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

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Triphenylhalophosphonium halides, Ph_3PX_2 form crystals comprising bridged linear cations $[\text{Ph}_3\text{P-X-X-PPh}_3]^+$ where X_3 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 stabilized 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.¹ Extended versions of such systems such as 5c-6e cases were identified later² and the area is now of substantial current interest.^{3,4} For example, Nakanishi and co-workers³ 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.*⁴ 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 electronegative atom.⁵ This extremely active current area has seen XB established in the formation of solid state structures, molecular association, medicinal chemistry and supramolecular processes.^{5,6} However relatively little is known about such interactions involving a P-X moiety.⁷

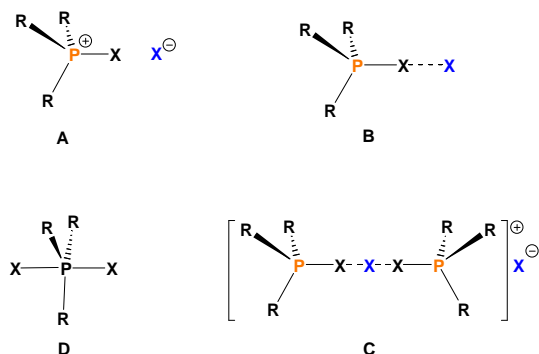
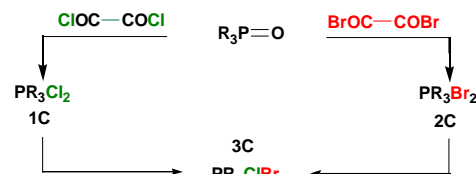


Chart 1. The principal dihalophosphorane structures (orange – nominal positive charge; blue – nominal negative charge).

Dihalophosphoranes R_3PX_2 show remarkable structural diversity^{8,9} 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,⁸ solid state Ph_3PX_2 (**1**, X = Cl; **2** X = Br) had commonly been thought to occur in just two structural types (Chart 1): the type **A** tetracoordinate salt $[\text{Ph}_3\text{PX}]^+\text{X}^-$ **1A** and the type **D** pentacoordinate trigonal bipyramidal species, **1D**. However a third spoke-geometry **B** was subsequently identified for species $\text{R}_3\text{P-X-X}$ (Chart 1, X = Br, I) bearing strong electron-donating alkyl substituents and the structure of **B** was studied theoretically.⁹



Scheme 1 Preparation of dihalides **1C**, **2C** and mixed halide **3C**.

We now report that we have identified a self-organised extended 5c-6e PXXXXP motif. Our observations are based on an earlier report by Godfrey, McAuliffe and co-workers¹⁰ 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 $[\text{Ph}_3\text{P-Cl-Cl-Cl-PPh}_3]^+$, and chloride anions Cl^- rather than individual $[\text{Ph}_3\text{P-Cl}]^+$ 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 $\text{Ph}_3\text{P-Cl-Br}$, **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.^{9,10} We had an interest in alternative preparations, which arose from their central role in our asymmetric Appel-type processes for *P*-stereogenic phosphorus compounds.¹¹ Specifically, we wished to establish

that the reaction of phosphine oxides with oxalyl halides¹² (COX)₂ (X = Cl, Br) leads to the same halide structural types as shown in Chart 1.¹³ When a solution of Ph₃PO in DCM (0.1 M) was treated with (COCl)₂ vigorous effervescence was followed by precipitation of colourless symmetrical crystals. The decoupled ³¹P NMR spectrum in DCM (sharp singlet at 62.1 ppm),^{8,14} and the ¹H and ¹³C 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 Å) was identical to the earlier reported¹⁰ chloride **1C** and contained the bridged linear moieties [Ph₃P-Cl-C-Cl-PPh₃] 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.

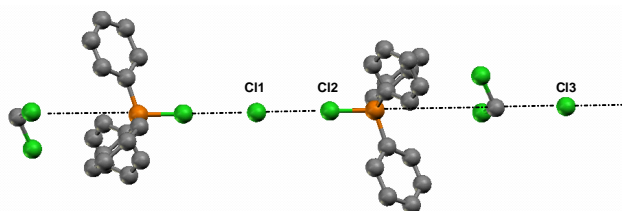


Fig. 1 X-ray crystal structure¹⁰ of the dichloride **1C** showing linear spatial arrangement of the bridge moiety P-Cl-Cl-P, anions Cl(3) and solvent molecules (all hydrogens are omitted for clarity).

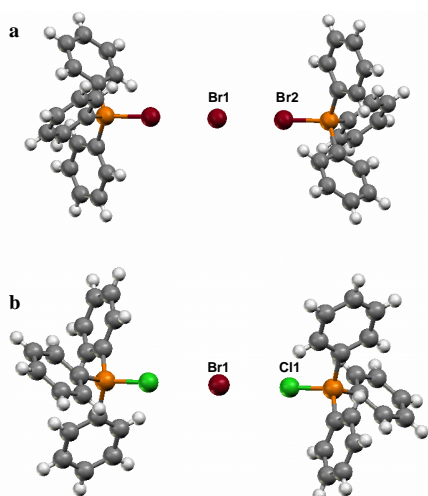


Fig. 2 X-ray crystal structure of: a) dibromide **2C** showing linear bridge P-Br-Br-P; b) mixed halide **3C** showing linear P-Cl-Br-P unit (isolated counteranions and solvent molecules are omitted).

The analogous bromide **2** was prepared by treatment Ph₃PO 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 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 ratio¹⁵ 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 Ph₃PCl-Br-ClPPh₃ (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 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**

		Cl-Cl-Cl	Cl-Br-Cl	Br-Br-Br
<i>a</i>		15.995	15.974	16.162
<i>d</i> _(P-X)	Exp	2.01	2.00	2.17
	Calc	1.97 ^a / 2.06 ^b	2.06 ^a / 2.06 ^b	2.17 ^a / 2.26 ^b
<i>d</i> _(XXX)	Exp	6.56	6.52	6.37
	Calc	6.11 ^a / 5.58 ^b	6.53 ^a / 5.93 ^b	6.47 ^a / 5.85 ^b
<i>d</i> _(P...X)		8.56 ^c	8.57 ^c	8.64 ^c

^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*_(ClClCl) 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 2nd and 4th positions as pointed out by Farnham, Dixon and Calabrese.^{2a} 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 PXXXX 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 PXXXX 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.

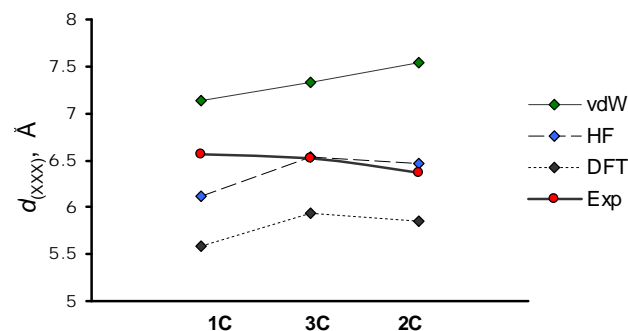


Fig. 3 Experimentally observed (red) lengths of the XXX bridge in **1C-3C** as compared to the van der Waals prediction (green), HF (blue) and DFT (grey) calculated geometries.

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 pair¹⁶ whereby the molecules CH_2Cl_2 and isolated anions X^- are aligned with the axis P-X-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 $[\text{Ph}_3\text{P-X-X-X-PPh}_3]^+$, 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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† ESI available: preparation of **1**, **2** and **3**, crystallographic, computational and NMR data.

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