

# 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  $\sigma^*$ -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<sup>1,2</sup> 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  $2Ph_3PS \cdot 3I_2$ .<sup>3</sup> All reactions were performed in carbon tetrachloride solution. An X-ray crystallographic study<sup>3</sup> 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  $\sigma^*$ -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 Meyers<sup>1</sup> 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).

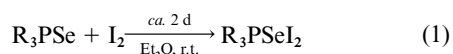
We are currently engaged in a study of the interaction of organo Group 15 and 16 donor atoms with dihalogens.<sup>4–11</sup> We have found that the nature of the products formed is dependent

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.<sup>8</sup> 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  $\psi$ -trigonal bipyramidal structure.<sup>11</sup> 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,  $Ph_3P-I-I$ .<sup>4</sup> Conversely, Dillon and Waddington<sup>12</sup> 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) Å<sup>4</sup> whereas with the more basic parent tertiary phosphine,  $PhMe_2PI_2$ ,  $d(I-I)$  is 3.408(2) Å.<sup>5</sup> 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 Meyers<sup>1</sup> 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

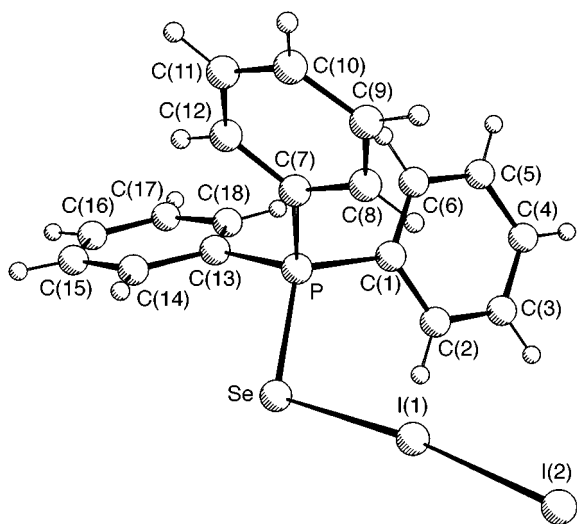


quantitative yield. In all cases, recrystallisation of the resultant red powders from diethyl ether–dichloromethane (1 : 1) solution at 50 °C produced a large quantity of dark red crystals on standing at room temperature for *ca.* 2 d. From these a crystal was chosen for analysis by single-crystal X-ray diffraction. The structures of  $\text{Ph}_3\text{PSeI}_2$ ,  $(\text{Me}_2\text{N})_3\text{PSeI}_2$  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

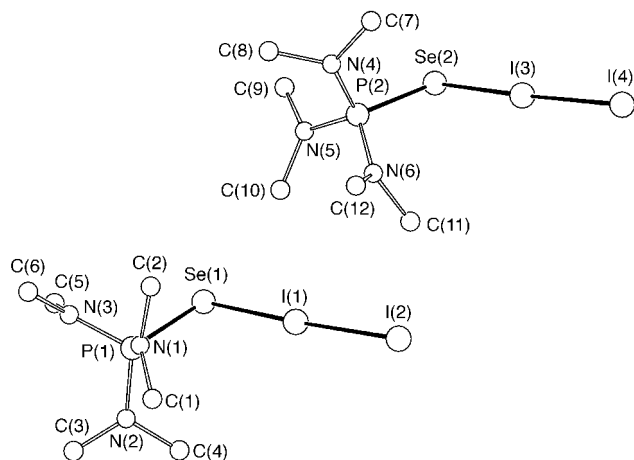
**Table 1** Selected bond lengths (Å) and angles (°) for  $\text{R}_3\text{PSeI}_2$  (R = Ph,  $\text{Me}_2\text{N}$  or  $\text{Et}_2\text{N}$ )

Bond or angle	$\text{Ph}_3\text{PSeI}_2$	$(\text{Me}_2\text{N})_3\text{PSeI}_2^*$	$(\text{Et}_2\text{N})_3\text{PSeI}_2$
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

