Tertiary Phosphine Adducts of Mixed Halogens, R_3PIBr; Synthesis and Structure in the Solid State and Solution†

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The first extensive solid-state study of compounds of formula R_3PIBr [R_3 = (p-$ClC_6H_4)_3$, Ph_3, Ph_2Pr^n, Ph_2Me, $PhMe_2$ or $Bu^n{}_3$] has been made, most having not previously been described. The crystal structure of Ph_3PIBr shows it to be a surprisingly complex molecule containing dual occupancy of the halogen sites within the unit cell, existing predominantly as Ph_3PIBr. Nevertheless, it is clear that the molecule is a further example of the four-co-ordinate molecular 'spoke' structure, Ph_3P–X–X, previously established for Ph_3PX_2 (X = Br or I) and Ph_3AsI_2. X-Ray powder diffraction studies on analytically pure samples of Ph_3PIBr prepared the same way indicated that subtly different compounds are formed containing varying degrees of occupancy for the two sites described above; however, the molecule is always predominantly Ph_3P–I–Br. Raman spectroscopic studies on all the R_3PIBr compounds illustrate the dominance of the P–I bond in the spectrum; however, in some cases a minor peak assignable to ν(P–Br) was noted, in agreement with the crystallographic studies. Solution ^{31}P-{H} NMR studies in $CDCl_3$ indicate complete ionisation of the compounds R_3P–I–Br to $[R_3PI]Br$; no evidence for the corresponding $[R_3PBr]I$ was observed. Results for the compound $Bu^n{}_3PIBr$ were inconclusive however. This suggests halogen exchange occurs in solution, in agreement with the findings of previous workers.

Although there is a great deal of current interest[1-7] in the nature of compounds formed between triorganophosphines and dihalogens, reports concerning such compounds containing mixed halogens are much rarer and have been confined almost exclusively to solution studies.[8,9] This is in contrast to purely inorganic compounds of stoichiometry $[PCl_nBr_{4-n}]^+$ which have been characterised by Dillon and Gates.[10]

Compounds of stoichiometry $R_3PX(X')$ (R = Ph; X = Br, X' = I) were first investigated by Harris and co-workers[8] using conductimetric titration methods. These workers clearly demonstrated that in MeCN solution ionic products were formed; however, although attempts to isolate Ph_3PIBr were unsuccessful, a product which analysed as $Ph_3PI_{1.5}Br_{0.5}$ was isolated. A number of products were also isolated from the 2:1 reaction of IBr and PPh_3, all of which were assigned ionic structures, $R_3PX_nX'_{4-n}$, based on conductimetric results. Similarly, the compounds Ph_3PI_3Br and Ph_3PIBr_3 were synthesised from the 1:1 reaction of IBr with Ph_3PI_2 and Ph_3PBr_2, respectively, and both compounds were assigned an ionic structure.[8]

More recently the reaction of trialkylphosphines with IBr was investigated by Harris and McKechnie,[8] again using conductance techniques. Interestingly, evidence for the formation of a number of compounds was noted. In the conductimetric titration of IBr with PR_3 (R = n-butyl, octyl or cyclohexyl) breaks in the mole ratio *vs.* conductance graph were observed at the 0.5:1, 1:1 and 2:1 ratios. This led to the postulation of the formation of adducts of stoichiometry $R_3PX_{0.5}X'_{0.5}$, $R_3PX(X')$ and $R_3PX_2X'_2$. The high conductivity values at the breaks in the graph, corresponding to the formation of these adducts, indicated that they are all ionic in MeCN solution. Attempts to isolate a compound of stoichiometry $R_3PX_{0.5}X'_{0.5}$ were unsuccessful, however, and it was thus concluded that such 0.5:1 IBr:PR_3 adducts are not stable as solids. Satisfactory analytical data were reported for both the 1:1, $R_3PX(X')$, and the 2:1, $R_3PX_2X'_2$, adducts.

