# The Acceptor Properties of some Organophosphorus(V) Bromides

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The acceptor properties of the organophosphorus(V) bromides $PBr_3(cat)$ (cat = benzene-1,2-diolate), $PBr(cat)_2$, and $PBr_4Ph$, and of the $PBr_3Ph^+$ cation, towards Lewis bases such as halide ions and uni- or bi-dentate pyridines have been investigated, mainly by means of $^{31}P$ n.m.r. spectroscopy. Several new complexes have been isolated, and characterised by elemental analysis and (in some instances) n.m.r. or vibrational spectroscopy.

In recent years the acceptor properties of several chlorophosphorus(V) species, including $PCl_5$,[1] the $PCl_4^+$ ion,[2] $PCl_4Ph$,[3] $PCl_3(cat)$[4] (cat = benzene-1,2-diolate, $C_6H_4O_2$), $PCl(cat)_2$,[4] $PCl_4Me$,[5] $PCl_4Et$,[5] and derivatives thereof, towards the Lewis bases $Cl^-$ and uni- or bi-dentate pyridines, have been described. The Lewis acid behaviour of phosphorus(V) bromide is not readily investigated, since it dissociates when dissolved in solvents of low polarity, equation (1), and is

$$PBr_5 \longrightarrow PBr_3 + Br_2 \qquad (1)$$

stabilised (as the $PBr_4^+$ ion) only in polar, oxidising solvents such as liquid $Br_2$ or 25-oleum (containing 25% $SO_3$).[6] The acceptor properties of the organophosphorus(V) bromides $PBr_3(cat)$, $PBr(cat)_2$, and $PBr_4Ph$, together with those of $[PBr_3Ph][BBr_4]$ towards halide ions and pyridine bases are now reported. There have been no previous studies in this area, although the formation of an adduct by $PBr(cat)_2$ with a bidentate pyridine such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) was expected to lead to the same cationic species $[P(cat)_2L]^+$ (L = bipy or phen) as those formed by $PCl(cat)_2$ under similar conditions.[4,7] Several new compounds have been isolated and characterised by elemental analysis, $^{31}P$ n.m.r. spectroscopy (where possible), and in some cases vibrational spectroscopy.

## Experimental

All manipulations, including n.m.r. sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Chemicals of the best available commercial grade were used, in general without further purification except for tetra-alkylammonium chlorides which were dried as described previously.[8] PBr(cat) was prepared by the method of Gross and Karsch,[9] and $PCl(cat)_2$ as described previously.[4,10] The compound $PBr(cat)_2$ was prepared by adding an excess of bromine to a solution of $PCl(cat)_2$ in $CH_2Cl_2$, giving rise to a very effervescent reaction. The solution was left to stir for a few minutes, and the solvent then removed *in vacuo* to give a white solid product (Found: C, 44.0; H, 2.5; Br, 24.5; P, 9.5. $C_{12}H_8BrO_4P$ requires C, 44.1; H, 2.5; Br, 24.4; P, 9.5%). Tetrabromo(phenyl)phosphorane, $PBr_4Ph$, was prepared by bromination of $PBr_2Ph$ in an inert solvent ($CH_2Cl_2$), as described previously.[6] The preparation of other new complexes is described below, and their elemental analyses are given in Table 1. Light petroleum used was that fraction boiling at 30—40 °C.

