Direct evidence of a multicentre halogen bond: unexpected contraction of the P-XXX-P fragment in triphenylphosphine dihalides

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Triphenylhalophosphonium halides, Ph₃PX₂, form crystals comprising bridged linear cations [Ph₃P-X-X-PPh₃]⁺ where X₃ bridge is shortened from 6.56 Å in Cl-Cl-Cl to 6.36 Å in Br-Br-Br system. It is proposed that this structure is stabilised by five-centre/six-electron (5c-6e) hypervalent interactions.

The idea of multicentre hypervalent interaction, such as the three-centre, four-electron (3c-4e) bond, developed alongside those of classical covalent bonding. Extended versions of such systems such as 5c-6e cases were identified later and the area is now of substantial current interest. For example, Nakanishi and co-workers have extensively developed extended hypervalent bonds in pre-designed naphthalene and anthracene structures involving strings incorporating moderately polar functional groups as individual components. Related to this are the extensive studies by Kilian et al. of sub van der Waals contacts in peri-substituted naphthalenes. In the case of the halogens, hypervalent interactions have helped to rationalise the nature of the halogen bond (XB) connecting a covalently bonded halogen atom X to an electron-rich electron-negative atom. This extremely active current area has seen XB established in the formation of solid state structures, molecular association, medicinal chemistry and supramolecular processes. However relatively little is known about such interactions involving a P-X moiety.

Dihalophosphoranes R₂PX₂ show remarkable structural diversity and they have been the subject of investigation especially owing to the possible co-existence and interconversion of both ionic and covalent species with, in many cases, a fine energy balance between them. In the earliest studies, solid state Ph₃PX₂ (1, X = Cl; 2 X = Br) had commonly been thought to occur in just two structural types (Chart 1): the type A tetracoordinate salt [Ph₃PX]⁺X Br⁻ and the type D pentacoordinate trigonal bipyramidal species, 1D. However a third spoke-geometry B was subsequently identified for species R₂P-X-X (Chart 1, X = Br, I) bearing strong electron-donating alkyl substituents and the structure of B was studied theoretically.

We now report that we have identified a self-organised extended 5c-6e PXXXP motif. Our observations are based on an earlier report by Godfrey, McAuliffe and co-workers of yet another unique bridged structure for dichlorophosphoranes (Chart 1, C). They found that 1 crystallised from dichloromethane (DCM), shows an unexpected linear cationic species [Ph₃P-Cl-Cl-Cl-PPh₃]⁺, and chloride anions Cl⁻ rather than individual [Ph₃PCl]⁻ and Cl⁻. They also noted that, while this structure is essentially ionic, the Cl...Cl distance (3.28 Å) between the adjacent bridging chlorines in 1C is markedly shorter than the sum of Van der Waals radii (3.56 Å). Since the bridged structure C, similarly to B, can be viewed as a case of polycentre XB, we were interested to establish whether the spatial organisation in C is driven by the propensity of 1 to form such bridged structures. Here we present new data on the dibromide 2 and mixed chloride-bromide Ph₃PClBr, 3 (Scheme 1). Our findings suggest that the configuration of bridged species is indeed driven by polycentre covalent interactions and that phosphane halides show an example of robust hypervalent interactions capable of maintaining their integrity within a range of geometrical parameters of the crystal structure.

