'Soft–soft' halogen–halogen interactions in solid ion pairs of solvent-free $Pr^i_3PCl_2$ and CH_2Cl_2-solvated $Pr^i_3PBr_2$: structural features of chloro- and bromo-triisopropylphosphonium salts

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An X-ray crystallographic study of solvent-free $Pr^i_3PCl_2$ and dichloromethane-solvated $Pr^i_3PBr_2$ reveals that both halogenophosphonium halides exist as monomeric ion pairs $Pr^i_3P^+$–X···X^-; elongations of P–Cl and P–Br bonds are associated with Cl···Cl and Br···Br interactions.

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 in solution ('fluxional P^{III}–P^V systems'), as detected by ^{31}P and ^1H NMR spectroscopy[1–3] (Scheme 1). In the solid state, I···I interactions of iodophosphonium ions $R_nPI_{4-n}{}^+$ with iodide counter ions lead, depending on the number of iodine atoms adjacent to phosphorus, to 'spoke' structures with approximately linear P–I···I units (n = 3; R_3PI_2)[3–7] to rings, helices and zigzag chains (n = 2, R_2PI_3),[8–11] or to interpenetrating puckered layers and three-dimensional networks (n = 1, RPI_4).[12]

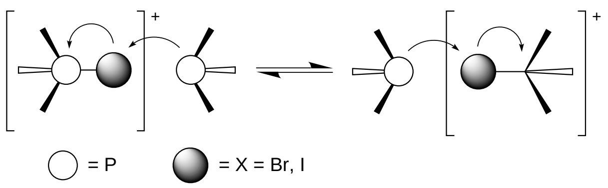
Evidence for related structures with Br···Br or even Cl···Cl interactions is still extremely scarce. McAuliffe *et al.* found that Ph_3PBr_2 also exists (as do Ph_3PI_2[4] and Ph_3PIBr[13]) as a 'molecular charge-transfer-like spoke';[14] dichloromethane-solvated Ph_3PCl_2, however, contains $[Ph_3PCl···Cl···ClPPh_3]^+$ cations that are well separated from Cl^- anions.[15] Is there a general difference between the solid state structures of compounds R_3PCl_2 compared with R_3PI···I and R_3PBr···Br, or is the structure of dichloromethane-solvated Ph_3PCl_2 an exceptional case? 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_3PCl_2 and of a solvated species R_3PBr_2 (R = alkyl). Fortuitously, the crystallisation behaviour of triisopropylphosphane derivatives $Pr^i_3PX_2$ (X = Cl **1**,[17] X = Br **2**[16]) 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_3PCl_2. **2**, however, gave crystals containing 0.5 equiv. of CH_2Cl_2 under comparable conditions. Both solid compounds contain R_3P^+–X···X^- ion pairs with approximately linear P–X···X units;[3,4] the bromide ions of two such ion pairs of **2** are 'bridged' by a CH_2Cl_2 molecule (Figs. 1 and 2). We have since found that the corresponding P–I compound $[(Pr^i_3PI_2)_2·CH_2Cl_2]$[18] is isostructural. The Br^-···H–C–H···Br contacts can be understood as bromide solvation by ion–dipole interactions.

The Cl···Cl distance within ion pairs of **1** [3.234(1) Å] is slightly shorter than those of $Ph_3PCl···Cl···ClPPh_3]^+$ [3.279(6) Å];[15] the degree of interaction by (valence-shell expanding) Cl → Cl n → σ* 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 $Ph_3PCl_2·CH_2Cl_2$[15] and **1**. A reinvestigation of the structure of $[Pr^i_3PCl]^+[N(SO_2CH_3)_2]^-·CH_2Cl_2$[19] **3** reveals that here chlorine atoms of a well ordered CH_2Cl_2 approach the Cl atom of the $[Pr^i_3PCl]^+$ cation [3.407(2) Å] to satisfy its Lewis-acidic needs, which apparently cannot be met by the $[N(SO_2Me)_2]^-$ counter ion.

$$R_3P\text{-}X^+ \;\; X^- \rightleftharpoons R_3P\text{-}X{\leftarrow}X \qquad \text{(i)}$$

$$R_3P\text{-}X^+ \; + \; PR_3{}^* \rightleftharpoons R_3P \; + \; X\text{-}R_3P^{+*} \qquad \text{(ii)}$$



