DALTON
FULL PAPER

Crystal structure of triphenylphosphine sulfide diiodine; the first crystallographically characterised 1 : 1 molecular charge-transfer complex of a tertiary phosphine sulfide with diiodine

David C. Apperley,[a] **Neil Bricklebank,***[†,b] **Sally L. Burns,**[b] **David E. Hibbs,**[c] **Michael B. Hursthouse**[c] **and K. M. Abdul Malik**[c]

[a] *Industrial Research Laboratories, University of Durham, Durham, UK DH1 3LE*
[b] *Division of Chemistry, Sheffield Hallam University, Sheffield, UK S1 1WB*
[c] *Department of Chemistry, University of Wales Cardiff, Cardiff, Park Place, PO Box 912, Cardiff, UK CF1 3TB*

In CH_2Cl_2 solution, Ph_3PS and diiodine react to form a molecular 1 : 1 charge-transfer complex. The complex has been studied in solution using ^{31}P-{H} NMR and UV/VIS spectroscopy. Single-crystal X-ray diffraction and solid-state ^{31}P-{H} NMR studies of $Ph_3PS\cdot I_2$ show that the molecular structure is maintained in the solid phase. The structure of $Ph_3PS\cdot I_2$ is novel and contradicts previous results which indicated that a 1 : 1 ($Ph_3PS : I_2$) complex could not be isolated in the solid state. The I–I distance [2.823(1) Å] and the S–I distance [2.753(2) Å] in $Ph_3PS\cdot I_2$ are comparable with those in charge-transfer complexes of related sulfur donors. However, the I–I distance in $Ph_3PS\cdot I_2$ is shorter than that in $Ph_3PSe\cdot I_2$ reflecting the weaker donor power of the Ph_3PS towards diiodine. The NMR spectroscopic results on $Ph_3PS\cdot I_2$ and the analogous Ph_3PO and Ph_3PSe compounds indicate that the stability of the $Ph_3PE\cdot I_2$ complexes increases in the order E = Se > S ⩾ O.

During the past decade there has been renewed interest in the structures, properties and reactions of dihalogen derivatives of organo Group 15[1,2] and 16[3–5] donors. These studies have identified several different structural archetypes and have established a general pattern of reactivity which is dependent not only on the dihalogen and the basicity of the donor, but also on the reaction solvent.

Dihalogen complexes of tertiary phosphine chalcogenides were first reported in the early 1960's by Zingaro and co-workers,[6–10] who characterised the compounds using IR and UV/VIS spectroscopy. Zingaro's studies showed that all R_3PE (R = alkyl or aryl) compounds except Ph_3PS form 1 : 1 adducts with I_2, IBr and ICl, in both the solid state and in CCl_4 solution.[6–10] Triphenylphosphine sulfide formed 1 : 1 complexes with these dihalogens in solution, but in the solid state the complex with diiodine was found to have an unusual 2 : 3 ($Ph_3PS : I_2$) stoichiometry. Zingaro and co-workers were unable to isolate a 1 : 1 complex between Ph_3PS and I_2 in the solid state, despite the fact that the adduct could be identified in solution.[7] The structure of $2Ph_3PS\cdot 3I_2$ has been determined[11] and represents the only structural data for a tertiary phosphine sulfide dihalogen complex. The structure (Fig. 1) consists of two Ph_3PS–I–I units linked by a third molecule of diiodine which is coplanar and collinear with the terminal iodine atoms of the Ph_3PS–I–I molecules.[11] The structure of $2Ph_3PS\cdot 3I_2$ has been investigated using ^{129}I Mössbauer spectroscopy which indicated that the iodine bonds were polarised: $Ph_3PS–I^{\delta+}\cdots I^{\delta-}\cdots I–I\cdots I^{\delta-}\cdots I^{\delta+}–SPPh_3$.[12]