**Table 1.** Elemental analyses [a]

| Compound | Analysis (%) | | | | |
|---|---|---|---|---|---|
| | C | H | N | P | Br |
| $[PBr_2(cat)(py)_2][Br_3]$ | 27.5 | 2.1 | 3.9 | 4.2 | 61.0 |
| | (27.6) | (2.0) | (4.0) | (4.4) | (57.3) |
| $[PBr_2(cat)(bipy)]_2[Br_3]Br$ | 31.6 | 1.7 | 4.9 | 5.1 | 51.8 |
| | (31.3) | (2.0) | (4.6) | (5.0) | (52.0) |
| $[PBr_2(cat)(bipy)][BBr_4]$ | 24.1 | 1.6 | 3.5 | 3.9 | 59.6 |
| | (24.5) | (1.5) | (3.6) | (3.9) | (61.0) |
| $[PBr_2(cat)(phen)][Br_3]$ | 30.5 | 1.9 | 4.0 | 4.5 | 54.9 |
| | (30.1) | (1.7) | (3.9) | (4.3) | (55.6) |
| $[N(n-C_5H_{11})_4][PBrCl(cat)_2]$ [b] | 59.7 | 9.1 | 2.4 | 4.6 | 12.0 |
| | (58.1) | (7.9) | (2.1) | (4.7) | (12.1) |
| $PBr(cat)_2{\cdot}py$ | 50.8 | 3.0 | 4.6 | 7.6 | 19.4 |
| | (50.3) | (3.2) | (3.4) | (7.6) | (19.7) |
| $[P(cat)_2(bipy)]_2[Br_3]Br$ | 45.7 | 3.3 | 4.8 | 5.8 | 28.5 |
| | (46.9) | (2.9) | (5.0) | (5.5) | (28.4) |
| $[P(cat)_2(phen)]_2[Br_3]Br$ | 48.2 | 3.1 | 4.4 | 5.3 | 26.0 |
| | (49.1) | (2.7) | (4.8) | (5.3) | (27.2) |
| $[PBr_3Ph(bipy)][BBr_4]$ | 22.8 | 1.5 | 3.4 | 3.8 | 66.8 |
| | (23.0) | (1.6) | (3.4) | (3.7) | (67.0) |
| $[PBr_3Ph(phen)][BBr_4]$ | 25.2 | 1.6 | 3.2 | 3.5 | 64.8 |
| | (25.2) | (1.5) | (3.3) | (3.6) | (65.2) |

[a] Calculated values are given in parentheses. [b] Cl, 5.3 (5.4%).

$[PBr_2(cat)(py)_2][Br_3]$ (py = *pyridine*).—PBr(cat) (0.76 g, 3.47 mmol) was dissolved in a small amount of $CH_2Cl_2$, and bromine (0.2 cm$^3$, 3.88 mmol) was added, with stirring, to produce a pale orange solution. Pyridine (0.56 cm$^3$, 6.94 mmol) was added cautiously, and an orange precipitate was instantly formed. The product was separated, washed with low-boiling light petroleum and dried *in vacuo* to give a fine orange powder.

$[PBr_2(cat)(bipy)]_2[Br_3]Br$.—This salt was similarly prepared from PBr(cat) (1.298 g, 5.92 mmol), bromine (0.33 cm$^3$, 6.40 mmol) and 2,2′-bipyridine (0.926 g, 5.93 mmol), the base being dissolved in the minimum quantity of $CH_2Cl_2$ before addition. The product was isolated as above as a bright orange solid.

$[PBr_2(cat)(bipy)][BBr_4]$.—A mixture of bromine and PBr(cat) in $CH_2Cl_2$ was prepared as above, and an equimolar quantity of $BBr_3$ was added to the solution, with stirring. A solution of 2,2′-bipyridine in $CH_2Cl_2$ was added, and the solution left to stir for 5 min. A yellow precipitate then formed, and was isolated in a similar manner to the above compounds.

$[PBr_2(cat)(phen)][Br_3]$.—Bromine (0.5 cm$^3$, 9.70 mmol) was added, with stirring, to a solution of PBr(cat) (2.07 g, 9.45 mmol) in $CH_2Cl_2$. A solution of 1,10-phenanthroline (1.708 g, 9.48 mmol) in the same solvent was then added slowly, with constant stirring. The yellow precipitate which immediately formed was isolated as above, washed with $CH_2Cl_2$ and low-boiling light petroleum and dried *in vacuo*.

$[N(n-C_5H_{11})_4][PBrCl(cat)_2]$.—$PBr(cat)_2$ (0.448 g, 1.37 mmol) was dissolved in a small amount of $CH_2Cl_2$, and $N(n-C_5H_{11})_4Cl$

(0.463 g, 1.39 mmol) was added to the solution, with stirring. The solvent was removed *in vacuo* to yield a white solid.

$PBr(cat)_2 \cdot py$.—Pyridine was dripped into an equimolar quantity of $PBr(cat)_2$ dissolved in $CH_2Cl_2$, with stirring. The white precipitate which immediately formed was isolated as above and washed with low-boiling light petroleum.

$[P(cat)_2(bipy)]_2[Br_3]Br$.—$PBr(cat)_2$ was dissolved in $CH_2Cl_2$ and an equimolar quantity of 2,2′-bipyridine was added, with stirring. The yellow precipitate which immediately formed was isolated and washed as above. Analysis indicated the approximate composition $[P(cat)_2(bipy)]^+{}_2[Br_3]^-Br^-$.

