Donor-Acceptor Complexes between Simple Phosphines. First Structural Data for an Almost Forgotten Class of Compounds

Gerhard Müller, Hans-Joachim Matheus a, and Martin Winkler b

Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, D-78464 Konstanz, Germany
a Present address: in – integrierte informationssysteme GmbH, Am Seerhein 8, 78467 Konstanz, Germany
b Present address: Industrielack AG, Alpenblickstr. 3-5, 8853 Lachen, Switzerland

Reprint requests to Prof. Dr. Gerhard Müller. E-mail: gerhard.mueller@chemie.uni-konstanz.de

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Hypervalence, Phosphines, Lewis Acid-Base Adducts

Lewis acid-base adducts between simple phosphines have been structurally characterized for the first time in the form of \( \text{Me}_3\text{P} \cdot \text{PBr}_3 \) (I) and \( \text{Me}_3\text{P} \cdot \text{PBz}'_3 \) (2; \( \text{Bz}' = 3,5\text{-dimethyl-benzyl} \)). On the basis of its solid-state structure the bonding situation in I may be described as intermediate between a neutral donor-acceptor complex containing hypervalent phosphorus(III) and an ion pair, according to the resonance formulae \( \text{Me}_3\text{P} \rightarrow \text{PBr}_3 \rightleftharpoons \left[ \text{Me}_3\text{P} \cdot \text{PBr}_3 \right]^+ \text{Br}^- \). The weak (incomplete) bond formation to the third bromine atom clearly reflects the reluctance of trivalent phosphorus to accommodate more than four electron pairs in its valence shell. (Crystal data for I: monoclinic \( \text{P}_2_1/n \), \( a = 7.142(3) \), \( b = 16.844(2) \), \( c = 8.139(4) \AA, \beta = 106.24(2)^\circ, Z = 4 \). Both compounds have short P-P bonds (I: 2.264(2); 2: 2.236(2) \AA). The results are compared with previous IR/Raman and NMR investigations on 1:1 and 2:1 adducts between organophosphines (as donors) and phosphorus trihalides (as acceptors).

Introduction

Lewis acid-base adducts between simple phosphines as donors and phosphines as acceptors have already been reported in 1958 [1]. These early investigations were based mainly on vapor pressure measurements as an indicator for complex formation and yielded, inter alia, evidence for 2:1 adducts like \( \text{Me}_3\text{P}_2\text{PCl}_3 \) of unknown structure. In sharp contrast to numerous investigations on Lewis acid-base adducts between phosphine donors and acceptor molecules of the heavier main group elements, including arsenic, antimony, and bismuth [2], formation, structure, and bonding in adducts between phosphines as donors and acceptors have received astonishingly little attention as yet. Adducts \( \text{Me}_3\text{P}_2\text{PX}_3 \) (\( X = \text{Cl}, \text{Br} \)) with 2:1 stoichiometry were mentioned again in 1970, but the data reported were limited to a (correct) elemental analysis for the bromo compound [3]. In 1976 a detailed vibrational study (IR/Raman) of \( \text{Me}_3\text{P}_2\text{PBn}_3 \) was reported [4]. It interpreted \( \text{Me}_3\text{P}_2\text{PBn}_3 \) as a covalent 2:1 adduct between two molecules \( \text{PMe}_3 \) as donors and one molecule \( \text{PBr}_3 \) as acceptor, the latter containing a six-coordinate pseudo-octahedral central phosphorus atom (including the lone pair) with the \( \text{PMe}_3 \) substituents being trans to each other (formula I).

In 1985 an extensive \( ^{31}\text{P} \) NMR investigation of the complex formation between \( \text{PBn}_3 \) and \( \text{PPhMe}_3 \) as donors and \( \text{PX}_3 \) (\( X = \text{Cl}, \text{Br} \)) as acceptors was undertaken in methylene chloride solution [5, 6]. It clearly showed the formation of 1:1 adducts. In the case of \( \text{PCl}_3 \) also 2:1 adducts were observed [7]. The adducts were formulated as ion pairs II and III.