Scheme 1 The positions of equilibria i and ii depend on R

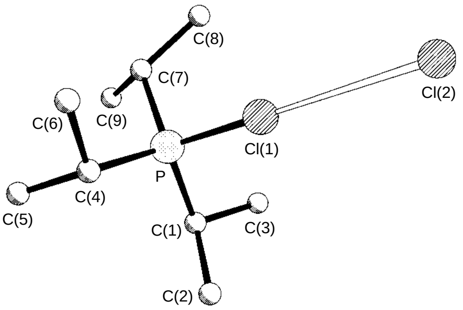


Fig. 1 Molecular structure of **1**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P–Cl(1) 2.002(1), Cl(1)···Cl(2) 3.234(1); P–Cl(1)···Cl(2) 177.5(1).

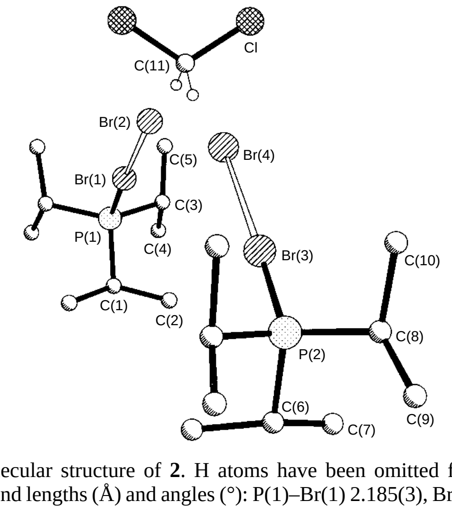


Fig. 2 Molecular structure of **2**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–Br(1) 2.185(3), Br(1)···Br(2) 3.369(2), P(2)–Br(3) 2.174(3), Br(3)···Br(4) 3.315(2); P(1)–Br(1)···Br(2) 175.0(1), P(2)–Br(3)···Br(4) 176.5(1).

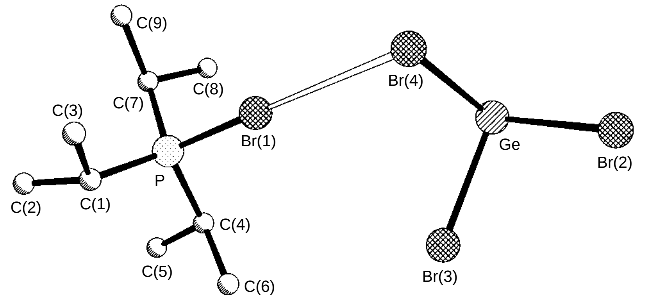


Fig. 3 Molecular structure of **4**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P–Br(1) 2.155(2), Br(1)···Br(4) 3.415(1), Ge–Br(4) 2.556(1), Ge–Br(2) 2.481(1), Ge–Br(3) 2.480(1); P–Br(1)···Br(4) 177.8(1).

Bromotrialkylphosphonium tribromogermanates(II) and tribromostannates(II) have been identified spectroscopically as the products from reactions of bulky phosphanes with germanium and tin tetrabromides;[2] structural evidence by X-ray methods, however, has not yet been provided. In salts $[R_3PBr]^+[MBr_3]^-$ ($M = Ge^{II}, Sn^{II}$), cation–anion interactions might occur *via* $Br\cdots M^I$ or $Br\cdots Br$ contacts. In the latter case, the $Br\cdots Br$ contacts would provide an interesting comparison with those of compound **2**. We therefore reacted Pr^i_3P with $GeBr_4$: the new compound $Pr^i_3PBr^+GeBr_3^-$ **4**, formed in high yield, provides the first crystallographic characterisation of a product from a germanium or tin tetrahalide/tertiary phosphane redox reaction.[2,20,21] 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 and the P–Br bond in **4** [2.155(2) Å] is slightly shorter than those in **2** (Fig. 2) or in Ph_3PBr_2 {*d*(Br–Br) 3.123(2), *d*(P–Br) 2.181(3) Å} (Fig. 3).[14]

P–I bonds of iodophosphonium ions are affected by $n \longrightarrow \sigma^*$ overlap from nucleophiles attacking the I atoms. P–Br bond lengths [**2**, 2.185(3), 2.174(3) Å; **4**, 2.155(2) Å] are less affected by cation–nucleophile interactions than P–I bond lengths and the related impact on P–Cl bond lengths [**1**, 2.002(1) Å; **3**, 1.994(2) Å;[19] $Me_3PCl^+SbCl_6^-$, 1.986(2) Å[22]] is even smaller.