The nature of Ph_3PS–diiodine interaction in CCl_4 solution was re-examined by Sobczky and co-workers[13] who observed the formation of a 1 : 1 charge-transfer complex. However, Kaur and Lobana[14] reported that Ph_3PS formed a 2 : 3 ($Ph_3PS : I_2$) complex in CCl_4 and a 1 : 1 complex in CH_2Cl_2. The diphosphine sulfide $Ph_2P(S)CH_2P(S)Ph_2$ gave similar results, whereas (p-$CH_3C_6H_4)_3PS$ formed a 1 : 1 [(p-$CH_3C_6H_4)_3PS : I_2$] complex in both solvents. These differences were attributed to the differing basicities of the donors.[14]

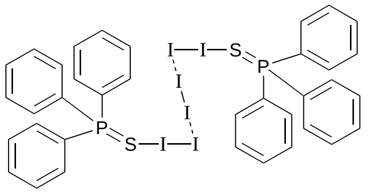

Fig. 1 Structure of $2Ph_3PS\cdot 3I_2$

More recently, structural data have been reported for a number of tertiary phosphine selenide diiodine complexes. Rudd *et al.*[15] have studied the structures of the tetraiodo complexes, R_3PSeI_4 (R = morpholino or Me_2N), which are ionic $[R_3PSeI]I_3$. In contrast, Godfrey *et al.*[16] have characterised the 1 : 1 complexes, $Ph_3PSe\cdot I_2$, $(Me_2N)_3PSe\cdot I_2$ and $(Et_2N)_3PSe\cdot I_2$, all of which adopt molecular charge-transfer type structures.

The apparent inability of Ph_3PS to form a 1:1 complex with diiodine seemed somewhat anomalous and has prompted us to reinvestigate the interaction of tertiary phosphine chalcogenides and diiodine. Herein we describe the synthesis and solid-state structure of the elusive $Ph_3PS\cdot I_2$.

Results and Discussion

A compound of stoichiometry $Ph_3PS\cdot I_2$ was prepared by the direct reaction of equimolar quantities of triphenylphosphine sulfide and diiodine in dichloromethane. The UV/VIS spectrum of the resulting brown solution showed a single band at 436 nm, which corresponds to the blue shifted diiodine absorption in the 1 : 1 charge-transfer complex. This result is in good agreement with those obtained by previous workers.[10,13,14] The solvent was then allowed to evaporate slowly producing a crop of large, red-brown crystals in quantitative yield. Single-crystal X-ray analysis of one of these crystals revealed that the compound has a molecular charge-transfer type structure.

We have also attempted to prepare the analogous Ph_3PSe and Ph_3PO compounds in CH_2Cl_2. The adduct $Ph_3PSe\cdot I_2$ forms as large red-brown crystals, whose structure is identical to that reported recently for this compound by Godfrey *et al.* who prepared their $Ph_3PSe\cdot I_2$ in diethyl ether.[16] This shows that for this

---

[†] E-Mail: N.Bricklebank@SHU.ac.uk

Table 1 Selected bond lengths (Å) and angles (°) in $Ph_3PS{\cdot}I_2$ and a comparison with the equivalent distances and angles in $2Ph_3PS{\cdot}3I_2$[11] and $Ph_3PSe{\cdot}I_2$[16]

	$Ph_3PS{\cdot}I_2$	$2Ph_3PS{\cdot}3I_2$	$Ph_3PSe{\cdot}I_2$
P–E	1.998(2)	2.007(3)	2.156(4)
E–I(1)	2.753(2)	2.729(2)	2.803(3)
I(1)–I(2)	2.8230(11)	2.838(1)	2.881(3)
E–I(1)–I(2)	175.51(3)	175.23(5)	173.69(6)
P–E–I(1)	108.78(7)	107.6(1)	106.0(1)
C(1)–P–E	113.2(2)	112.0(3)	113.6(5)
C(7)–P–E	105.5(2)	106.1(2)	104.2(5)
C(13)–P–E	114.5(2)	113.7(2)	113.4(4)