These two descriptions (covalent versus ionic) are prototypal as they represent the possible bonding extremes for such simple adducts. For a 1:1 complex the covalent adduct would be \( \text{R}_3\text{P} \rightarrow \text{PX}_3 \) which contains a hypervalent P(III)X_3 center with a...
valence shell of five electron pairs. As indicated in formula I, in a covalent 2:1 adduct (R3P)2PX3 there would be even six electron pairs in the valence shell of the central phosphorus(III) atom.

Hypervalence (the formal accomodation of more than 4 electron pairs in the valence shell of a main group element) [8] at phosphorus(III) has been well documented [9, 10], the majority of cases being those with five electron pairs at the P(III) atom. To our knowledge, the coordination number 6 at P(III) has recently been tried to achieve by intramolecular nitrogen coordination employing far more elaborate ligands [12].

We report here on an investigation of the adduct formation between PMe3 and PBz'Me2 (Bz' = 3,5-dimethylbenzyl) as donors and PBr3 as acceptor in solution (by 31P NMR), and on the structure of the 1:1 adducts (Me3P)PBr3 (I) and (Me3P)PBr2Bz' (2) in the solid state (by X-ray diffraction).

Results and Discussion

Reactions

Our experiments were first aimed at the synthesis of 2:1 adducts between the organophosphines PMe3 and PBz'Me2 and PBr3. The addition of excess PMe3 to PBr3 at room temperature without solvent results in intractable reaction mixtures. Therefore, further attempts to synthesize adducts between the components were undertaken at -80 °C. If a two-fold excess of PMe3 is added to PBr3 (both in Et2O) at -80 °C a slightly yellow solid rapidly forms (see Experimental Section). After removal of solvent and excess PMe3 and warming to room temperature the solid turns bright yellow to orange. The color change is due to redox reactions resulting in P(V) species (mainly Me3PBr2) and methyl polyphosphanes. Above 60 - 80 °C the solid turns brown-orange and no further color change is observed. If the solid is constantly kept below -40 °C without solvent, it may be stored largely unchanged for several days. It is virtually insoluble in diethyl ether, benzene and toluene, and slightly soluble in chloroform. Good solubility is observed in methylene chloride and acetonitril. In both solvents the decomposition (disproportionation) of the compounds is markedly faster, however, making immediate NMR measurements at low temperatures mandatory. They were done exclusively in CH2Cl2 and indicated the formation of predominantly the 1:1 adduct (Me3P)PBr3 and, to a lesser extent, the 2:1 adduct (Me3P)2PBr3 (see below).

Adduct synthesis between PMe3 and PBr3 was also attempted at -80 °C in the absence of solvent by adding PBr3 to a two- and a three-fold excess of PMe3. In both cases mainly the 1:1 adduct is formed.

Reactons between PBz'Me2 and PBr3 were carried out in Et2O at -50 °C by adding PBr3 to a two-fold excess of PBz'Me2. As in the reaction of PMe3 with PBr3, the formation of 1:1 and 2:1 adducts was observed by NMR.

NMR characterization

The yellow solids obtained in the reactions in Et2O as described above were dissolved in CD2Cl2 and examined by 31P NMR (Table 1). The spectra clearly indicate the presence of both the 1:1 as well as the 2:1 adducts, the 1:1 species being clearly

<table>
<thead>
<tr>
<th>System</th>
<th>1:1 Adduct</th>
<th>2:1 Adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe3/PBr3</td>
<td>1:1</td>
<td>2:1</td>
</tr>
<tr>
<td>PBz'Me2/PBr3</td>
<td>1:1</td>
<td>2:1</td>
</tr>
<tr>
<td>P' Bu3/PBr3 and PPhMe2/PBr3</td>
<td>1:1</td>
<td>2:1</td>
</tr>
</tbody>
</table>

Table 1. 31P NMR data for the systems PMe3/PBr3 and PBz'Me2/PBr3. Literature values for P' Bu3/PBr3 and PPhMe2/PBr3 are included for comparison.
the majority product. The amount of the 2:1 adduct formed under these conditions is at most 10% at low temperatures. The individual values are virtually unchanged from -60 to 0 °C but the amount of the 2:1 adduct is clearly diminished at higher temperatures. The $^{31}$P shifts and P-P coupling constants of the 1:1 adducts agree fairly well with those observed previously in the systems P$n$Bu$_3$/PBr$_3$ and PPhMe$_2$/PBr$_3$ (Table 1) [5, 13]. In contrast to those findings, we did not observe species like [R$_3$P=P-PR$_3$]$^+$ X$^-$ and [R$_3$P-PX-PX-PR$_3$]$^{2+}$ 2X$^-$, however.