$[P(cat)_2(phen)]_2[Br_3]Br$.—This salt was prepared in a similar manner to the previous one, except that the 1,10-phenanthroline was dissolved in $CH_2Cl_2$ prior to addition. A yellow solution resulted, which when placed in a refrigerator overnight yielded a yellow precipitate. This was treated as above.

$[PBr_3Ph][BBr_4]$.—An equimolar quantity of $BBr_3$ was added cautiously to a slurry of $PBr_4Ph$ in $CH_2Cl_2$.[6] The mixture was left to stir for 15 min, when a white precipitate was observed. The compound was isolated as above.

$[PBr_3Ph(bipy)][BBr_4]$.—The salt $[PBr_3Ph][BBr_4]$ was dissolved in $CH_2Cl_2$ and an equimolar quantity of 2,2′-bipyridine was added, with stirring. A yellow precipitate was observed. The solution was left to stir for 30 min, and the solid then isolated and washed in the usual manner.

$[PBr_3Ph(phen)][BBr_4]$.—This salt was similarly prepared from $[PBr_3Ph][BBr_4]$ and 1,10-phenanthroline. The yellow solid which separated immediately on mixing was isolated as above.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer, as described previously.[8] Chemical shifts were measured relative to external $H_3PO_4$, with the downfield direction taken as positive. Boron-11 n.m.r. spectra were recorded at the same temperature on a multinuclear Fourier-transform spectrometer, which has been described before in relation to $^{119}Sn$ n.m.r. spectra.[11] Chemical shifts are similarly expressed relative to external $B(OMe)_3$. Microanalyses (C, H, N, P, Cl, and Br) and i.r. spectra were obtained as described in earlier papers,[6,8,12] while Raman spectra were recorded on a Cary 82 spectrometer by Mrs. J. Slegrova, using an argon laser.

## Results and Discussion

(*a*) $PBr_3(cat)$.—This compound was first prepared by Gross, Gloede and co-workers,[13,14] and has been widely used in the preparation of acidic bromides.[15] It was found to be soluble in most common organic solvents, and $^{31}P$ chemical shifts of −188.6 p.p.m. in $CS_2$, −186.9 p.p.m. in $CH_2Cl_2$, −189.0 p.p.m. in $CHCl_3$, and −190.1 ± 1 p.p.m. in the solid state were measured, in excellent agreement with the previous solution value from $CHCl_3$.[16] These shifts indicate that the compound has a five-co-ordinate molecular structure in both solid and solution.

When a small amount of $NBu^n{}_4Br$ was added to a solution of $PBr_3(cat)$ in $CH_2Cl_2$, the $^{31}P$ n.m.r. spectrum showed two peaks, at 197.6 and −195.1 p.p.m., the latter ascribed to starting material. Addition of more of the bromide resulted in the appearance of a single resonance at 196.7 p.p.m., which may be readily assigned to PBr(cat).[16] These results suggest that $PBr_3(cat)$ does not show acceptor properties towards the bromide ion, unlike $PCl_3(cat)$ which forms $[PCl_4(cat)]^-$ with $Cl^-$ ions,[4] but decomposes to PBr(cat) with formation of the tribromide ion, equation (2). Analogous behaviour towards

$$PBr_3(cat) + Br^- \longrightarrow PBr(cat) + Br_3^- \qquad (2)$$

$Br^-$ ions is shown by both $PBr_5$ [17] and $PBr_4Ph$ (see later).

Lewis acid characteristics were shown, however, towards pyridine bases. When a 1 : 1 : 2 mixture of PBr(cat), $Br_2$ [to form $PBr_3(cat)$ *in situ*], and pyridine was prepared in $CH_2Cl_2$, an orange precipitate was immediately formed and no solution signals could be observed. The solid was isolated, and analysed as $[PBr_2(cat)(py)_2][Br_3]$ (Experimental section). It did not give a solid-state spectrum, but in $PhNO_2$ showed a single sharp peak at −217.6 p.p.m. Although three geometrical isomers are possible for $[PBr_2(cat)(py)_2]^+$, the observation of one resonance only suggests that either one isomer is formed preferentially, or else there is rapid exchange between the isomers. Similar behaviour has been observed for the $[PCl_2(cat)(py)_2]^+$ cation, formed from $[PCl_2(cat)][SbCl_6]$ and py.[4] Confirmation of the presence of the $Br_3^-$ ion was provided by the Raman spectrum, which showed a band at 168 cm⁻¹.[18] Formation of $Br_3^-$ implies some reduction of $PBr_3(cat)$ to PBr(cat), equation (3). No signal was detected from the