Remarkably, solid-state studies on compounds of stoichiometry R_3PIBr are limited to Ph_3PIBr which was reported only recently.[11] An ionic structure $[Ph_3PI]Br$ was assigned based on the solid-state ^{31}P-{H} NMR results. This is in contrast to the solution studies of Harris and co-workers[8] who postulated from electronic spectroscopic and conductimetric studies that a MeCN solution of Ph_3PIBr existed as $[Ph_3PBr]I$, *i.e.* the lighter halogen is bound to the phosphorus in the cation. The reason for this discrepancy was rationalised to be due to the instability of the Ph_3PIBr in polar solvents. Dillon and Lincoln[11] prepared their sample of Ph_3PIBr from dichloromethane, whereas Harris and co-workers studied Ph_3PIBr in the much more polar MeCN, and it was reasoned that in this case the P–I bond in the cation would be attacked by the Br^- ions to form $[Ph_3PBr]I$.

We are currently investigating[1,2,12] a large number of compounds of stoichiometry R_3PX_2 (X_2 = Br_2, I_2 or IBr) and have found that, in addition to the generally accepted five-co-ordinate molecular R_3PX_2 structure and the tetrahedral ionic structure $[R_3PX]X$, a third structural form exists, the molecular four-co-ordinate Ph_3P–X–X (X = Br[1] or I[2]) and Ph_3As–I–I.[13] Extensive studies on the compounds R_3PI_2 suggest that this novel structure may be common to compounds of this stoichiometry.[12]

We now report a study of compounds of stoichiometry R_3PIBr. We chose to investigate the nature of these compounds because, first, very little is known about their structures, especially in the solid state, and secondly we were intrigued to know that if the compounds R_3PIBr adopted the molecular four-co-ordinate structure R_3P–X–X, which halogen would be bound to the phosphorus? This question seemed especially interesting since there is some disagreement as to the nature of these compounds as reported by previous workers.[8,11]

Results and Discussion

The compounds R_3PIBr [R_3 = (p-$ClC_6H_4)_3$, Ph_3, Ph_2Pr^n,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and spectroscopic data for the compounds R_3PIBr

		Analysis (%)[a]				$\delta(^{31}P-\{H\})$[b]			
Compound	Colour	C	H	I	Br	R_3PIBr	R_3PI_2[c]	R_3PBr_2[d]	$\nu(P-I)/cm^{-1}$
$(p-ClC_6H_4)_3PIBr$	Yellow	38.0 (37.7)	2.3 (2.1)	22.2 (22.1)	13.6 (14.0) 18.1 (18.6)Cl	38.7	41.8	48.1	148
Ph_3PIBr	Yellow	45.8 (46.1)	3.0 (3.2)	26.9 (27.1)	16.5 (17.0)	44.2	44.8	49.2	164
Ph_2Pr^nPIBr	Pale yellow	41.0 (41.4)	3.8 (3.9)	29.9 (29.2)		49.1	50.1	55.0	187
$Ph_2MePIBr$	Yellow	38.0 (38.3)	3.3 (3.2)	33.6 (31.2)		53.0	52.6	63.0	182
$PhMe_2PIBr$	Buff	28.1 (27.8)	3.5 (3.2)	36.9 (36.8)	23.0 (23.2)	61.9	61.9	67.7	200
$Bu^n{}_3PIBr$	Buff	35.8 (35.2)	6.3 (6.6)	29.4 (31.1)	17.5 (19.5)	103.3	102.3	102.5	206

[a] Calculated values in parentheses. [b] In $CDCl_3$ solution, 85% phosphoric acid as standard. [c] Ref. 12. [d] Ref. 14.

Table 2 Selected bond lengths (Å) and angles (°) in $Ph_3PI_{1.29}Br_{0.71}$

I(1Br)–Br(2I)	3.062(2)	Br(2I)–I(1Br)–P	178.0(1)
I(1Br)–P	2.461(5)	I(1Br)–P–C(1)	109.6(6)
P–C(1)	1.79(1)	I(1Br)–P–C(7)	110.3(6)
P–C(7)	1.78(2)	I(1Br)–P–C(13)	107.7(5)
P–C(13)	1.77(2)	C(1)–P–C(7)	109.1(7)
		P–C(1)–C(2)	120(1)