The 1:1 and 2:1 adducts in the previous study [5] were formulated as ion pairs II and III. Although we do not have direct evidence, we are also inclined to formulate our adducts as ion pairs. We do so because methylene chloride is a good ionizing solvent, and the structure determinations on (Me$_3$P)PBr$_3$ (1) and (Me$_3$P)PBr$_2$Bz$'$ (2) reported below indicate a partial ion-pair character of these compounds also in the solid state.

**Solid-state structure determinations**

No single crystals suitable for X-ray diffraction could be obtained in the above experiments. This is certainly due to the mixture of compounds present, and to the rapid decomposition of the CH$_2$Cl$_2$ solutions. Yellow single crystals of the 1:1 adducts (Me$_3$P)PBr$_3$ (1) and (Me$_3$P)PBr$_2$Bz$'$ (2) could be obtained by slow diffusion of PMe$_3$ into toluene solutions of PBr$_3$ and PBr$_2$Bz$'$, respectively (see Experimental Section) [14].

(Me$_3$P)PBr$_3$ (1) crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units in the unit cell. Fig. 1 shows the molecular structure, important structural parameters are summarized in Table 2. The donor PMe$_3$ is firmly bonded to the acceptor PBr$_3$. The bonding angles at P$_2$ are grouped around the tetrahedral value and are thus enlarged with respect to uncoordinated, “free” PMe$_3$, while the P-C distances (Table 2) are slightly shorter than those in PMe$_3$ [15], as is always observed when phosphines act as strong donors. The P-P bond (2.264(2) Å) is at the upper end of the range encompassed in a wide variety of P-P compounds with coordination numbers 3, 4, [16] and 5 [17] at phosphorus. Of particular interest is the geometry at the acceptor phosphorus atom P$_1$. While two of the bromine atoms are bonded closer to it (P-Br$_1$ 2.424(2), P-Br$_2$ 2.250(2) Å), the third shows a longer P-Br distance (P-Br$_3$ 2.677(2) Å). It is the latter bromine atom which bridges two of the acceptor phosphines resulting in a dimer with crystallographic inversion symmetry (Fig. 1). It should be noted that the bridging bromine has strongly unequal P-Br$_3$ distances, the second one (Br$_3$-P$_1'$) being 3.327(2) Å. The angle P$_1$-Br$_3$-P$_1'$ is 93.67(5)$^\circ$. It should also be noted
that the bromine atom Br1 trans to the more strongly bonded bridging bromine Br3 has a longer P-Br bond than Br2 which is trans to the weaker bonded Br3'. The overall geometry at the acceptor phosphorus atom is octahedral with one lone pair. Although this is in agreement with VSEPR theory [18] for a total of 6 electron pairs, we would like to point out that the geometry at P1 may be described alternatively as pyramidal if only the shortest bonds to P2, Br1, Br2 are considered (solid bonds in Fig. 1). The longer ones to Br3/Br3' are then formed along the vectors of the bonds P-Br1 and P-Br2, respectively, and, in view of their inherent weakness, may be regarded as secondary bonds [19-21]. Dimer formation through secondary P-Br bonds in a way similar to 1 has also been observed for the anion in $[\text{Me}_3\text{P}]^+\text{PBr}_3^-$ [11 a]).

On the basis of its molecular structure, bonding in 1 is probably best described as intermediate between a neutral donor-acceptor complex containing hypervalent phosphorus(III) and an ion pair, according to the resonance formulae $\text{Me}_3\text{P} \rightarrow \text{PBr}_3 \rightarrow \text{[Me}_3\text{P-PBr}_3]^+\text{Br}^-$. Despite the loose dimer formation, the weak (incomplete) bond formation to the bridging bromine atoms clearly reflects the reluctance of trivalent phosphorus to accommodate more than four electron pairs in its valence shell.