In contrast to the above-mentioned rapid I^+ or Br^+ transfer between phosphanes,[1,2] which is also observed in mixtures of **2** and Pr^i_3P in CH_2Cl_2 solution at room temperature (1 : 1 mixture: δ_P 57), comparable R_3PCl^+–R_3P systems do not give averaged P^{III}–P^V NMR signals, indicating that transition states $[R_3P–X–PR_3]^+$ are of higher energy when X = Cl. ^{31}P NMR shifts of the cations of **1**–**4** are only slightly anion dependent (δ_P in CH_2Cl_2 solution: **1**, 120.1; **2**, 114.9; **3**, 119.8;[19] **4**, 114.3).

In conclusion, phosphoranes with one I or Br atom bonded to pentacoordinated phosphorus are known;[23,24] however all as 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 and the increasing accessibility of $[R_3P\cdots X\cdots PR_3]^+$ transition states (Cl ≪ Br < I) associated with 'soft–soft' ($n \longrightarrow \sigma^*$) interactions are all consistent with the known range of increasing electrophilicity and polarisability of the heavier halogens.

Footnotes and References

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† *Crystal data*: **1**: $C_9H_{21}Cl_2P$; *M* = 231.13, orthorhombic, space group $P2_12_12_1$, *a* = 9.437(2), *b* = 10.101(2), *c* = 13.262(2) Å, *U* = 1264.1(4) Å^3, *Z* = 4, D_c = 1.214 Mg m^{-3}, μ = 0.596 mm^{-1}, *F*(000) = 496, 2629 independent reflections to 2θ max. 55°, *T* = 173 K, *S* = 1.027, $R[F, > 4\sigma(F)]$ = 0.0394, $wR(F^2)$ = 0.0902, 45 restraints and 116 parameters, highest peak 0.471 and deepest hole −0.196 e Å^{-3}, absolute structure parameter *x* = 0.06(11).

2: $C_{9.5}H_{22}Br_2ClP$; *M* = 362.51, orthorhombic, space group *Pnma*, *a* = 15.576(2), *b* = 10.594(2), *c* = 18.219(2) Å, *U* = 3006.4(8) Å^3, *Z* = 8, D_c = 1.602 Mg m^{-3}, μ = 5.644 mm^{-1}, *F*(000) = 1448, 2766 independent reflections to 2θ max. 50°, *T* = 173 K, *S* = 0.958, $R[F, > 4\sigma(F)]$ = 0.599, $wR(F^2)$ = 0.1518, 44 restraints and 142 parameters, highest peak 1.357 and deepest hole −0.765 e Å^{-3}. The displacement parameters of some isopropyl C atoms are slightly higher than expected for low-temperature structures (*ca.* 0.15 Å^2), which may be due to slight disorder.

4: $C_9H_{21}Br_4GeP$; *M* = 552.46, monoclinic, space group $P2_1/n$, *a* = 10.717(3), *b* = 8.285(3), *c* = 18.765(4) Å, β = 91.80(3)°, *U* = 1665.3(8) Å^3, *Z* = 4, D_c = 2.203 Mg m^{-3}, μ = 11.507 mm^{-1}, *F*(000) = 1048, 2930 independent reflections to 2θ max. 50°, *T* = 143 K, *S* = 1.107, $R[F, > 4\sigma(F)]$ = 0.0443, $wR(F^2)$ = 0.1156, 143 parameters, highest peak 1.058 and deepest hole −0.894 e Å^{-3}.

All X-ray datasets were collected with monochromated Mo-Kα radiation (λ = 0.710 73 Å) on a Siemens P4 (**1**, **2**) or a Stoe STADI-4 (**4**) four-circle diffractometer. Absorption corrections were based on ψ-scans. The structures were solved by direct (**1**, **4**) or heavy-atom methods (**2**) and refined anisotropically by full-matrix least squares on F^2. H atoms were included using a riding model for all non-methyl group protons. Methyls were refined as rigid groups except C(10) in **2** (riding). CCDC 182/576.

‡ ^{31}P NMR data (300 K CH_2Cl_2–C_6D_6): **1**, δ 120.1; **2**, δ 114.9; **4**, δ 114.3.

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Received in Basel, Switzerland, 3rd July 1997; 7/04684G