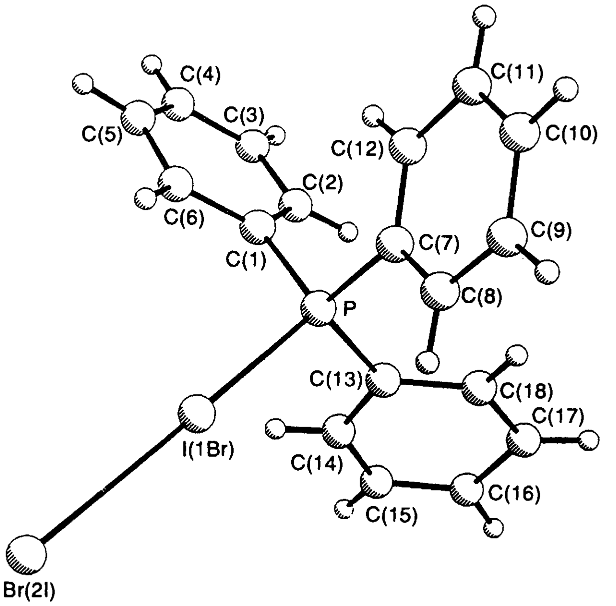

Fig. 1 Crystal structure of $Ph_3PI_{1.29}Br_{0.71}$

Ph_2Me, $PhMe_2$, or $Bu^n{}_3$], Table 1, were synthesised under strictly anaerobic and anhydrous conditions. Addition of PR_3 to a saturated diethyl ether solution of IBr proved to be the most successful method (see Experimental section). Characterisation data are contained in Table 1.

The crystal structure of Ph_3PIBr is shown in Fig. 1. This compound was recrystallised from an analytically pure sample of Ph_3PIBr in diethyl ether–1,2-dichloroethane (1:1). Despite this fact, the crystal selected is rich in iodine compared to bromine and had the empirical formula $Ph_3PI_{1.29}Br_{0.71}$, from X-ray analysis results, Tables 2 and 3. Additionally, the nature of the compound proved to be far more complex than we expected. Although existing predominantly as the species Ph_3P–I–Br, evidence for Ph_3PI_2, Ph_3PBr_2 and/or Ph_3P–Br–I were all detected within the unit cell. The structure of Ph_3PIBr clearly illustrates it to be a further example of the molecular four-co-ordinate spoke structure exemplified by Ph_3PX_2 (X = Br or I)[1,2] and Ph_3AsI_2.[13] Unequivocal assignment of halogen atoms in the I–Br bond of Ph_3PIBr is difficult, since both crystallographic sites are of mixed-halogen occupancy. The halogen atom bound directly to the phosphorus atom is 86(2)% I and 14(2)% Br (% atom), whereas the halogen atom bound directly to the other halogen atom is 57(2)% Br and 43(2)% I (% atom). The dual occupancy of the halide sites may explain the confusion generated by earlier workers who have assigned both the structures Ph_3PBrI and Ph_3PIBr to this molecule. Although from this crystallographic study the predominant mixed-halide species is Ph_3PIBr, the situation is clearly more complex than this suggests and the possibility of confusion without crystallographic data obviously exists. Nevertheless, the iodine–bromine bond is 3.062(2) Å which although lengthened with respect to molecular I–Br (2.52 Å) is still within bonding distance when compared to the van der Waals radii of the individual ions (4.1 Å). Furthermore, the weakening of the I–Br bond in charge-transfer complexes has been predicted from charge-transfer theory[15] and would be expected since electron density is being put into the antibonding orbitals of the halogens by the tertiary phosphine donor. The weakening of the I–Br bond has been demonstrated spectroscopically[16,17] and subsequently illustrated from single-crystal X-ray diffraction studies[18,19] on such compounds containing sulfur or nitrogen donors.

Table 3 Fractional atomic coordinates for the non-hydrogen atoms in $Ph_3PI_{1.29}Br_{0.71}$

Atom	*x*	*y*	*z*
I(1Br)	0.917 68(8)	0.755 5(1)	0.355 5(1)
Br(1I)	0.917 7	0.755 5	0.355 5
Br(2I)	0.985 2(1)	0.820 0(1)	0.083 2(1)
I(2Br)	0.985 2	0.820 0	0.083 2
P	0.862 6(3)	0.709 6(3)	0.576 3(5)
C(1)	0.790(1)	0.809(1)	0.646(2)
C(2)	0.798(1)	0.829(1)	0.779(2)
C(3)	0.740(2)	0.904(1)	0.833(2)
C(4)	0.673(2)	0.953(2)	0.758(3)
C(5)	0.661(1)	0.933(1)	0.630(3)
C(6)	0.721(1)	0.861(1)	0.568(2)
C(7)	0.785(1)	0.601(1)	0.572(2)
C(8)	0.813(2)	0.521(1)	0.497(2)
C(9)	0.751(2)	0.438(1)	0.493(2)
C(10)	0.660(2)	0.439(2)	0.556(2)
C(11)	0.628(1)	0.516(1)	0.630(2)
C(12)	0.692(2)	0.598(1)	0.630(2)
C(13)	0.975(1)	0.691(1)	0.671(1)
C(14)	1.045(1)	0.766(2)	0.681(2)
C(15)	1.132(1)	0.762(2)	0.751(2)
C(16)	1.153(2)	0.674(2)	0.810(2)
C(17)	1.084(2)	0.593(2)	0.810(2)
C(18)	0.997(2)	0.603(2)	0.734(2)