$\text{(Me}_3\text{P})\text{PBr}_3\text{Bz'}$ (2) crystallizes in the orthorhombic space group $P 2_12_12_1$ with 4 formula units in the unit cell. Fig. 2 shows the molecular structure, important structural parameters are summarized in Table 3. As in 1, the donor PMe$_3$ is firmly bonded to the acceptor phosphine PBr$_3$Bz'. The P-P bond in 2 (2.236(2) Å) is even shorter than in 1. The coordination at P1 is completed by two bromine atoms and the benzyl substituent. Again, one of the bromine atoms (Br1) is firmly bonded (P1-Br1 2.327(2) Å) while the second one is substantially further away (P1-Br2 2.957(2) Å). The latter distance is even longer than the corresponding one in 1. Thus, the inferior acceptor properties of PBr$_3$Bz' as compared to PBr$_3$ are not manifested in a longer P-P (donor-acceptor) bond but in a more extensive dissociation of one bromine atom. In other words, the ionic character of 2 according to the formula $[\text{Me}_3\text{P-PBr}_3\text{Bz'}]^+\text{Br}^-$ is more pronounced than in 1. No dimer formation is observed in 2. Although at first glance the overall geometry at P1 may be regarded as trigonal-bipyramidal with one lone pair in equatorial position, we prefer a description as pyramidal (solid bonds in Fig. 2) with a weak secondary bond to one bromine (Br2; open bond in Fig. 2) along the bond vector to the most electronegative substituent Br1 at P1. We do so because the equatorial angle P2-P1-C4 (100.8 (2)°) is substantially smaller than the 120° standard. It seems improbable to us that this is entirely due to lone-pair repulsion.

**IR spectra and conclusions**

We have shown that PMe$_3$ forms stable 1:1 adducts with the bromophosphines PBr$_3$ and PBr$_2$Bz' which can be isolated as crystalline solids. In the
solid state they are partially ionic. The adduct 2 has more ion-pair character than 1 which is due to the reduced acceptor properties of $\text{PBr}_3$ as compared to PBr$_3$. In good ionizing solvents the dissociation of the adducts into ion pairs should be even more pronounced. There is still the question whether of the adducts into ion pairs should be even more so to PBr$_3$. In good ionizing solvents the dissociation of 2:1 adducts between alkylphosphines and bromophosphines (or other halophosphines), which are observable in solution, are stable enough to be isolated in the solid state, and what their exact nature (covalent nature of adduct 1 or ion pairs with bromide counterions) would be. Under the conditions we obtained single crystals of the 1:1 adducts 1 and 2, the formation of 2:1 adducts is highly improbable, but this does not rule out their existence [3]. As our results show that already the 1:1 adducts are partially ion pairs, 2:1 adducts should be even more so [22]. Hence, an entirely covalent nature, as implied by formula 1, is improbable. As 1 was suggested on the basis of detailed vibrational spectra (770 - 100 cm$^{-1}$) of solid (Me$_3$P)$_2$PBr$_3$ [4], we determined the IR spectra of 1 and 2 in the range 710 - 30 cm$^{-1}$ in polyethylene. The spectra are summarized in Table 4 together with the IR data reported for (Me$_3$P)$_2$PBr$_3$ [4]. In order to identify bands of decomposition products, IR spectra of decomposed samples of 1 and 2 were also recorded. They are included in Table 4. As can be clearly seen, virtually all of the IR bands reported for (Me$_3$P)$_2$PBr$_3$ [4] agree with ours of the 1:1 adduct or its decomposition products. We therefore conclude that the presumed 2:1 adduct (Me$_3$P)$_2$PBr$_3$ investigated in the vibrational study [4] was essentially the 1:1 adduct (Me$_3$P)PBr$_3$ (1).

**Experimental**

All experiments were carried out under exclusion of air and moisture under purified dry argon in standard Schlenk tube glassware or in a glove box. Solvents were dried under argon over sodium-potassium alloy (Et$_2$O) or CaH$_2$ (CHCl$_3$/CDCl$_3$, CH$_2$Cl$_2$/CD$_2$Cl$_2$) and freshly distilled prior to use. Reagents: PMe$_3$ (Aldrich), PM$_3$ (23), PBr$_3$/Bz’ [24], PBr$_3$/Et$_2$O [24]. Spectra: $^{31}$P NMR: JEOL JNM-GX-400 (162 MHz; ext. 85% H$_3$PO$_4$); FT-IR spectra: Perkin-Elmer System 2000 in dry, oxygen-free polyethylene (UVASOL; Merck).