$$2PBr_3(cat) + 2\ py \longrightarrow [PBr_2(cat)(py)_2][Br_3] + PBr(cat) \quad (3)$$

phosphorus(III) species, possibly because the precipitate rapidly filled the coil region of the spectrometer probe. Since excess pyridine would also be present (because of the 1 : 1 : 2 molar ratio), an alternative possibility is weak complex formation between PBr(cat) and the base, giving rise to a broad exchange peak which may not have been detected. Similar behaviour, with formation of either mixed $Br^-$ and $Br_3^-$ counter ions, or $Br_3^-$ alone as the counter ion, was found with bidentate pyridine bases, as indicated below.

A 1 : 1 : 1 mixture of PBr(cat), $Br_2$, and bipy in $CH_2Cl_2$ yielded an orange precipitate and a single $^{31}P$ resonance at −198.2 p.p.m., assigned to the complex cation $[PBr_2(cat)(bipy)]^+$. Again only one n.m.r. signal was seen, indicating the formation of one isomer only or rapid exchange between the two possible geometric isomers. The cation $[PCl_2(cat)(bipy)]^+$ similarly gave a single peak only in $CH_2Cl_2$, although evidence for the existence of a second isomer was found from one experiment in $PhNO_2$ as solvent.[4] When the same solution was monitored after 1 h, no signal could be detected. The solid product was isolated, and analysed as $[PBr_2(cat)(bipy)]_2[Br_3]Br$. The expected Raman band for the $Br_3^-$ ion was observed at 173 cm⁻¹.[18] The solid gave a broad $^{31}P$ peak at −198 ± 3 p.p.m., in excellent agreement with the solution shift. The compound $[PBr_2(cat)(bipy)][BBr_4]$ was also prepared; its solid-state $^{31}P$ spectrum consisted of a broad peak at −193.5 ± 4 p.p.m., and in $PhNO_2$ it gave a single resonance at −195.1 p.p.m. Its i.r. spectrum between 650 and 250 cm⁻¹ (Nujol mull) was very similar to that of $[PBr_2(cat)(bipy)]_2[Br_3]Br$, except for an additional broad band at 590 cm⁻¹, readily assigned to the $BBr_4^-$ ion.[19,20] It gave a solid-state $^{11}B$ resonance at −53.5 p.p.m., in good agreement with the value of −52.5 p.p.m. reported for $[NEt_4][BBr_4]$,[21] while the shift of −44.5 p.p.m. in $PhNO_2$ also agrees well with literature values [22–24] for this ion in solution. A Raman frequency of 244 cm⁻¹ was ascribed to the $BBr_4^-$ ion.[25]

When an equimolar amount of 1,10-phenanthroline was added to a PBr(cat)–$Br_2$ mixture in $CH_2Cl_2$, a yellow precipitate was immediately formed and no $^{31}P$ solution spectrum could be observed. The product was isolated, and analysed as $[PBr_2(cat)(phen)][Br_3]$. Unfortunately no solid-state n.m.r. signals could be detected from this salt. A Raman band at

**Table 2.** I.r. frequencies (650—400 $cm^{-1}$) for $PBr(cat)_2$ and related species

| Compound | $\nu/cm^{-1}$ |
|---|---|
| $PBr(cat)_2$ | 636s, 590w, 578s, 552br, 538w, 504br, 470w, 420s, 400w |
| $[PBrCl(cat)_2]^-$ | 624s, 584m, 572s, 560w, 530s, 500s, 470br, 430m, 420w |
| $[PCl_2(cat)_2]^-$ * | 640s, 628w, 590m, 578m, 562w, 550w, 540m, 530w, 500s, 470w, 460s, 430s |

* Ref. 4.