The X-ray powder diffraction patterns of bulk Ph_3PX_2 (X_2 = Br_2, I_2 or IBr) are compared in Fig. 2 and clearly establish that Ph_3PIBr is not merely a statistical mixture of Ph_3PI_2 and Ph_3PBr_2. All three patterns are very similar, as expected since the three structures are isomorphous, see Table 4.

However, X-ray powder diffraction studies of two compounds of formula Ph_3PIBr (which were analytically pure from elemental analysis results) show that the two compounds

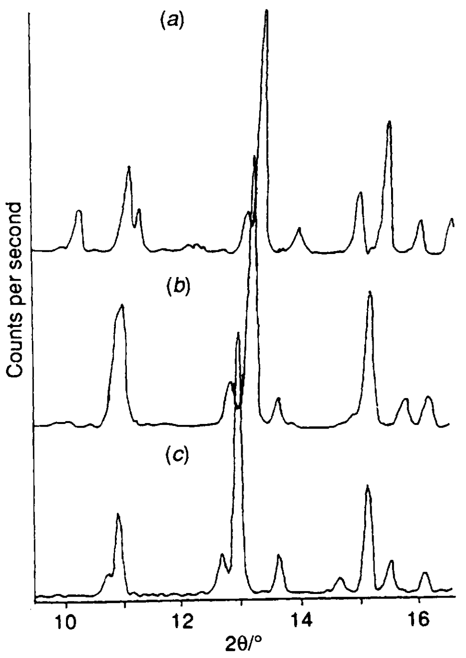

Fig. 2 X-Ray powder diffraction patterns of the compounds Ph_3PX_2 [X_2 = Br_2 (*a*), IBr (*b*) or I_2 (*c*)]

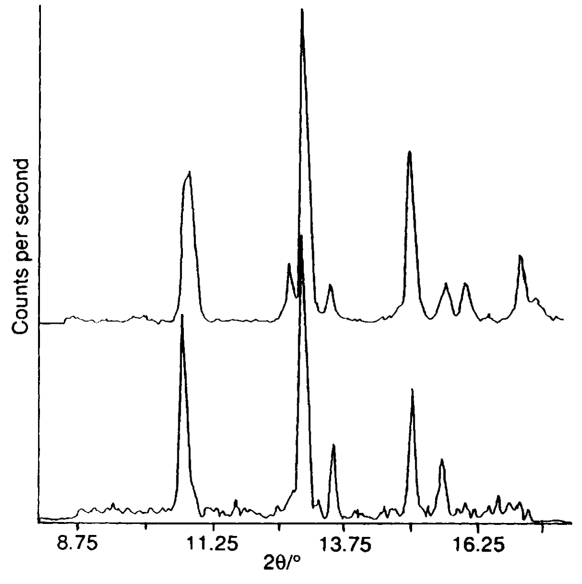

Fig. 3 X-Ray powder diffraction patterns of two independent samples of Ph_3PIBr prepared using identical techniques

Table 4 Unit-cell dimensions (Å) for the compounds Ph_3PX_2 (X_2 = Br_2, I_2 or IBr)

Compound	Space group	*a*	*b*	*c*
Ph_3PI_2	$P2_12_12_1$	12.993(1)	13.673(3)	10.461(6)
Ph_3PIBr	$P2_12_12_1$	12.996(8)	13.479(7)	10.288(6)
Ph_3PBr_2	$P2_12_12_1$	12.729(10)	13.312(5)	10.030(5)

prepared independently using the same experimental conditions are, in fact, not identical, Fig. 3, suggesting that the occupancy of the four different crystallographic sites described above may vary in each sample of a compound of stoichiometry R_3PIBr, despite the fact that analytically the compounds appear to be identical and the compounds are prepared in an identical manner.