Dihalides 1 and 2 were previously prepared by halogenation of phosphines. We had an interest in alternative preparations, which arose from their central role in our asymmetric Appel-type processes for P-stereogenic phosphorus compounds. Specifically, we wished to establish...
that the reaction of phosphine oxides with oxalyl halides \(^{12}\) (COX)\(_2\) (X = Cl, Br) leads to the same halide structural types as shown in Chart 1.\(^{13}\) When a solution of Ph\(_3\)PO in DCM (0.1 M) was treated with (COCl)\(_2\) vigorous effervescence was followed by precipitation of colourless symmetrical crystals. The decoupled \(^{31}\)P NMR spectrum in DCM (sharp singlet at 62.1 ppm),\(^{8,14}\) and the \(^1\)H and \(^31\)C NMR spectra were consistent with the tetracoordinate chlorophosphonium cation structure (see ESI section). The X-ray diffraction analysis of this material clearly indicated that its cubic crystal structure (\(a = 15.995 \text{ Å}\)) was identical to the earlier reported\(^{10}\) chloride 1C and contained the bridged linear moieties [Ph\(_3\)P-Cl-CI-Cl-PPh\(_3\)] as shown in Figure 1. This confirmed that crystallisation of the dichloride 1 from DCM leads to 1C regardless of the method by which 1 is generated in solution.

**Fig. 1** X-ray crystal structure\(^{10}\) of the dichloride 1C showing linear spatial arrangement of the bridge moiety P-Cl-Cl-Cl-P; anions Cl(3) and solvent molecules (all hydrogens are omitted for clarity).

The analogous bromide 2 was prepared by treatment of Ph\(_3\)PO in DCM with oxalyl bromide (see Scheme 1). X-ray diffraction analysis of the bright yellow crystals of 2 revealed a bridged tribromo(bis)triphenylphosphonium bromide 2C (Figure 2a) fully isostructural with 1C. The parameters of 2C exhibit several interesting features. First, its cubic unit cell is somewhat larger (\(a = 16.162 \text{ Å}\)) compared to the chloride 1C (Table 1). Second, the position of the isolated counteranions is significantly, by 1.1 Å, disordered and the average distance to the phosphorus, \(d(P_{-}Br)\) is longer, 8.64 Å. Third, and most striking, the distance between the two terminal bridge bromines Br(2) in 2C is shorter (6.37 Å), than in the analogous chloride 1C (6.56 Å) despite the bigger size (1.15 Å) and greater van der Waals radius (1.85 Å) of bromine.

We were able to go a step further. When solutions of 1 and 2 were mixed in a 2:1 ratio\(^{15}\) and the solvent was gradually removed, new pale yellow cubic crystals were isolated. X-ray diffractometry indicated that this material, 3C, contained only one type of bridged fragment Ph\(_3\)P(Cl-Br-CI-Cl-PPh\(_3\)) (Figure 2b) and the isolated anionic occupancies were 0.62 and 0.38 for Cl and Br respectively which is very close to their statistical distribution in solution. The unit cell of 3C is smaller (\(a = 15.974 \text{ Å}\)) than that of 1C making 3C the most densely packed of all three dihalides. In comparing 1C-3C (Table 1, Fig. 3), it is apparent that the X-X-X bridge interconnecting the two phosphorus centres contracts progressively as the sum of VDW sizes of the three halogens involved is increased. The trihalide bridge in the dibromide 2C (6.37 Å) is the shortest, despite the fact that its unit cell is the largest (16.162 Å) and the P-X covalent bond is the longest (2.169 Å). This intriguing contraction phenomenon is, to the best of our knowledge, exceptional. However, it can be rationalised by postulating that a polycentre covalent bond is responsible for the formation of the bridged trihalide structures.

**Table 1** Geometric parameters (Å) of 1C-3C.

<table>
<thead>
<tr>
<th></th>
<th>Cl-Cl-Cl</th>
<th>Cl-Br-Cl</th>
<th>Br-Br-Br</th>
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<tbody>
<tr>
<td>(a)</td>
<td>15.995</td>
<td>15.974</td>
<td>16.162</td>
</tr>
<tr>
<td>(d(P_{-}X))</td>
<td>Exp. 2.01</td>
<td>2.00</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Calc. 1.97(^{a}) / 2.06(^{b})</td>
<td>2.06(^{a}) / 2.06(^{b})</td>
<td>2.17(^{a}) / 2.26(^{b})</td>
</tr>
<tr>
<td>(d(XXX))</td>
<td>Exp. 6.56</td>
<td>6.52</td>
<td>6.37</td>
</tr>
<tr>
<td></td>
<td>Calc. 6.11(^{a}) / 5.58(^{b})</td>
<td>6.53(^{a}) / 5.93(^{b})</td>
<td>6.47(^{a}) / 5.85(^{b})</td>
</tr>
<tr>
<td>(d(P_{-}X))</td>
<td>8.56(^{a})</td>
<td>8.57(^{c})</td>
<td>8.64(^{c})</td>
</tr>
</tbody>
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\(^{a}\) HF calculations; \(^{b}\) DFT B3LYP; \(^{c}\) Isolated counteranions X.