**Table 3.** I.r. frequencies (650—250 $cm^{-1}$) of some Lewis base derivatives of $PBr(cat)_2$

| Compound | $\nu/cm^{-1}$ |
|---|---|
| $PBr(cat)_2{\cdot}py$ | 650s, 620w, 610w, 586w, 572m, 546s, 510w, 504m, 460m, 426s, 366br, 320m, 306w |
| $[P(cat)_2(bipy)]_2[Br_3]Br$ | 640s, 616s, 564s, 542s, 526m, 480s, 460w, 440m, 432s, 416w, 400m, 350m, 320w, 300w, 290w, 284w |
| $[P(cat)_2(phen)]_2[Br_3]Br$ | 646s, 626s, 600s, 572m, 564m, 510s, 500s, 472s, 450s, 438s, 400w, 390w, 350m, 330w, 300w, 280w |

168 $cm^{-1}$ was ascribed to a vibration of a symmetrical tribromide ion,[18] although different frequencies have been reported for unsymmetrical $Br_3^-$ ions.[26]

The results thus show that $PBr_3(cat)$ possesses Lewis acid properties towards pyridine bases, resulting in the formation of six-co-ordinate cations. Similar compounds were formed by bipy and phen with $PCl_3(cat)$, but the molecular species $PCl_3(cat){\cdot}py$ (both isomers) was formed preferentially by py, even though $[PCl_2(cat)(py)_2]^+$ was also present.[4] With $PBr_3(cat)$ the ionic form $[PBr_2(cat)(py)_2]^+$ is clearly favoured by rapid precipitation of the complex from $CH_2Cl_2$.

(*b*) $PBr(cat)_2$.—This compound had not been reported previously in the literature, but was prepared as described in the Experimental section. It was readily soluble in organic solvents, and $^{31}P$ chemical shifts of $-27.5$ p.p.m. in $CH_2Cl_2$ and $-29.1$ p.p.m. in $PhNO_2$ were recorded, as well as a broad solid-state resonance at $-29.1$ p.p.m. These results suggest a five-co-ordinate molecular structure for the compound, possibly similar to that of $PCl(cat)_2$.[27]

When $NBu^n_4Br$ was added to a solution of $PBr(cat)_2$ in $CH_2Cl_2$, a slight upfield movement of the single resonance to $-29.1$ p.p.m. was observed. This was not considered significant, and no further upfield shift took place on addition of excess $Br^-$ ions, indicating that $[PBr_2(cat)_2]^-$ is not formed under the experimental conditions The route of decomposition to a phosphorus(III) compound, with formation of $Br_3^-$ ions, is not open to $PBr(cat)_2$. Rather surprisingly, however, $PBr(cat)_2$ showed acceptor properties towards chloride ions. Addition of $N(n\text{-}C_5H_{11})_4Cl$ to a solution of $PBr(cat)_2$ in $PhNO_2$ caused the single $^{31}P$ peak to move upfield, and a limiting shift of $-69.5$ p.p.m. was established, ascribed to the $[PBrCl(cat)_2]^-$ ion. A white solid isolated from equimolar amounts of $N(n\text{-}C_5H_{11})_4Cl$ and $PBr(cat)_2$ analysed as $[N(n\text{-}C_5H_{11})_4][PBrCl(cat)_2]$. No solid-state n.m.r. signal could be obtained, but its i.r. spectrum between 650 and 400 $cm^{-1}$ showed marked differences from that of $PBr(cat)_2$, and also differed from that[4] of $[PCl_2(cat)_2]^-$ (Table 2). $PCl(cat)_2$ similarly showed acceptor properties towards chloride ions, and salts containing the $[PCl_2(cat)_2]^-$ ion have been isolated,[4] but its reaction with bromide ions was not investigated.

When pyridine was added to a dilute solution of $PBr(cat)_2$ in $CH_2Cl_2$, a single $^{31}P$ resonance was found at $-85.5$ p.p.m., attributed to the molecular species $PBr(cat)_2{\cdot}py$, or an equilibrium peak between $PBr(cat)_2$ and $PBr(cat)_2{\cdot}py$.[4,7] Although two isomers are possible for $PBr(cat)_2{\cdot}py$, the observation of a single peak suggests either preferential formation of one isomer or a rapid equilibrium between them. Similar behaviour has been observed in the $PCl(cat)_2$–py system, although in this case the ionic species $[P(cat)_2(py)_2]^+$ was also detected.[4,7] The solution deposited a white solid after some time, and the solution signal disappeared, showing that complete reaction had occurred. When the experiment was repeated on a preparative scale using more concentrated solutions, the precipitate formed immediately. It analysed as the 1 : 1 molecular adduct $PBr(cat)_2{\cdot}py$, but failed to give a solid-state $^{31}P$ n.m.r. spectrum.