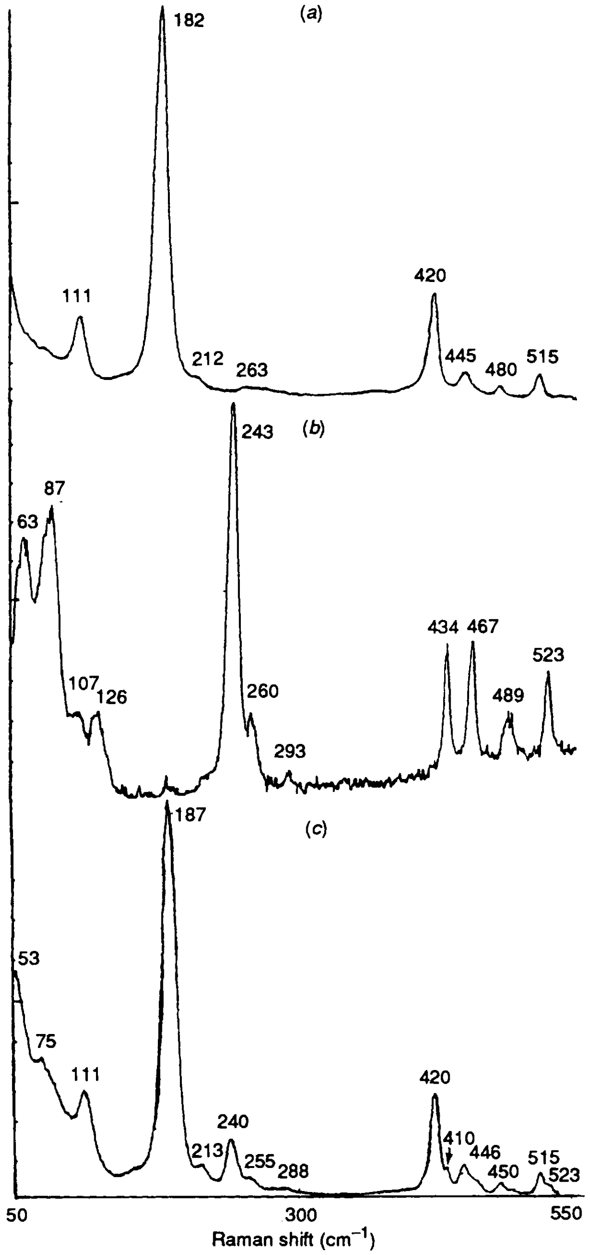

Fig. 4 Low frequency Raman spectra of the compounds $Ph_2Pr^nPX_2$ [X_2 = I_2 (*a*), Br_2 (*b*) or IBr (*c*)]

Further evidence for the complex nature of compounds of stoichiometry R_3PIBr is afforded from their low-frequency Raman spectra. In most cases the spectra exhibited an intense peak which, by comparison with data for the analogous diiodo compound, R_3PI_2, is assignable to ν(P–I).[12] In all cases this peak dominates the spectrum. However, a smaller peak at higher frequencies was noted for the compounds R_3PIBr which is absent in the spectra of the compounds R_3PI_2. Consequently, we synthesised the respective dibromophosphoranes, R_3PBr_2, for comparative purposes.[14] The low-frequency Raman spectra of the compounds $Ph_2Pr^nPX_2$ (X_2 = Br_2, I_2 or IBr) are compared in Fig. 4; $Ph_2Pr^nPI_2$ and Ph_2Pr^nPIBr show intense bands at 182 and 187 cm^{-1}, respectively, assignable to ν(P–I).[12] The spectrum of Ph_2Pr^nPIBr also exhibits a smaller peak at 240 cm^{-1}, which by comparison with data for $Ph_2Pr^nPBr_2$ [ν(P–Br) at 243 cm^{-1}, Fig. 4] is assignable to ν(P–Br).

Clearly, in agreement with crystallographic data, Raman data show that whilst compounds of stoichiometry R_3PIBr exist predominantly as the molecular species R_3P–I–Br in the solid state, a minor quantity of the species R_3P–Br–I is also present.