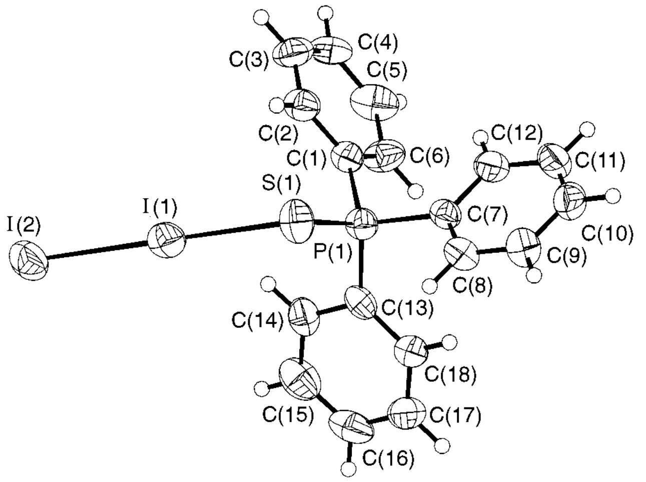

Fig. 2 X-Ray structure of $Ph_3PS{\cdot}I_2$

Table 2 NMR data for $Ph_3PO{\cdot}I_2$, $Ph_3PS{\cdot}I_2$ and $Ph_3PSe{\cdot}I_2$

	δP(ppm)[b]	
Compound[a]	Solution	Solid state
Ph_3PO	29.61	28.99
$Ph_3PO{\cdot}I_2$	30.20	31.20
Ph_3PS	43.36	46.37
$Ph_3PS{\cdot}I_2$	41.70	39.74
Ph_3PSe	35.36 (728)	37.91 (737)
$Ph_3PSe{\cdot}I_2$	30.60 (645)	26.06 (623)

[a] Data for Ph_3PO, Ph_3PS and Ph_3PSe from ref. 20. [b] All $^{31}P\text{-}\{^1H\}$ NMR data are referenced to external 85% H_3PO_4. Values in brackets correspond to $^1J(^{31}P\text{–}^{77}Se)$ Hz.

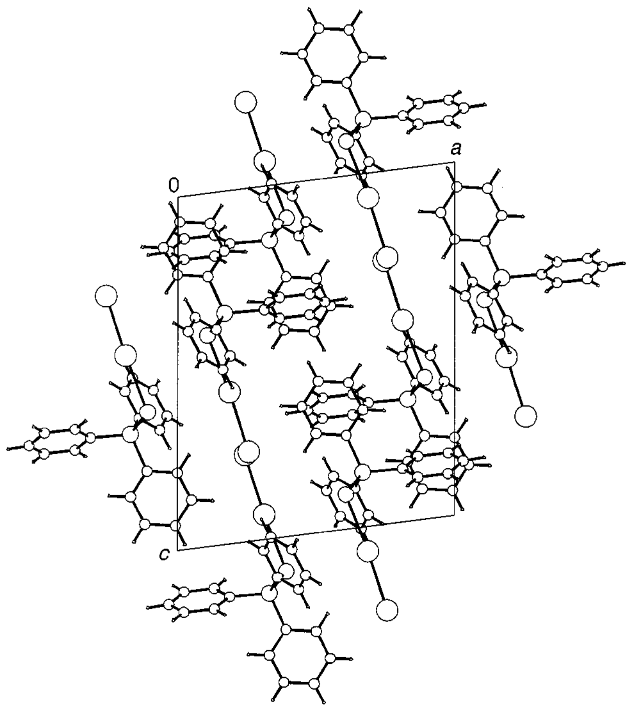

Fig. 3 Molecular packing in $Ph_3PS{\cdot}I_2$, viewed along *b*

compound at least the structure adopted is independent of the reaction solvent. In contrast, $Ph_3PO{\cdot}I_2$ formed as a brown microcrystalline solid which readily lost diiodine, suggesting that in this compound the diiodine is only very weakly bound.