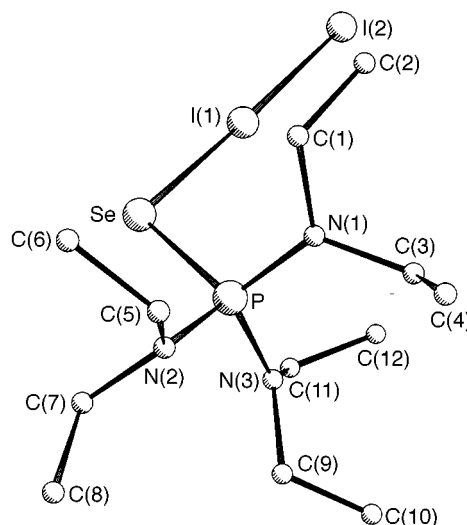


**Fig. 1** Crystal structure of  $\text{Ph}_3\text{PSeI}_2$



**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

phosphine selenide and represent a further example of molecular ‘spoke’ structures first established by our group for triphenylphosphine–diiodine.<sup>4</sup> The  $d(\text{I}–\text{I})$  for  $\text{R}_3\text{PSeI}_2$  are 2.881(2) (R = Ph), 2.959(2), 2.965(2) (R =  $\text{Me}_2\text{N}$ ), 2.985(2) (R =  $\text{Et}_2\text{N}$ ), significantly lengthened with respect to molecular iodine (2.71 Å) but considerably shorter than  $\text{Ph}_3\text{PI}_2$ , 3.142(5) Å.<sup>4</sup> These values are more similar to those of the analogous Group 16 compound  $\text{Me}_2\text{SeI}–\text{I}$ , 2.916(3) Å.<sup>11</sup> The P–Se–I bond angles are 106.0(1) (R = Ph), 99.6(2), 101.1(2) (R =  $\text{Me}_2\text{N}$ ) and 106.4(1)° (R =  $\text{Et}_2\text{N}$ ). The complexes  $\text{R}_3\text{PSeI}_2$  may therefore be considered as donation of electron density from the selenium atoms to the  $\sigma^*$ -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 (VSEPR) model]. The Se–I–I linkages are essentially linear, 173.69(6) (R = Ph), 177.33(8), 176.6(1) (R =  $\text{Me}_2\text{N}$ ), and 178.04(5) (R =  $\text{Et}_2\text{N}$ ), in common with all crystallographically characterised charge-transfer complexes of diiodine. The P–Se bond in  $\text{Ph}_3\text{PSeI}_2$ , 2.156(4) Å, is considerably lengthened with respect to free triphenylphosphine selenide [2.112(1) Å],<sup>13</sup> as expected upon co-ordination of diiodine. However, it is interesting that it is intermediate between those of free  $\text{Ph}_3\text{PSe}$  and a typical P–Se single bond, *e.g.* as in  $\text{P}_4\text{Se}_3$  [2.24(1) Å].<sup>14</sup> Clearly the P–Se bond in  $\text{Ph}_3\text{PSeI}_2$  retains considerable double-bond character. This phenomenon has previously been observed in the complex  $\text{Ph}_3\text{PSe} \cdot \text{AlCl}_3$  by Burford *et al.*<sup>15</sup> 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  $\text{Ph}_3\text{PSe}$  is 560  $\text{cm}^{-1}$ , and falls to 540  $\text{cm}^{-1}$  for the adduct  $\text{Ph}_3\text{PSeI}_2$ , Table 2. A similar shift was observed by previous workers<sup>2</sup> for the compounds  $\text{Ph}_3\text{PSe}$  (560  $\text{cm}^{-1}$ ) and  $\text{Ph}_3\text{PSeI}–\text{Br}$  (535  $\text{cm}^{-1}$ ). A comparison of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of free  $\text{Ph}_3\text{PSe}$  ( $\delta$  35.8) and  $\text{Ph}_3\text{PSeI}_2$  ( $\delta$  31.1), reveals only a slight shift (4.7 ppm). This again supports the assertion that the charge-transfer complex  $\text{Ph}_3\text{PSeI}_2$  contains significant P–Se double-bond character since the perturbation of the phosphorus atom in  $\text{Ph}_3\text{PSe}$  is relatively small upon co-ordination of diiodine. The crystal structure of  $\text{Ph}_3\text{PSeI}_2$  therefore verifies the spectroscopic data of Zingaro and Meyers<sup>1</sup> and illustrates the greater donor power of  $\text{Ph}_3\text{PSe}$  towards diiodine compared to  $\text{Ph}_3\text{PS}$ , namely  $\text{Ph}_3\text{PSe}$  forms a stable 1 : 1 adduct with diiodine, whereas, for  $\text{Ph}_3\text{PS}$ , a stable adduct can only be formed with two triphenylphosphine sulfide–diiodine moieties and a supporting diiodine molecule.<sup>3</sup>