To examine the electronic structure of the P-X-X-X-P multicentre systems, we compared the experimental and VDW distances to quantum chemistry calculation results (Figure 3). The equilibrium geometries in vacuum were optimised at the most commonly used HF and DFT levels using 6-31G* basis set. Both approaches provide linear symmetrical geometries of the P-X-X-X-P fragment and realistic P-X covalent bond lengths (Table 1). Clearly, the experimentally observed distances \(d(XXX)\) are significantly shorter than VDW prediction, as mentioned above, and they are inversely proportional to the halide size (Figure 3). Interestingly, quantum chemistry calculations give even shorter interatomic distances \(d(XXX)\); for instance, the calculated \(d(XXX)\) in vacuum is shorter than in crystalline 1C. Importantly, the calculations predict contraction of the XXX fragment in the bromide 3C when compared to mixed halide 2C which is in good agreement with the trend experimentally observed in solid state (Figure 3). This indicates, possibly, an expected strengthening of the 5c6e bond with the introduction of the less electronegative bromines at the 2\(^{nd}\) and 4\(^{th}\) positions as pointed out by Farnham, Dixon and Calabrese.\(^{24}\) Nevertheless, calculations under these artificial conditions (i.e. in vacuum and in the absence of counterions) cannot be...
expected to fully replicate experimental data. The discrepancies can possibly be accounted for by electrostatic interactions with counter-ions and compression between intersecting linear chains in crystal lattice leading to elongation of relatively weak contacts.

Analysis of the calculated electrostatic charge distributions, appears to suggest that a linear PXXXP geometry is unlikely to arise purely from electrostatic interactions. In 2C for example, (Figure S2, ESI section) the terminal bromines of the bridge are essentially electrically neutral as their Mulliken charges are +0.001. We therefore propose that the observed tendency of the triphenylphosphine dihalides to form linear PXXXP trihalide structures can be attributed to a five-centre hypervalent bond (5c-6e) involving three electron pairs: one is provided by the central halide anion and other two by P-X bonds of the halophosphonium fragments.

Another intriguing feature of dihalides 1C-3C is that the isolated anions are separated from the cationic phosphorus centres by a solvent molecule. This is shown explicitly for 1C (Fig. 1) where it can be seen that the arrangement mimics that of a solvent separated ion pair\(^\text{15}\) whereby the molecules CH\(_2\)Cl\(_2\) and isolated anions X\(^-\) are aligned with the axis P-X-X-P. This arrangement could be seen as a snap-shot of a process in which the isolated anion is liable, upon loss of the solvent molecule, to replace the covalently attached halogen in a nucleophilic exchange process. A study of processes of this type is underway in our group.

In conclusion, phosphonium dihalides tend to form crystals comprising of complex bridged trihalophosphonium dications, molecules of solvent and individual halide anions positioned potentially to effect nucleophilic attack on the phosphorus. We propose that the linear structure of the bridged cations [Ph\(_2\)P-X-X-X-PPh\(_3\)]\(^+\), is stabilised by hypervalent 5c-6e interactions. This finding is significant for better understanding of chemical bonding in Main Group chemistry.

**Notes and references**

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15. When equal amounts of the chloride 1 and bromide 2 were mixed only yellow cubic crystals of 2C were formed.