**Reaction of PMe$_3$ with PBr$_3$ in Et$_2$O**

At -80 °C 5 ml (3.7 g, 48.3 mmol) of PMe$_3$ in 10 ml of Et$_2$O was added dropwise to a stirred solution of 2 ml (5.8 g, 21.3 mmol) of PBr$_3$ in 10 ml of Et$_2$O. A slightly yellow precipitate formed immediately which was separated by centrifugation and decantation of the liquid.

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Table 4. Infrared data (cm$^{-1}$) for (Me$_3$P)$_2$PBr$_3$, 1, 2, and the decomposition products of 1 and 2.

<table>
<thead>
<tr>
<th>(Me$_3$P)$_2$PBr$_3$ $^a$</th>
<th>1 $^b$ (dec.) $^c$</th>
<th>2 $^b$ (dec.) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>671 (mw)</td>
<td>673 (w)</td>
<td>678 (vs)</td>
</tr>
<tr>
<td>638 (vw)</td>
<td>547 (vw)</td>
<td>545 (vw)</td>
</tr>
<tr>
<td>433 (w)</td>
<td>412 (vw)</td>
<td>411 (vs)</td>
</tr>
<tr>
<td>390 (s)</td>
<td>391 (s)</td>
<td>390 (m, sh)</td>
</tr>
<tr>
<td>371 (m, sh)</td>
<td>376 (s)</td>
<td>383 (s, sh)</td>
</tr>
<tr>
<td>334 (w)</td>
<td>315 (w)</td>
<td>339 (vw, sh)</td>
</tr>
<tr>
<td>~ 290 (w, sh)</td>
<td>277 (s)</td>
<td>268 (w)</td>
</tr>
<tr>
<td>~ 274 (m)</td>
<td>254 (s)</td>
<td>245 (s)</td>
</tr>
<tr>
<td>~ 249 (m)</td>
<td>217 (m, br)</td>
<td>208 (w)</td>
</tr>
<tr>
<td>~ 194 (mw, br)</td>
<td>152 (w)</td>
<td>159 (vw)</td>
</tr>
<tr>
<td>132 (m)</td>
<td>90 (w, sh)</td>
<td>85 (s, br)</td>
</tr>
<tr>
<td>70 (vw)</td>
<td>66 (w)</td>
<td></td>
</tr>
<tr>
<td>52 (vw)</td>
<td>51 (w)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. [4]. $^b$ The numbers in one row do not necessarily denote identical vibration modes for the different compounds. $^c$ The IR spectra of the decomposition products of 1 and 2 were obtained by dissolving the adducts in CH$_2$Cl$_2$ and warming the solutions to the boiling point whereupon they turn orange. After removing the solvent, amorphous orange solids remain the IR spectra of which were recorded.
It was dried at \(-40\) °C \textit{in vacuo} and used for the NMR measurements.

\textbf{Reaction of PMe}_3 \textit{with PBr}_3 \textit{without solvent}

At \(-80\) °C 1 ml (2.9 g, 10.6 mmol) of PBr\(_3\) was added dropwise to 3 ml (2.2 g, 29.0 mmol) of PMe\(_3\) under heavy stirring. A white precipitate formed immediately. The reaction mixture including excess liquid PMe\(_3\) was left at \(-30\) °C. After several days additional small yellowish crystals formed which proved to be the 1:1 adduct according to diffractometer measurements. By NMR also the bulk product was essentially the 1:1 adduct.

\textbf{Reaction of PBz’Me\(_2\) with PBr\(_3\) in Et\(_2\)O}

At \(-50\) °C 0.5 ml (1.3 g, 5 mmol) of PBr\(_3\) was added dropwise to a stirred solution of 1.8 g (9.9 mmol) of PBz’Me\(_2\) in 7 ml of Et\(_2\)O. A yellowish precipitate formed which was separated by removing all volatiles \textit{in vacuo}. It was investigated by NMR.