The structure of $Ph_3PS{\cdot}I_2$ is illustrated in Fig. 2. Selected bond lengths and angles are listed in Table 1 together with the equivalent lengths and angles in $2Ph_3PS{\cdot}3I_2$ and $Ph_3PSe{\cdot}I_2$ for comparative purposes. The I–I bond in $Ph_3PS{\cdot}I_2$ [2.8230(11) Å] is shorter and the S–I bond [2.753(2) Å] longer than those in $2Ph_3PS{\cdot}3I_2$ [$d_{I\text{–}I}$, 2.838(1) Å; $d_{S\text{–}I}$, 2.729(2) Å].[11] These differences are directly attributable to greater polarization of the S–I–I bonds in $2Ph_3PS{\cdot}3I_2$, which results from the interaction of this group with a second molecule of diiodine (Fig. 1).[11] The P=S distances in $Ph_3PS{\cdot}I_2$ and $2Ph_3PS{\cdot}3I_2$ [$d_{P=S}$: $Ph_3PS{\cdot}I_2$, 1.998(2) Å; $2Ph_3PS{\cdot}3I_2$, 2.007(3) Å[11]] are almost identical and both are lengthened with respect to that in unco-ordinated Ph_3PS [$d_{P=S}$ 1.950(3) Å].[17] Conversely, the average P–C bond length in $Ph_3PS{\cdot}I_2$ [1.806(5) Å] is shorter than that in Ph_3PS [1.817(8) Å].[17] As expected, the S–I–I linkage is almost linear [175.51(3)° *cf.* 173.69(6)° in $Ph_3PSe{\cdot}I_2$ and 175.23(5)° in $2Ph_3PS{\cdot}3I_2$]. The I–I bond in $Ph_3PS{\cdot}I_2$ is lengthened with respect to that of molecular diiodine (2.667 Å),[18] but is clearly within bonding distance when compared to the van der Waals' radius of diiodine (4.3 Å).[19] Both the I–I and the S–I distances are consistent with those reported in diiodine complexes of related organo-sulfur donors.[3,4] The I–I distance in $Ph_3PS{\cdot}I_2$ is shorter than that in $Ph_3PSe{\cdot}I_2$, consistent with Ph_3PS donating less electron density than $Ph_3PSe{\cdot}I_2$ to diiodine.

The structure of $2Ph_3PS{\cdot}3I_2$ revealed an intermolecular interaction between one of the phenyl rings and the iodine bound to the sulfur. These interactions resulted in a slight deviation in the S–P–C angles from those of a regular tetrahedron. In the present case also, the S–P–C angles show some deviations from the ideal tetrahedral angle, but these cannot be attributed to any short I···C contacts. In $Ph_3PS{\cdot}I_2$ (Fig. 3) the molecules pack fairly loosely in the crystal and are held together by van der Waals forces. The shortest intermolecular contacts involving a pair of non-hydrogen atoms [C(11)···C(15) at $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$] are 3.609(10) Å. As can be seen from Table 1, the bond angles in $Ph_3PS{\cdot}I_2$, $2Ph_3PS{\cdot}3I_2$ and $Ph_3PSe{\cdot}I_2$ are very similar. Godfrey *et al.*[16] suggested that the deviation of the angles around the phosphorus in $Ph_3PSe{\cdot}I_2$ is due to the retention of significant P–Se double bond character, and because the lone pairs on larger atoms tend to cause the angles between bonds to be appreciably smaller than the tetrahedral angle. Clearly, these arguments would apply equally well to both $Ph_3PS{\cdot}I_2$ and $2Ph_3PS{\cdot}3I_2$.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of $Ph_3PS{\cdot}I_2$, $Ph_3PSe{\cdot}I_2$ and $Ph_3PO{\cdot}I_2$ have been recorded in both the solid state and in $CDCl_3$ solution. The data are summarised in Table 2. The solution data for $Ph_3PSe{\cdot}I_2$ concur with those reported previously for this compound.[16] The solid-state and solution spectra each exhibit single signals, with reasonable agreement in chemical shifts, indicating that each compound adopts the same structure in both phases. The signals for $Ph_3PS{\cdot}I_2$ and $Ph_3PSe{\cdot}I_2$ are shifted to a higher frequency than those of uncomplexed Ph_3PS and Ph_3PSe.[20] The magnitude of the change in chemical shift between the diiodine and the free phosphine chalcogenide is greatest for the selenium complex, reflecting the enhanced donor ability of Ph_3PSe over Ph_3PS. The spectra of the selenium-containing complex show the expected satellites due to ^{31}P–^{77}Se coupling with good agreement in the solution and solid-state values of $J(^{31}P–^{77}Se)$. Both the solid state and the solution coupling constants for $Ph_3PSe{\cdot}I_2$, 645 and 623 Hz respectively, are much smaller than those observed for Ph_3PSe; reported values for $J(^{31}P–^{77}Se)$ are 728 Hz ($CDCl_3$ solution) and 737 Hz (solid).[20] The reduction in the size of $J(^{31}P–^{77}Se)$ is consistent with the shift in electron density from selenium to iodine leading to a lengthening of the phosphorus–selenium bond.[21] The signal for $Ph_3PO{\cdot}I_2$ is shifted only very slightly from that of uncomplexed Ph_3PO, confirming that any interaction between the donor and acceptor is very weak.