The $^{31}P-\{H\}$ NMR data for the compounds R_3PIBr are in Table 1 and compared to the values recorded for the compounds R_3PX_2 (X = Br or I). All the spectra were run as $CDCl_3$ solutions. All previous studies into compounds of formula R_3PX_2 (X = Br or I) have shown that ionisation occurs in solution to form $[R_3PX]X$.[1,2,6,8,9,11,14] The $^{31}P-\{H\}$ NMR spectra of the compounds R_3PIBr all display a single peak indicating a single phosphorus environment. Clearly then, in solution R_3PIBr exist entirely as $[R_3PI]Br$ or $[R_3PBr]I$. The $^{31}P-\{H\}$ NMR spectra of the compounds R_3PX_2 (X = Br or I), Table 1, yield the $^{31}P-\{H\}$ chemical shifts for the cations $[R_3PBr]^+$ and $[R_3PI]^+$ respectively and therefore, by comparison with the shifts recorded for the compounds R_3PIBr, assignment of which halogen is bound to the phosphorus in solution should be straightforward.

From Table 1 the compounds R_3PIBr [R = $(p\text{-}ClC_6H_4)_3$, Ph_3, Ph_2Pr^n, Ph_2Me or $PhMe_2$] all adopt the iodophosphonium bromide structure $[R_3PI]Br$, all the values for these compounds corresponding to the iodophosphonium cation, $[R_3PI]^+$. Since a single peak is observed in each case and the values are significantly different to those recorded for the cation $[R_3PBr]^+$, it may be deduced that there is no evidence for the bromophosphonium iodide structure, $[R_3PBr]I$. However, the value for $[Ph_2MePBr]^+$ reported here differs from that previously reported[20] (δ 51.6). We do not observe any peak at this value for the $[Ph_2MePBr]Br$ described herein, and the shift is similar to that observed for the iodophosphonium cation $[Ph_2MePI]X$ (X = Br or I), δ 53.0 and 52.6, respectively.

The situation for the tributylphosphine–dihalogen adducts is less clear cut. Values recorded for the compounds $Bu^n{}_3PX_2$ (X_2 = Br_2, I_2 or IBr) are δ 102.5, 102.3 and 103.3 respectively. Previous $^{31}P-\{H\}$ NMR studies[21,22] on $Bu^n{}_3PBr_2$ have shown values of δ 105 and 102, in fairly good agreement with the present value. There are no previous literature reports concerning the $^{31}P-\{H\}$ NMR shifts for $Bu^n{}_3PX_2$ (X_2 = I_2 or IBr) described here but a number of $^{31}P-\{H\}$ NMR studies on the cation $[Bu_3PCl]^+$ have been reported, giving shifts varying from δ 105 to 100.7.[22,23] It would therefore appear that the $^{31}P-\{H\}$ NMR shift for the cation $[Bu^n{}_3PX]^+$ is largely halide independent. Although this appears curious, we have previously recorded the $^{31}P-\{H\}$ NMR shifts for the compounds $[Pr^n{}_3PX]X$ (X = Br[14] or I[12]), δ 101.5 and 102.4, respectively, and that for $[Pr^n{}_3PCl]Cl$ has previously been reported at δ 101.0 by Appel and Scholer.[23] Again, these results indicate that the $^{31}P-\{H\}$ NMR shift for the cation $[Pr^n{}_3PX]^+$ is also halide independent. These results suggest that, as the tertiary phosphine become more basic, the effect on the $^{31}P-\{H\}$ NMR shift for the cation $[R_3PX]^+$ of changing X (Cl, Br or I) is largely insignificant.

These results contrast with the solid-state studies for the compounds R_3PIBr described herein. These $^{31}P-\{H\}$ NMR solution studies clearly indicate that considerable halogen exchange occurs and, in most cases, the cation is present exclusively as the iodophosphonium ion and no $[R_3PBr]I$ is present. However, no definite conclusions can be drawn regarding the solution structure of $Bu^n{}_3PIBr$ since the shifts for the cations $[Bu^n{}_3PX]^+$ (X = Br or I) are nearly identical. The Raman spectrum of this compound in the solid state does exhibit a strong band at 206 cm^{-1}, assignable to ν(P–I) indicating that Bu_3PIBr does exist predominantly with the heavier halogen bound to the phosphorus, at least in the solid state, in agreement with the observations regarding the other R_3PIBr compounds described herein. In contrast to the solid-state structures of the R_3PIBr compounds, the solution structures all exist as a single species suggesting equilibration in solution. The equilibrium nature of solutions of compounds of stoichiometry $R_3PX(X')$ has previously been reported. However, the results presented here, *i.e.* that the solution structures of R_3PIBr is $[R_3PI]Br$, conflicts with reports by Harris and coworkers[8] who concluded, from electronic spectroscopic and conductivity measurements, that compounds of stoichiometry R_3PIBr existed as ionic $[R_3PBr]I$ in MeCN solution, *i.e.* the lighter halogen is bound directly to the phosphorus atom in the cation.

