



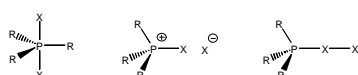
X-Ray Crystallographic Studies on Ion Pairs of Triisopropylphosphonium Salts: The Influence of Cation-Anion Interactions and Solvation in the Solid State

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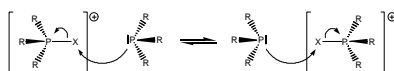
Introduction

Compounds of the general formula R_3PX_2 (R = alkyl, phenyl; X = Br, I) had been described as phosphonium salts $R_3P^+X^-$ (possibly in equilibria with phosphoranes) until X-ray studies on solid compounds with $X = I$ (various R [1,2]) and $X = Br$ ($R = Ph$ [3]) showed the presence of monomeric ion pairs with approximately linear arrangements $P-X-X$. These structures (described as „spokes“ $R_3P^+ \leftarrow X^-$ with $X = I$ or Br) are due to interactions of the soft nucleophilic anions with the „acceptor“ halogen atoms adjacent to the phosphonium centers (Scheme 1).



Scheme 1. Structure alternatives for the compounds R_3PX_2

In solution iodine atoms and bromine atoms adjacent to phosphonium centers behave as soft electrophiles. Nucleophilic attack by tertiary phosphanes R_3P at I (of R_3PI^+) or Br (of R_3PBr^+) leads to rapid I^- or Br^- transfer (‘‘fluxional P^{III}/P^V systems’’), as detected by ^{31}P - and 1H -NMR [1,4,5] (Scheme 2).

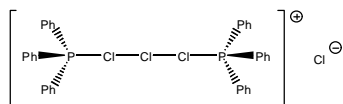


Scheme 2. Halogen transfer of R_3P/R_3PX^+ in solution

Evidence for the above mentioned ‘‘spoke’’ structures with $Cl \cdots Cl$ interactions is still extremely scarce.

McAuliffe *et al.* found that dichloromethane-solvated Ph_3PCl_2 , however, contains $[Ph_3PCl \cdots Cl \cdots ClPPh_3]^+$ cations that are well-separated from Cl^- anions [6] (Scheme 3).

Is there a general difference between the solid state structures of compounds R_3PX_2 compared with $R_3PI \cdots I$ and $R_3PBr \cdots Br$, or is the structure of dichloromethane-solvated Ph_3PCl_2 an exceptional case?



Scheme 3. Structure of $[Ph_3PCl \cdots Cl \cdots ClPPh_3]^+ Cl^-$

Solvation effects

To determine whether ion-dipole interactions of the anion with dichloromethane or other effects contribute to the latter ‘‘exceptional’’ structure, it was desirable to solve the structure of a related solvent-free species R_3PX_2 ($X = I, Br; R = alkyl$). Fortunately, the crystallisation behaviour of triisopropylphosphane derivatives $i-Pr_3PX_2$ ($X = Cl: 1$ [7], $X = Br: 2$ [8], $X = I: 3$ [9]) was found to meet just the above requirements.

Crystallisation from dichloromethane provided solvent-free **1**, which is, to the best of our knowledge, the first crystallographically characterised solvent-free compound of stoichiometry R_3PX_2 . **2**, however, gave crystals containing $1/2$ equivalent of dichloromethane under comparable conditions.

Both solid compounds contain $R_3P^+X^- \cdots X^-$ ion pairs with approximately linear $P-X \cdots X$ units [1,2]; the bromide ions of two such ion pairs of **2** are ‘‘bridged’’ by a CH_2Cl_2 molecule (Figure 1, 2). The $X \cdots H-C-H \cdots X$ contacts can be understood as halogenide solvation by ion-dipole interactions.

We have since found that the corresponding P-I compound $[(i-Pr_3PBr_2)_2 \cdot CH_2Cl_2]$ [9] (**3**) is isostructural.

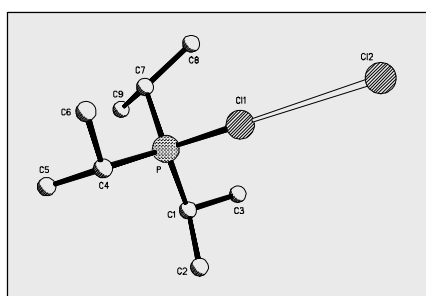


Figure 1. Structure of **1**

The $Cl \cdots Cl$ distance within ion pairs of **1** (3.234(1) Å) is slightly shorter than those of $[Ph_3PCl \cdots Cl \cdots ClPPh_3]^+$ (3.279(6) Å) [6]; the degree of interaction by (valence shell expanding) $Cl \cdots Cl$ $n \rightarrow \sigma^*$ overlap is obviously not very dependent on the coordination number of the donating chloride ion. Packing and anion solvation effects might both contribute to the structural difference between $[Ph_3PCl_2 \cdot CH_2Cl_2]$ [8] and **1**.