One difference between the spectra of the three complexes is the direction in the shift of the signal from the parent triphenyl phosphine chalcogen upon co-ordination of diiodine; the signals for $Ph_3PS{\cdot}I_2$ and $Ph_3PSe{\cdot}I_2$ are shifted to higher frequency, whereas that for $Ph_3PO{\cdot}I_2$ is shifted to lower frequency. This disparity cannot be attributed entirely to the differences in the electronegativity of the chalcogen. Analysis of the sideband data for the complexes indicates that the shielding tensors are similar for the $Ph_3PS{\cdot}I_2$ and $Ph_3PSe{\cdot}I_2$ complexes and that these are significantly different to that for $Ph_3PO{\cdot}I_2$. The same observation has been reported for Ph_3PSe, Ph_3PS and Ph_3PO.[22]

We have also recorded the IR and Raman spectra of the three complexes. The ν(P=E) bands in the parent Ph_3PE donors occur at 1190 (E = O), 637 (E = S) and 560 cm^{-1} (E = Se).[23] Co-ordination of diiodine to the Ph_3PE molecule results in a decrease in the ν(P=E) stretching frequency to 1175 (E = O), 590 (E = S) and 537 cm^{-1} (E = Se). These results are in agreement with previous IR studies of these compounds.[6,7,16] Zingaro[7] reported that ν(P=S) in $2Ph_3PS{\cdot}3I_2$ occurs at 590 cm^{-1} which concurs with the value reported here for $Ph_3PS{\cdot}I_2$, which has an identical P–S bond length. We were unable to observe the fundamental I–I vibrations in the complexes, which usually occur below 200 cm^{-1}, due to instrumental limitations. However, the Raman spectrum of each complex contains weak bands in the region 230–330 cm^{-1} which are assignable to ν(I–I) overtone bands.[4]

Conclusion

From these results it is evident that Ph_3PS forms a stable 1 : 1 charge-transfer complex with diiodine not only in solution but also in the solid state. Solid-state and solution $^{31}P\text{-}\{^1H\}$ NMR spectroscopic studies show that the stability of triphenylphosphine chalcogenide diiodine complexes follow the order $E = Se > S \geqslant O$. Godfrey *et al.*,[16] when comparing the structures of $Ph_3PSe{\cdot}I_2$ and $2Ph_3PS{\cdot}3I_2$, suggested that Ph_3PS does not form a stable 1 : 1 complex because it is a weaker donor towards diiodine than Ph_3PSe. X-Ray and NMR data for $Ph_3PS{\cdot}I_2$ and $Ph_3PSe{\cdot}I_2$ show that Ph_3PSe is indeed a stronger donor towards diiodine than Ph_3PS, and thus forms a more stable charge-transfer complex. However, the supposition that Ph_3PS and diiodine only form a 1 : 1 adduct in solution is clearly incorrect.

Experimental

Synthesis

Triphenylphosphine sulfide, triphenylphosphine selenide and triphenylphosphine oxide were prepared using standard literature procedures.[9,21] Diiodine (Aldrich) and dichloromethane were used as received. The compounds reported here were prepared by direct reaction of the tertiary phosphine chalcogen and diiodine in dichloromethane. The synthesis of $Ph_3PS{\cdot}I_2$ is typical: diiodine (0.86 g, 3.4 mmol), dissolved in dichloromethane, was added slowly to a solution of Ph_3PS (1 g, 3.4 mmol) in dichloromethane, with stirring. After *ca.* 4 h, the solution was removed to a fume cupboard and the solvent allowed to evaporate slowly, yielding the $Ph_3PS{\cdot}I_2$ product as red-brown crystals (yield 1.8 g, 96%). M.p. 110 °C (Found: C, 39.4; H, 2.64. $C_{18}H_{15}I_2PS$ requires C, 39.9; H, 2.76%). IR spectrum/cm^{-1} (KBr disc) 1476m, 1432m, 1101s, 995m, 745s, 713m, 690s, 618m, 590s, 504m. Raman spectrum/cm^{-1} 1183m, 1094m, 1025m, 997s, 744m, 634m, 616m, 589m, 337s, 275w, 264w, 249m.