However, Dillon and Lincoln[11] found from solid-state $^{31}P-\{H\}$ NMR measurements on Ph_3PIBr that in the solid state the compound existed with the heavier halogen bound to the phosphorus, in agreement with the work presented here. The reason for this discrepancy was rationalised by Dillon and Lincoln[11] as being due to the susceptibility of the P–I bond to attack by bromide anions in highly polar solvents. Harris prepared Ph_3PIBr from the highly polar MeCN, whereas Dillon and Lincoln[11] prepared their Ph_3PIBr from the less-polar dichloromethane, and demonstrated the susceptibility of the P–I bond to attack by Br^- in MeCN solution using $^{31}P-\{H\}$ NMR solution spectroscopy. The compounds R_3PIBr reported here were prepared from the essentially non-polar diethyl ether and would therefore be expected to exist with the heavier halogen present in the cation, in agreement with Dillon and Lincoln.[11]

The crystal structure of the Ph_3PIBr reported here clearly shows that the molecule adopts the molecular four-co-ordinate structure $Ph_3P\text{–}X\text{–}X'$, isostructural and isomorphous with Ph_3PX_2 (X = Br or I), Figs. 1 and 2, and is considerably more complicated than its stoichiometric formula would suggest, there being crystallographic and spectroscopic evidence for the existence of significant quantities of Ph_3PBrI, Ph_3PI_2 and Ph_3PBr_2 within the unit cell. The 'I–Br' distance in the compounds is 3.062(2) Å, which clearly constitutes a genuine bond when compared to the van der Waals radius of I–Br (4.1 Å). However, the situation is complicated due to the presence of excess of iodine. Nevertheless, the compound is isostructural with both Ph_3PI_2 and Ph_3PBr_2 and represents one example of the statistical distribution of halide ions in a crystal formed when Ph_3PIBr is brought into solution. It seems highly probable that a statistical distribution of crystal phases would form with varying quantities of I and Br. The reason for this may be related to the greater solubility of Ph_3PI_2 compared to Ph_3PBr_2 in diethyl ether. The situation is complex in any case since the 'bromine' site in the crystal structure of Ph_3PIBr has 43% iodine character and the 'iodine' site has 14% Br. Therefore, unequivocal assignment of the positions of the halogens in Ph_2PIBr is not possible; however, the halogen bound to the phosphorus has predominantly (86%) iodine character.

Conclusion

In contrast to the dihalogen compounds R_3PX_2 (X = Br or I), compounds of formula R_3PIBr have complicated structures which, from crystallographic and spectroscopic evidence, contain molecules with various halogen combinations within the unit cell and are not adequately structurally described by the simple stoichiometric formula R_3PIBr. The compound Ph_3PIBr exists predominantly as $Ph_3P\text{–}I\text{–}Br$ from crystallographic studies, *i.e.* with the heavier halogen bound to the phosphorus. Raman spectroscopic studies suggest that this is the case for all the R_3PIBr compounds described here. This is in agreement with the work of Dillon and Lincoln[11] who concluded that for Ph_3PIBr the heavier halogen was bound directly to the phosphorus. However, from the present study the compounds R_3PIBr appear to be considerably more complicated than suggested by Dillon and Lincoln,[11] and Ph_3PIBr has clearly been shown to adopt the molecular four-co-ordinate structure $Ph_3P\text{–}X\text{–}X'$ and is isostructural with both Ph_3PI_2 and Ph_3PBr_2. Therefore the ionic structure $[Ph_3PI]Br$ assigned by Dillon and Lincoln[11] to their sample of Ph_3PIBr seems rather simplistic; the possibility remains that this could be due to solvent effects, however.