Addition of either bipy or phen to a solution of $PBr(cat)_2$ in $CH_2Cl_2$ resulted in a yellow precipitate, instantly in the case of bipy where no solution peak was apparent. Two resonances were found for the phen solution, however, at $-29.1$ [$PBr(cat)_2$] and $-90.4$ p.p.m. The higher field resonance was assigned to the $[P(cat)_2(phen)]^+$ cation, and is in good agreement with the reported value of $-89.9$ p.p.m. for $[P(cat)_2(phen)][SbCl_6]$ in $PhNO_2$.[4] When more phen was added, the peak from the starting material disappeared, showing that reaction was complete. Only the bipy adduct gave a solid-state signal, at $-85.5 \pm 2$ p.p.m. This compares with a solution shift of $-93.4$ p.p.m. for $[P(cat)_2(bipy)][SbCl_6]$ in $PhNO_2$.[4] {A larger difference between solid-state and solution shifts has been observed previously[4] for $[P(cat)_2(phen)]^+$.} Both solid complexes analysed approximately as $[P(cat)_2L]_2[Br_3]Br$ (L = bipy or phen). The formation of the $Br_3^-$ ion in these reactions is rather puzzling, since the only source of bromine was $PBr(cat)_2$, and there is no ready route for its decomposition to a phosphorus(III) species, unlike $PBr_3(cat)$, $PBr_4Ph$, or $PBr_5$. The Raman spectrum of the phen complex showed the expected band for $Br_3^-$ at 167 $cm^{-1}$.[18] The i.r. spectra of the adducts with pyridine bases differed appreciably from that of $PBr(cat)_2$ below 650 $cm^{-1}$, and the frequencies are listed in Table 3.

Hence $PBr(cat)_2$ shows acceptor properties towards $Cl^-$ ions, py, bipy, and phen, but not towards $Br^-$ ions under the experimental conditions. Its reactions with pyridine bases appear to be simpler than those of $PCl(cat)_2$, with only a single phosphorus-containing species being formed in each instance, possibly stabilised by rapid precipitation in the case of py. The bidentate ligands seem to displace $Br^-$ readily, unlike $PCl(cat)_2$ where phen in particular reacted very slowly,[4] although it was noticeable here that precipitation of the complex was much faster with bipy than with phen. The apparent instability of $[PBr_2(cat)_2]^-$ explains the non-observation of a second exchanging peak, as was found in the $PCl(cat)_2$–bipy reaction.[4]

(*c*) $PBr_4Ph$ *and* $[PBr_3Ph][BBr_4]$.—Tetrabromo(phenyl)phosphorane was first prepared by Michaelis and Köhler,[28] and may be readily obtained by bromination of $PBr_2Ph$ in an inert solvent.[6] A chemical shift of 23.0 p.p.m. in 25-oleum has been ascribed to the $PBr_3Ph^+$ cation, which is also known in salts such as $[PBr_3Ph][BBr_4]$, and in admixture with the other cations in the series $[PCl_nBr_{3-n}Ph]^+$.[6] The solid-state spectrum of the compound consisted of a broad resonance at 14.6 p.p.m., with apparent shoulders at 22.7 and 1.6 p.p.m., suggesting an ionic structure $[PBr_3Ph]^+Br^-$, similar to that of $PBr_5$. The compound was found to be insoluble in common organic solvents, and no solution data could be obtained, providing further support for an ionic rather than a covalent formulation.