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

**Table 2** Analytical and spectroscopic data for the compounds R<sub>3</sub>PSe and R<sub>3</sub>PSeI<sub>2</sub> (R = Ph, Me<sub>2</sub>N or Et<sub>2</sub>N)

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

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

The  $d$ (I–I) for (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>, 2.959(2) and 2.965(2) Å (there are two molecules in the asymmetric unit), is significantly longer than that observed for Ph<sub>3</sub>PSeI<sub>2</sub> (0.084 Å) thus illustrating that changing the R groups on R<sub>3</sub>PSeI<sub>2</sub> compounds does affect the  $d$ (I–I), but the effect is more subtle when compared to R<sub>3</sub>PI<sub>2</sub> compounds [ $d$ (I–I) for Ph<sub>3</sub>PI<sub>2</sub> is 3.142(5)<sup>4</sup> compared to 3.408(2) Å for PhMe<sub>2</sub>PI<sub>2</sub>,<sup>5</sup> a difference of 0.266 Å]. This is as expected, since for R<sub>3</sub>PSeI<sub>2</sub> 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 (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> are 2.185(7) and 2.175(8) Å, significantly lengthened when compared to the parent (Me<sub>2</sub>N)<sub>3</sub>PSe, 2.120(1) Å,<sup>15</sup> as expected upon co-ordination of diiodine. The P–Se bond lengthening in (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>, 0.060(8) Å, is greater than that observed for Ph<sub>3</sub>PSeI<sub>2</sub>, 0.044(5) Å, suggesting greater perturbation on the P–Se double bond. Nevertheless, significant double-bond character is still retained in (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> 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  $\nu$ (P=Se) for (Me<sub>2</sub>N)<sub>3</sub>PSe is 530 cm<sup>-1</sup> which falls to 507 cm<sup>-1</sup> for the adduct (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>, Table 2. There is greater variation in the <sup>31</sup>P-{H} NMR spectra of the compounds (Me<sub>2</sub>N)<sub>3</sub>PSe ( $\delta$  83.2) and (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> ( $\delta$  66.7), again suggesting that the perturbation of the phosphorus atom in (Me<sub>2</sub>N)<sub>3</sub>PSe upon co-ordination of diiodine is greater for (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> than observed for Ph<sub>3</sub>PSeI<sub>2</sub>. Consequently, from X-ray crystallographic data and <sup>31</sup>P-{H} NMR studies, greater P–Se double-bond character is observed for Ph<sub>3</sub>PSeI<sub>2</sub> than for (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>. As a consequence, different  $d$ (I–I) are observed [2.881(2) and 2.962(2) Å (average), respectively].

As expected, (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> also adopts the molecular ‘spoke’ structure (Et<sub>2</sub>N)<sub>3</sub>PSeI–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 (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> [ $d$ (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 R<sub>3</sub>PSeI<sub>2</sub> from Me<sub>2</sub>N to Et<sub>2</sub>N. 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 R<sub>3</sub>PSeI<sub>2</sub>. The  $d$ (P–Se) for (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>, 2.203(3) Å, is similar to that of (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> [2.180(8) Å (average)] but cannot be compared to that of the parent tertiary phosphine selenide (Et<sub>2</sub>N)<sub>3</sub>PSe since this compound has not been crystallographically characterised. Again, a similar shift in the  $\nu$ (P=Se) in the infrared spectrum is observed for (Et<sub>2</sub>N)<sub>3</sub>PSe (553 cm<sup>-1</sup>) upon co-ordination of diiodine (530 cm<sup>-1</sup>), Table 2. Shifts in the <sup>31</sup>P-{H} NMR spectrum for (Et<sub>2</sub>N)<sub>3</sub>PSe and (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> ( $\delta$  77.1 and 60.1, respectively) and (Me<sub>2</sub>N)<sub>3</sub>PSe and (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> ( $\delta$  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 <sup>31</sup>P-{H} NMR spectra of (Et<sub>2</sub>N)<sub>3</sub>PSe and (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> 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 CDCl<sub>3</sub>. The com-

pound (Et<sub>2</sub>N)<sub>3</sub>PSe exhibits two small peaks (*ca.* 4% compared to the central phosphorus resonance) at  $\delta$  72.3 and 81.9, giving a coupling constant  $J$ (<sup>77</sup>Se–P) of 794 Hz. This coupling constant shifts to a lower value upon co-ordination of diiodine [(Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> exhibits two small peaks at  $\delta$  56.2 and 64.0,  $J$ (<sup>77</sup>Se–P) = 632 Hz].

