R. Perhaps surprisingly, there is even a significant difference in d (I–I) for the compounds (Me₂N)₃PSeI₂ and (Et₂N)₃PSeI₂ [2.962(2) (average) and 2.985(2) Å, respectively]. This clearly shows that even subtle changes in R for R₃PSeI₂ compounds have an effect on d (I–I) despite the fact that the R groups are not bound directly to the donor atom. Significant lengthening of the P=Se bond is also observed for the compounds R₃PSeI₂ (R = Ph, Me₂N or Et₂N) compared to the parent tertiary phosphine selenide, as expected upon co-ordination of diiodine. In all cases however, some retention of phosphorus–selenium double-bond character is retained when compared to a typical P–Se single bond.¹⁴ In agreement with previous work,^{1,2} this may also be deduced from a comparison of the infrared spectra of the R₃PSeI₂ compounds and their parent tertiary phosphine selenides, the ν (P=Se) band being shifted *ca.* 20 cm⁻¹ downfield upon co-ordination of diiodine. The compounds R₃PSeI₂ (R = Ph, Me₂N or Et₂N) represent the first examples of tertiary phosphine selenide dihalides to be crystallographically characterised and the d (I–I) dependency on R is in agreement with our previous observations on R₃PI₂ compounds, although, as expected, the effect on d (I–I) is more subtle for R₃PSeI₂ compounds as the R groups are not bound directly to the donor atom. No R₃PSeI₂ compound has previously been the subject of a ³¹P-{H} NMR study. For all the compounds a decrease in ³¹P-{H} NMR resonance is seen compared to that of the parent tertiary phosphine selenide, as expected since electron density is removed from the selenium atom upon co-ordination of diiodine.

Experimental

The R₃PSeI₂ compounds (R = Ph, Me₂N or Et₂N) described were prepared from direct reaction of the appropriate tertiary phosphine selenide with diiodine under strictly anaerobic and anhydrous conditions. However, it was later noted that the products formed were air and moisture stable and therefore it

Table 3 Crystal data and details of refinement for R₃PSeI₂ (R = Ph, Me₂N or Et₂N)

	Ph ₃ PSeI ₂	(Me ₂ N) ₃ PSeI ₂	(Et ₂ N) ₃ PSeI ₂
Formula	C ₁₈ H ₁₅ I ₂ PSe	C ₆ H ₁₈ I ₂ N ₃ PSe	C ₁₂ H ₃₀ I ₂ N ₃ PSe
<i>M</i>	595.06	495.96	580.13
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2₁/n</i> (no. 14)	<i>Pbca</i> (no. 61)	<i>P2₁2₁2₁</i> (no. 19)
<i>a</i> /Å	12.563(7)	15.136(3)	12.664(5)
<i>b</i> /Å	9.483(4)	17.779(3)	18.476(5)
<i>c</i> /Å	16.161(4)	22.738(5)	8.727(4)
β/°	97.64(7)	—	—
<i>U</i> /Å ³	1908(3)	6119(2)	2042(2)
<i>Z</i>	4	16	4
<i>D_c</i> /g cm ⁻³	2.071	2.153	1.887
<i>F</i> (000)	1112	3680	1112
μ/cm ⁻¹	52.28	65.68	48.85
Crystal size/mm	0.25 × 0.25 × 0.10	0.20 × 0.20 × 0.20	0.30 × 0.25 × 0.10
Maximum 2θ/°	50.1	50.0	50.0
Maximum, minimum transitions	1.00, 0.64	1.00, 0.70	1.00, 0.46
Total data measured	3769	5355	1872
No. unique reflections	3596	5355	1870
No. observed reflections [<i>I</i> > 3.00σ(<i>I</i>)]	1786	5343	1171
No. parameters	199	236	172
Minimum, maximum residual electron density/e Å ⁻³	-1.07, 0.81	-0.68, 0.78	-0.47, 0.40
Maximum least-squares shift-to-error ratio	0.15	<0.01	<0.01
Weighting scheme parameter <i>g</i> in <i>w</i> = 1/[σ ² (<i>F</i>) + <i>g</i> (<i>F</i>) ²]	0.02	0.01	0.03
<i>R</i>	0.046	0.067	0.031
<i>R</i> '	0.055	0.060	0.033

was decided to reprepare them without taking precautions to exclude air and moisture. The same products were obtained by both experimental procedures, thus demonstrating that the exclusion of air and moisture is not necessary. Triphenylphosphine selenide was obtained commercially (Lancaster) and used as received. Tris(dimethylamino)phosphine selenide was simply prepared from the direct stoichiometric reaction of tris(dimethylamino)phosphine (Aldrich) with elemental selenium in diethyl ether solution. The crude (Me₂N)₃PSe was recrystallised from diethyl ether to produce the analytically pure product; (Et₂N)₃PSe was prepared in an identical manner from commercially obtained tris(diethylamino)phosphine (Lancaster) and elemental selenium. Diiodine was obtained commercially (Aldrich) and used as received. Elemental analyses were performed by the analytical laboratory of this department, see Table 2. Infrared spectra were recorded on a Nicolet 5PC Fourier-transform spectrometer, ³¹P-{¹H} NMR spectra on a Bruker AC200 spectrometer (shifts were relative to 85% phosphoric acid standard).

Crystallography

Crystals of all three compounds were independently mounted in Lindemann tubes under an atmosphere of dry argon. Measurements were performed at 298 K on a Rigaku AFC6S [Ph₃PSeI₂ and (Et₂N)₃PSeI₂] or a Nonius Cad4 Mac 3 [(Me₂N)₃PSeI₂] diffractometer. Both diffractometers employing graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scans. The structures were solved by direct methods.¹⁶ Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. An adsorption correction was applied in each case using the azimuthal scan technique. Details of the X-ray measurements and subsequent structure determinations are presented in Table 3. Hydrogen atoms were confined to chemically reasonable positions. Neutral scattering factors were taken from ref. 17(a). Anomalous dispersion effects were taken from ref. 17(b). All calculations were performed using the TEXSAN¹⁸ crystallographic software package.

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References

- R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, 1962, **4**, 771.
- R. A. Zingaro, *Inorg. Chem.*, 1963, **5**, 192.
- W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, 1968, **5**, 1561.
- S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.
- N. Bricklebank, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 2421.
- N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.
- N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 2261.
- N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 3873.
- N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1994, 1759.
- S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1996, 2521.
- S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 1031.
- K. B. Dillon and T. C. Waddington, *Nature (London), Phys. Sci.*, 1971, **230**, 158.
- P. G. Jones, C. Kienitz and C. Thone, *Z. Kristallogr.*, 1994, **80**, 209.
- E. Keulen and A. Vos, *Acta Crystallogr.*, 1959, **12**, 323.
- N. Burford, B. W. Royan, R. E. H. Spence and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 2111.
- G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, Oxford University Press, 1985, p. 175.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (a) Table 2.2A, (b) Table 2.3.1.
- TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

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