$Ph_3PSe{\cdot}I_2$. This compound was prepared in an identical manner to $Ph_3PS{\cdot}I_2$. M.p. 120 °C (Found: C, 36.05; H, 2.4. $C_{18}H_{15}I_2PSe$ requires C, 36.0; H, 2.41%). IR spectrum/cm^{-1} (KBr disc) 1475m, 1433m, 1098s, 995m, 744s, 716m, 689s, 618m, 537s, 498m. Raman spectrum/cm^{-1} 1183m, 1095m, 1025m, 997s, 614m, 539m, 341m, 331w, 254m, 238w.

$Ph_3PO{\cdot}I_2$. Reaction of Ph_3PO with diiodine in CH_2Cl_2 yielded a brown microcrystalline solid which readily lost diiodine on standing. M.p. 102 °C. Elemental analysis of this compound consistently gave results high in carbon. IR spectrum/cm^{-1} (KBr disc) 1482m, 1434m, 1175s, 1117m, 1090m, 996m, 755m, 720s, 617m. Raman spectrum/cm^{-1} 1183m, 1092m, 1026m, 998s, 682m, 615m, 288w, 247m.

Elemental analyses were carried out by The University of Cambridge Elemental Analysis service and by MEDAC Ltd., UV/VIS spectroscopy was performed on a ATI Unicam UV2 instrument, IR spectra were recorded on a Mattson 4020 Galaxy series FT-IR. Raman spectra were recorded on a Renishaw Raman Microprobe spectrometer using a 632 HeNe laser.

Solid-state ^{31}P CP-MAS spectra were obtained using a Varian UNITYplus 300 spectrometer at an operating frequency of 121.4 MHz. All the spectra were recorded using cross-polarisation, high-power ^{1}H decoupling and magic-angle spinning. Solution ^{31}P spectra were recorded in $CDCl_3$ solution using a Bruker AC250, 250 MHz spectrometer. In all cases spectral referencing was with respect to an external sample of 85% H_3PO_4.

X-Ray crystallography

Single crystals of $Ph_3PS{\cdot}I_2$ suitable for X-ray work were obtained as described above.

Crystal data. $C_{18}H_{15}I_2PS$, $M = 548.13$, monoclinic, $a = 12.618(2)$, $b = 9.454(3)$, $c = 15.930(6)$ Å, $\beta = 97.400(8)°$, $U = 1884.5(10)$ Å^3 (by refinement of the diffractometer angles for 250 reflections within $1.94 \leqslant \theta \leqslant 25.14°$), $T = 293$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 3.53$ mm^{-1}, 7642 reflections measured, 2875 unique ($R_{int} = 0.0489$).

Intensity data were recorded on a Delft Instruments FAST TV area detector diffractometer by following previously described procedures.[24] The structure was solved by Patterson methods (SHELXS 86)[25] and difference syntheses, and refined on F^2 by full-matrix least squares (SHELXL 93)[26] using all unique data corrected for Lorentz and polarisation factors, and also for absorption effects (DIFABS).[27] Non-hydrogen atoms were refined anisotropically and the hydrogen atoms included in calculated positions (riding model) with U_{iso} tied to the U_{eq} of the parent carbons. The structure refined to final $R1$ [on F, $F_o > 3\sigma(F_o)$] = 0.0270 and $wR2$ (on F^2, all data, 199 parameters) = 0.0572. Sources of scattering factors as in ref. 24. The diagrams were drawn with SNOOPI.[28] The calculations were done on a Pentium personal computer. Selected bond lengths and angles are given in Table 1.

CCDC reference number 186/910.