In solution, the evidence points to the existence of the compounds R_3PIBr as $[R_3PI]Br$ with no evidence for the corresponding bromophosphonium iodides, $[R_3PBr]I$. The results for $Bu^n{}_3PIBr$ are inconclusive however, due to the similarity of the ^{31}P-{H} NMR shifts of the cations $[Bu^n{}_3PX]^+$ (X = Cl, Br or I). The existence of a single peak in the ^{31}P-{H} NMR spectra of all the compounds R_3PIBr indicates that considerable halogen exchange occurs in solution, in agreement with the work of Harris[8] and Schmutzler and co-workers.[9]

Experimental

The compounds R_3PIBr are very moisture sensitive, therefore strictly anaerobic and anhydrous conditions were used for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmosphere HE-493 glovebox. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Tertiary phosphines were either synthesised by standard Grignard techniques or obtained commercially from Aldrich (PPh_3). The purity of all the tertiary phosphines used was confirmed by ^{31}P-{H} NMR spectroscopy prior to use. Iodine monobromide was obtained commercially (Aldrich) and used as received.

Synthesis of the compounds R_3PIBr was initially attempted from the direct reaction of PR_3 with IBr in diethyl ether, however elemental analysis results consistently showed that the compounds were rich in iodine and deficient in bromine. Additionally attempts to recrystallise the products generally resulted in the isolation of crystalline materials which were more impure than the original material. An improved, although not always successful, method of synthesis for the compounds is from the combination of a saturated solution of IBr in diethyl ether and a diethyl ether solution of PR_3 thus precipitating the product immediately. Even so the compounds R_3PIBr still had a tendency to be rich in iodine with respect to bromine. All the compounds were synthesised in a similar way, the synthesis of $PhMe_2PIBr$ being typical.

Dimethylphenylphosphine (1.00 g, 7.25 mmol) was added to diethyl ether (*ca.* 75 cm^3) and a saturated solution of IBr (1.5 g, 7.25 mmol) in diethyl ether was subsequently added. The resultant buff solid was isolated the same day using standard Schlenk techniques and dried *in vacuo*. The dry solid was then transferred to pre-dried argon-filled ampoules which were flame sealed. Synthesis of the compounds R_3PI_2[12] and R_3PBr_2[14] has been described elsewhere; elemental analyses on all such compounds described herein are in excellent agreement with the theoretical values.

Elemental analyses were performed by the analytical laboratory of this department, and the results are presented in Table 1. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 argon-ion laser and a SPEX 1403 0.85 m focal length double monochromator fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hammamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DMIB data station. Solution ^{31}P-{H} NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid standard. X-Ray powder diffraction patterns were recorded using a Scintag XRD2000 powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å).

X-Ray Crystallography.—Crystal data. $C_{18}H_{15}Br_{0.71}I_{1.29}P$, M_r = 469.10, orthorhombic, space group $P2_22_12_1$ (no. 19), a = 12.996(8), b = 13.479(7), c = 10.288(6) Å, U = 1802(3) Å^3 (by least-squares refinement of 25 accurately centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.729 g cm^{-3}, yellow block, 0.20 × 0.15 × 0.10 mm, μ(Mo-Kα) = 40.33 cm^{-1}, F(000) = 924.

Data collection and processing. Rigaku AFC6S diffractometer, ω–2θ mode with ω scan width 0.89 + 0.30 tan θ and scan speed 4.0° min^{-1} [with rescan up to a maximum of three times for weak reflections, $I < 10\sigma(I)$], graphite-monochromated Mo-Kα radiation; 1151 unique reflections measured ($0 < \theta < 24°$), 1001 observed reflections with $I > 2\sigma(I)$, Lorentz polarisation and absorption corrections applied. Intensity standards measured repeatedly showed no decline.

Structure solution and refinement. The structure was solved by heavy-atom methods[24] and subjected to full-matrix least-squares refinement based on F.[25] Atoms were refined anisotropically and hydrogen atoms were included in idealised positions (C–H 0.95 Å) with fixed isotropic thermal parameters. The I:Br ratio of the composite atom at each halogen site was also allowed to refine, while maintaining the total site population at 1.0, giving final agreement factors of R = 0.036 and R' = 0.037 where $w = 1/[\sigma^2(F_o) + 0.03F_o{}^2]$. The maximum and minimum peaks on the final Fourier difference map corresponded to 0.67 and 0.45 e Å^{-3}, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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