\textbf{X-ray structure analyses}

Single crystals of 1 and 2 were obtained from toluene. This was achieved by connecting two small Schlenk tubes with a glass tube. In one of the Schlenk tubes a solution of 2 ml of the respective phosphorus bromide in 10 ml of toluene was placed, while the other contained 2 ml of PMe\(_3\) in 10 ml of toluene. On standing for 2 to 3 days at 4 °C the more volatile PMe\(_3\) slowly evaporated into the other Schlenk tube containing the phosphorus bromide solution, whereupon yellow single crystals suitable for X-ray diffraction formed. They were mounted under nitrogen on glass fibers in an inert oil drop at 153(2) K [25]. The crystals were examined directly on a four-circle diffractometer (Enraf-Nonius CAD4) with graphite-monochromated Mo-K\(_\alpha\) radiation (\(\lambda = 0.71069 \text{ Å}\)). The crystal systems indicated by preliminary search and indexing procedures were checked for higher metrical symmetry by reduced-cell calculations (DELOS [26], LePage [27]). Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle reflexions from various parts of reciprocal space carefully centered on the diffractometer. Lp corrections were applied. Decay corrections (1: \(-0.5\%\); 2: \(-1.5\%\)) were not deemed necessary. Absorption was corrected for empirically on the basis of \(\psi\) scans around the diffraction vectors of 9 reflexions near \(\chi = 90^\circ\) which served to evaluate the transmission curves (1:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
  & 1 & 2 \\
\hline
Crystals & yellow prisms & yellow prisms \\
Crystal size [mm\(^3\)] & 0.20 \times 0.25 \times 0.30 & 0.2 \times 0.3 \times 0.4 \\
Formula & C\(_{3}\)H\(_{10}\)Br\(_3\)P\(_2\) & C\(_{12}\)H\(_{20}\)Br\(_2\)P\(_2\) \\
\(M_r\), [g/mol] & 346.74 & 386.02 \\
Crystal system & monoclinic & orthorhombic \\
Space group & \(P2_1/n\) (No. 14) & \(P2_2_2_2\) (No. 19) \\
a [Å] & 7.142(3) & 7.063(2) \\
b [Å] & 16.844(2) & 8.578(2) \\
c [Å] & 8.139(4) & 26.158(4) \\
\(\beta\) [deg.] & 106.24(2) & 90.0 \\
V [Å\(^3\)] & 940.1(6) & 1584.8(6) \\
\(Z\) & 4 & 4 \\
\(\rho_{\text{calc}}\) [g/cm\(^3\)] & 2.450 & 1.618 \\
\(\mu\) (Mo-K\(_\alpha\)) [cm\(^{-1}\)] & 131.3 & 52.9 \\
\(F(000)\) [e] & 648 & 768 \\
Scan type & \(\theta/2\theta\) & \(\theta/2\theta\) \\
\(\Delta\omega\) [deg.] & 0.9 + 0.35 tan \(\theta\) & 0.9 + 0.35 tan \(\theta\) \\
\((\sin\theta/\lambda)_{\text{max}}\) [Å\(^{-1}\)] & 0.656 & 0.639 \\
hkl Range & +9, +22, ±10 & +9, +10, +33 \\
Reflexions measured & 2449 & 1997 \\
Independent reflexions & 2279 & 1997 \\
\(R_{\text{int}}\) & 0.028 & — \\
Reflexions with \(I > 2\sigma(I)\) & 1722 & 1691 \\
Ref. parameters/restraints & 109/0 & 146/0 \\
(shift/error)\(_{\text{max}}\) & 0.00 & 2.01 (x parameter) \\
x (Flack) & — & 0.00(2) \\
\(R(F)/wR(F^2)\); all data\(^a\) & 0.036/0.082 & 0.034/0.073 \\
GoF (\(F^2\)) & 1.02 & 1.06 \\
\(\Delta\rho_{\text{iso}}\) (max./min.) [e/Å\(^3\)] & 0.82/−1.42 & 0.47/−0.47 \\
\hline
\end{tabular}
\caption{Crystal structure data for 1 and 2.}
\end{table}