When bromide ions (in the form $NR_4Br$) were added to a slurry of $PBr_4Ph$ in $CH_2Cl_2$ or $PhNO_2$, the only $^{31}P$ signal observed was at 153.1 p.p.m., readily assigned to $PBr_2Ph$.[29] The solutions were red, suggesting that reaction (4) occurs

$$PBr_4Ph + Br^- \longrightarrow PBr_2Ph + Br_3^- \qquad (4)$$

readily. This parallels the reactions of $PBr_5$ and $PBr_3(cat)$ with bromide ions. A solution of $PBr_4Ph$ in neat pyridine gave a single resonance at 146.0 p.p.m., slightly to high field of the literature value for $PBr_2Ph$.[29] Similarly the addition of excess pyridine to a slurry of $PBr_4Ph$ in $CH_2Cl_2$ led to a signal at 148.4 p.p.m. This upfield movement relative to $PBr_2Ph$ could be due to weak complex formation between $PBr_2Ph$ and py, equation (5), similar to that found for $PCl_3$ and py where a

$$PBr_4Ph + 2\ py \longrightarrow PBr_2Ph{\cdot}py + Br_2{\cdot}py \qquad (5)$$

single exchanging peak was detected.[1] No bromine colour was observed, possibly because of formation of the pyridine-bromine adduct, as shown in equation (5). When either bipy or phen was added to a slurry of $PBr_4Ph$ in $CH_2Cl_2$ or $PhNO_2$, no solution signals were detected, but a yellow precipitate separated. The product was prepared and isolated from $CH_2Cl_2$ in both instances, but analysed as $PBr_4Ph$, as well as giving an identical i.r. spectrum to the starting material. The results indicate that under the experimental conditions $PBr_4Ph$ has no acceptor properties towards pyridine bases, unlike $PCl_4Ph$ which forms stable six-co-ordinate compounds.[3]

The salt $[PBr_3Ph][BBr_4]$ was isolated as a white solid from stoicheiometric amounts of $PBr_4Ph$ and $BBr_3$. It gave a $^{31}P$ shift of 24.2 p.p.m. in $PhNO_2$, and a broad resonance at 21.1 p.p.m. in the solid state. Its $^{11}B$ solution spectrum in $PhNO_2$ consisted of a single peak at −38.9 p.p.m., close to literature values for the $BBr_4^-$ ion,[22–24] and the solid gave a broad signal, also at −38.9 p.p.m. Its i.r. spectrum was similar to that of $PBr_4Ph$, except for an additional broad band at 584 $cm^{-1}$, ascribed to the $BBr_4^-$ ion.[19,20] Addition of stoicheiometric quantities of either bipy or phen to a solution of $[PBr_3Ph][BBr_4]$ in $PhNO_2$ caused the appearance of a yellow precipitate, and no solution signals could be detected. The bipy complex was obtained on a preparative scale from $CH_2Cl_2$ solution as a yellow solid, which analysed as a 1 : 1 adduct and is formulated as $[PBr_3Ph(bipy)][BBr_4]$. No solid-state $^{11}B$ spectrum could be obtained for the complex, and the only signal in the corresponding $^{31}P$ spectrum was a sharp peak at −1.6 p.p.m., ascribed to an impurity since a resonance at much higher field is expected for the cation. It gave a single $^{11}B$ resonance in $PhNO_2$ solution at −42.3 p.p.m., assigned to the $BBr_4^-$ ion.[22–24] The phen complex was similarly isolated, and analysed as $[PBr_3Ph(phen)][BBr_4]$. No solid-state $^{31}P$ signal was found, but a broad $^{11}B$ resonance at −37.7 p.p.m. was detected, similar to values for other tetrabromoborates, although some variation with the cation has been observed.[21] The compound was insoluble in all common solvents attempted, and no solution data could be obtained. Despite these limitations, there is clear evidence for the formation of (presumably six-co-ordinate) compounds in these systems, showing that the $[PBr_3Ph]^+$ cation does possess some acceptor properties. The complexes were probably stabilised in this instance by rapid precipitation. It is plain, nevertheless, that the Lewis acid properties of $PBr_4Ph$ and its derivatives are markedly inferior to those of their chloro-analogues,[3] as reflected in the different structures of the phosphoranes themselves, where $PCl_4Ph$ is molecular in the solid [30] and $PBr_4Ph$ has a phosphonium salt structure.

The results overall show that several six-co-ordinate phosphorus(V) compounds with bromide ligands present may be prepared, but their stability is generally lower than that of analogous chloro-compounds unless rapid precipitation occurs. Anionic complexes in particular are noticeably reluctant to form, partly because of competing reactions between some bromophosphoranes [$PBr_5$, $PBr_3(cat)$, $PBr_4Ph$] and bromide ions. $[PBr_2(cat)_2]^-$ ions were not encountered under the experimental conditions, but $PBr(cat)_2$ did show acceptor properties towards chloride ions.

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