See http://www.rsc.org/suppdata/dt/1998/1289/ for crystallographic files in .cif format.

Acknowledgements

We are grateful to C. Paraskeva for her assistance in recording the IR spectra and Professor J. Yarwood and Dr. C. Sammon for their assistance in recording the Raman spectra.

References

1 F. Ruthe, W. W. du Mont and P. G. Jones, *Chem. Commun.*, 1997, 1947; S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1996, 252; M. A. H. A. Al-Juboori, P. N. Gates and A. S. Muir, *J. Chem. Soc., Dalton Trans.*, 1995, 1441; N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 2421; M. A. H. A. Al-Juboori, P. N. Gates and A. S. Muir, *J. Raman Spectrosc.*, 1995, **26**, 101; N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 2261; N. Bricklebank, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355; 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; W. W. du Mont, M. Bätcher, S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 912; F. A. Cotton and P. A. Kibala, *J. Am. Chem. Soc.*, 1987, **109**, 3308.

2 H. C. Wang, E. J. Gaffney, C. R. Dybowski and A. L. Rheingold, *J. Organomet. Chem.*, 1996, **512**, 21; 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; L. J. Baker, C. E. F. Rickard and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1995, 2895; N. Bricklebank, S. M. Godfrey, H. P. Lane, C A McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Dalton Trans.*, 1994, 175.

3 A. J. Blake, F. Cristiani, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1997, 1337; F. Freeman, J. W. Ziller, H. N. Po and M. C. Keindl, *J. Am. Chem. Soc.*, 1988, **110**, 2568.

4 F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, G. Saba and G. Verani, *J. Chem. Soc., Dalton Trans.*, 1992, 3553.

5 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 3501; S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and S. Sarwar, *J. Chem. Soc., Dalton Trans.*, 1997, 1031; M. Arca, F. Cristiani, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Heteroat. Chem.*, 1997, **8**, 139; *Polyhedron*, 1997, **16**, 1983; F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1994, **33**, 6315; F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1993, **32**, 3694.

6 R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, 1961, **65**, 1132.

7 R. A. Zingaro, *Inorg. Chem.*, 1963, **2**, 192.

8 R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, 1962, **1**, 771.

9 W. Tefteller and R. A. Zingaro, *Inorg. Chem.*, 1966, **5**, 2151.

10 R. A. Zingaro, R. E. McGlothlin and E. A. Meyers, *J. Phys. Chem.*, 1962, **66**, 2579.

11 W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, 1968, **72**, 1561; J. W. Bransford and E. A. Meyers, *Cryst. Struct. Commun.*, 1978, **7**, 697.

12 H. Sakai and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1625.

13 F. Lux, R. Paetzold, J. Danel and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 2*, 1975, 1610.

14 S. Kaur and T. S. Lobana, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2439; *J. Indian Chem. Soc.*, 1983, **60**, 126.

15 M. D. Rudd, S. V. Lindeman and S. Husebye, *Acta Chem. Scand.*, 1997, **51**, 689.

16 S. M. Godfrey, C. A. McAuliffe, S. L. Jackson and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1997, 4499.

17 P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1978, **34**, 3785.

18 I. L. Karle, *J. Chem. Phys.*, 1955, **23**, 1739.

19 N. N. Greenwood and A. Earnshaw, *The Chemistry of the Elements*, Pergamon, Oxford, 1984.

20 J. A. Davies, S. Dutremez and A. A. Pinkerton, *Inorg. Chem.*, 1991, **30**, 2380.

21 D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51.

22 J. B. Robert and L. Wiesenfeld, *Mol. Phys.*, 1981, **44**, 319.

23 G. Davidson, in *The Chemistry of Organophosphorus Compounds, Volume 2, Phosphine oxides, sulfides, selenides and tellurides*, ed. F. R. Hartley, Wiley Interscience, Chicester, 1992, p. 169.

24 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

25 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

26 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

27 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158; adapted for FAST geometry by A. I. Karaulov, University of Wales, Cardiff, 1991.

28 K. Davies, SNOOPI, Program for Crystal Structure Drawing, University of Oxford, 1983.

Received 22nd December 1997; *Paper* 7/09121D