\(^{a}\ w = 1/\sigma^2 (F_0^2) + (X-P)^2 + Y-P, P = [\max(F_0^2,0) + 2 F_\sigma^2]/3. 1: X = 0.0436, Y = 0.6775; 2: X = 0.0406, Y = 0.0.\)
Table 6. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1**. (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br1</td>
<td>-0.09688(8)</td>
<td>0.78246(3)</td>
<td>0.17024(7)</td>
<td>0.0283(2)</td>
</tr>
<tr>
<td>Br2</td>
<td>0.15293(9)</td>
<td>0.90440(3)</td>
<td>0.49820(6)</td>
<td>0.0266(2)</td>
</tr>
<tr>
<td>Br3</td>
<td>0.19295(8)</td>
<td>1.05943(3)</td>
<td>0.19890(6)</td>
<td>0.0239(2)</td>
</tr>
<tr>
<td>P1</td>
<td>0.0454(2)</td>
<td>0.91419(7)</td>
<td>0.1691(2)</td>
<td>0.0176(3)</td>
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<tr>
<td>P2</td>
<td>0.3294(2)</td>
<td>0.87224(7)</td>
<td>0.1691(2)</td>
<td>0.0167(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3615(9)</td>
<td>0.7669(3)</td>
<td>0.1841(9)</td>
<td>0.029(2)</td>
</tr>
<tr>
<td>C2</td>
<td>0.333(1)</td>
<td>0.9004(4)</td>
<td>-0.0422(7)</td>
<td>0.029(2)</td>
</tr>
<tr>
<td>C3</td>
<td>0.5381(9)</td>
<td>0.9136(4)</td>
<td>0.3210(8)</td>
<td>0.032(2)</td>
</tr>
</tbody>
</table>

T_{min}: 0.57, T_{max}: 1.00; **2**: T_{min}: 0.41, T_{max}: 1.00. The structure of **1** was solved by Patterson/direct methods (DIRDIF [28]), that of **2** by automated Patterson methods (SHELXS-86 [29]). All H atoms of **1** could be located in difference syntheses. For **2** 9 out of a total of 20 H atoms could be located, the remainder was calculated at idealized geometrical positions. Refinements on F^2 of all reflexions were done with anisotropic displacement parameters for the non-H atoms. For **1** the H atoms were refined freely with isotropic displacement parameters, those of **2** were included as fixed-atom contributions (U(iso) = 0.05 Å^2) into structure factor calculations (SHELXL-93 [30]). Other programs used included ORTEP-III [31] (structure drawings) and PLATON [32] (molecular geometry).

Crystal data and numbers pertinent to data collection and structure refinement are summarized in Tabl 5. Tables 6 and 7 contain the atomic coordinates.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166437 (1), -166438 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[7] As further products the formation of [R_3P=P=PR_3]^+ X^- and [R_3P=PX-PX-PX-PR_3]^+ 2X^- was observed.
[8] As the term “hypervalence” is used here only in a formal sense, no implication as to the exact number of electrons at the hypervalent atom is intended.
[13] 2:1 adducts have been observed previously only in the reaction of $P^\text{Bu}_3$ and $P\text{PhMe}_2$ with $P\text{Cl}_3$. See ref. [5].

[14] Similar experiments with $P(\text{CH}_2\text{Ph})\text{Me}_2/P\text{Br}_3$, $P\text{Me}_2/J\text{Br}_3$, and $P\text{Br}^2/\text{Br}_3$ failed to give single crystals.


[20] The secondary bonds are expected to form along the vector of the bond to the most electronegative substituent (Br in 1 and 2), and they do so by avoiding the lone pairs of the original geometry (pyramidal without the secondary bonds), which itself may be predicted by the VSEPR rules.

[21] In 1 the angle at P1 included by the more strongly bonded Br atoms is smaller than in PBr$_3$, however ($\angle(\text{Br-P-Br}) = 101.0(4)^\circ$; $d(\text{P-Br}) = 2.220(3)$ Å; GED): K. Kuchitsu, T. Shibata, A. Yokozeiki, C. Matsumura, Inorg. Chem. 10, 2584 (1971); X-ray: R. Enjalbert, J. Galy, Acta Crystallogr. B35, 546 (1979).

[22] AlCl$_4^-$ salts of triphosphane-1,3-di-ium ions, which may be regarded as 2:1 adducts with other counterions, have been described previously: A. Schmidpeter, S. Lochschmidt, K. Karaghiosoff, W. S. Sheldrick, J. Chem. Soc., Chem. Commun. 1985, 1447.