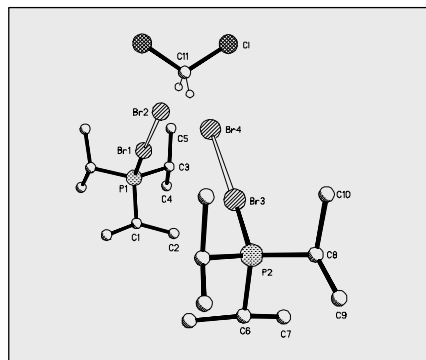


Figure 2. Structure of **2**

Nucleophilicity of the Anion

X-Ray studies of derivatives with anions of lower donor ability than Br and I would provide an interesting comparison with the $X \cdots X$ contacts in **2** and **3**.

A bromotrialkylphosphonium-tribromogermanate(II) has been identified spectroscopically as the product from a reaction of a bulky phosphane with germanium tetrabromide [5]; structural evidence by X-ray methods, however, has not yet been provided. In salts $[R_3PBr]^+ [GeBr_3]^-$, cation-anion interactions might occur via $Br \cdots Ge^IV$ or $Br \cdots Br$ contacts. The new compound $i-Pr_3P^+Br^- GeBr_3^-$ (**4**) provides the first crystallographic characterisation of a product from a germanium tetrahalide/tertiary phosphane redox reaction [5,10,11].

Consistent with the lower donor ability of the Br atoms of the $GeBr_3^-$ anion, cation-anion $Br \cdots Br$ contacts in **4** (3.415(1) Å) are slightly longer than those in **2** (3.369(2) and 3.315(2) Å) (Figure 3).

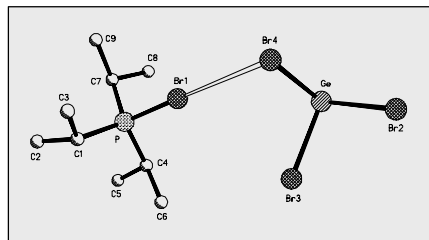


Figure 3. Structure of **4**

A derivative of **3** with an anion of lower nucleophilicity than I is the new compound **5** $i-Pr_3PI^+ I_3^-$. In solid state the compound forms independent layers of triiodide zigzag chains with each triiodide-triiodide contact pair asymmetrically ‘‘bridged’’ by an iodotriisopropylphosphonium ion (Figure 4). As expected, even the more significant $I \cdots I$ contacts (3.708(1) - 3.743(1) Å) in **5** are longer than those in **3** (3.383(1) and 3.372(1) Å). While P-I and P-Br bond lengths of halogenophosphonium ions are affected by $n \rightarrow \sigma^*$ overlap from nucleophiles attacking the I or Br atoms, the related impact on P-Cl bond length is smaller.

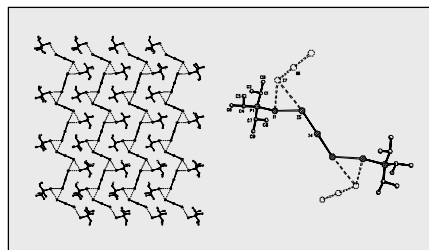


Figure 4. Packing diagram and structure of **5**

Summary

In conclusion, phosphoranes with one I or Br atom bonded to pentacoordinated phosphorus are known [12,13]; however the yet structurally characterised solid halogenophosphonium halides R_3PX_2 ($X = Cl, Br, I$) do not contain pentacoordinated phosphorus, but are ionic and exhibit similar types of cation-anion halogen-halogen interactions. The increasing significance of $X \cdots X$ interactions, the increasing extent of P-X bond lengthening, the increasing accessibility of $[R_3P^+ \cdots PR_3]^+$ transition states and anion dependency of the ^{31}P -NMR shifts ($Cl \ll Br \leq I$) associated with ‘‘soft-soft’’ ($n \rightarrow \sigma^*$) interactions are all consistent with the known range of increasing electrophilicity and polarisability of the heavier halogens.

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