## Conclusion

A single-crystal determination of Ph<sub>3</sub>PSeI<sub>2</sub> illustrates a molecular charge-transfer structure, Ph<sub>3</sub>PSeI–I, and thus confirms the conclusions of Zingaro and Meyers,<sup>1</sup> from their earlier spectroscopic studies. The compounds R<sub>3</sub>PSeI<sub>2</sub> (R = Me<sub>2</sub>N or Et<sub>2</sub>N) have not previously been reported, but, in agreement with Ph<sub>3</sub>PSeI<sub>2</sub>, they also adopt a molecular charge-transfer structure. There is significant variation in  $d$ (I–I) upon variation in R, that for Ph<sub>3</sub>PSeI<sub>2</sub>, 2.881(2) Å, being significantly shorter than for (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>, 2.962(2) Å (average), illustrating that the donor power of the selenium atom towards diiodine for R<sub>3</sub>PSeI<sub>2</sub> compounds is sensitive to R. Perhaps surprisingly, there is even a significant difference in  $d$ (I–I) for the compounds (Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> and (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub> [2.962(2) (average) and 2.985(2) Å, respectively]. This clearly shows that even subtle changes in R for R<sub>3</sub>PSeI<sub>2</sub> 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 R<sub>3</sub>PSeI<sub>2</sub> (R = Ph, Me<sub>2</sub>N or Et<sub>2</sub>N) 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.<sup>14</sup> In agreement with previous work,<sup>1,2</sup> this may also be deduced from a comparison of the infrared spectra of the R<sub>3</sub>PSeI<sub>2</sub> compounds and their parent tertiary phosphine selenides, the  $\nu$ (P=Se) band being shifted *ca.* 20 cm<sup>-1</sup> downfield upon co-ordination of diiodine. The compounds R<sub>3</sub>PSeI<sub>2</sub> (R = Ph, Me<sub>2</sub>N or Et<sub>2</sub>N) 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 R<sub>3</sub>PI<sub>2</sub> compounds, although, as expected, the effect on  $d$ (I–I) is more subtle for R<sub>3</sub>PSeI<sub>2</sub> compounds as the R groups are not bound directly to the donor atom. No R<sub>3</sub>PSeI<sub>2</sub> compound has previously been the subject of a <sup>31</sup>P-{H} NMR study. For all the compounds a decrease in <sup>31</sup>P-{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 R<sub>3</sub>PSeI<sub>2</sub> compounds (R = Ph, Me<sub>2</sub>N or Et<sub>2</sub>N) 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 R<sub>3</sub>PSeI<sub>2</sub> (R = Ph, Me<sub>2</sub>N or Et<sub>2</sub>N)

	Ph <sub>3</sub> PSeI <sub>2</sub>	(Me <sub>2</sub> N) <sub>3</sub> PSeI <sub>2</sub>	(Et <sub>2</sub> N) <sub>3</sub> PSeI <sub>2</sub>
Formula	C <sub>18</sub> H <sub>15</sub> I <sub>2</sub> PSe	C <sub>6</sub> H <sub>18</sub> I <sub>2</sub> N <sub>3</sub> PSe	C <sub>12</sub> H <sub>30</sub> I <sub>2</sub> N <sub>3</sub> PSe
<i>M</i>	595.06	495.96	580.13
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2<sub>1</sub>/n</i> (no. 14)	<i>Pbca</i> (no. 61)	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></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 <sup>3</sup>	1908(3)	6119(2)	2042(2)
<i>Z</i>	4	16	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	2.071	2.153	1.887
<i>F</i> (000)	1112	3680	1112
μ/cm <sup>-1</sup>	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 <sup>-3</sup>	-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 <sup>2</sup> ( <i>F</i> ) + <i>g</i> ( <i>F</i> ) <sup>2</sup> ]	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 (Me<sub>2</sub>N)<sub>3</sub>PSe was recrystallised from diethyl ether to produce the analytically pure product; (Et<sub>2</sub>N)<sub>3</sub>PSe 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, <sup>31</sup>P-{<sup>1</sup>H} 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 [Ph<sub>3</sub>PSeI<sub>2</sub> and (Et<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>] or a Nonius Cad4 Mac 3 [(Me<sub>2</sub>N)<sub>3</sub>PSeI<sub>2</sub>] 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.<sup>16</sup> 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 TEXSAN<sup>18</sup> crystallographic software package.

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