The Structure of Triphenylphosphorus–Dibromine, the First Crystallographically Characterised Bromophosphorane, a Compound which has the Novel Four-coordinate Molecular Ph₃P–Br–Br Geometry

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Triphenylphosphorus–dibromine is shown by X-ray crystallography to have a four-coordinate Ph_3P–Br–Br 'spoke' structure and is isostructural with Ph_3P–I–I and Ph_3As–I–I; thus forcing us to question the conventional belief that tertiary-organo group 15 adducts with dihalogens have either pentacoordinate R_3EX_2 or ionic $[R_3EX]^+X^-$ structures in the solid state.

The structural nature of halogenophosphoranes is of considerable current interest.[1–4] However, despite this, the amount of reported knowledge of their structural chemistry is scarce, a fact which has been commented upon by Cotton and Kibala.[4]

Triphenylphosphorus–dibromine has found significant use in organic chemistry as a synthetic reagent,[5–9] as well as a reagent for bond cleavage[10,11] and displacement[12,13] reactions. Work in this laboratory has also demonstrated the general use of dibromophosphoranes in the synthesis of novel transition metal complexes of tertiary phosphine ligands.[14] Clearly,

triphenylphosphorus–dibromine is a valuable and versatile synthetic reagent.

It is surprising then that very little work has been reported concerning the structural nature of bromophosphoranes of stoichiometry R_3PBr_2, particularly in the solid state; the only reports being an infrared spectral study of Me_3PBr_2[15] and a solid-state ³¹P NMR study on Ph_3PBr_2.[16] The conclusions of these earlier workers were that these compounds have an ionic $[R_3PBr]^+Br^-$ structure in the solid state; conclusions which were in agreement with solution studies, chiefly conducti-
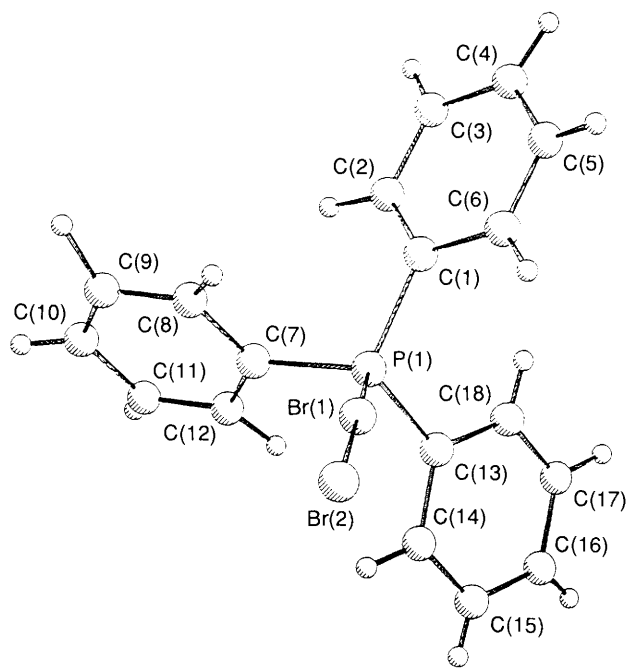
Fig. 1 Molecular structure of [Ph$_3$P·Br$_2$]. Selected bond lengths (Å) and angles(°): Br(1)–Br(2) 3.123(2); Br(1)–P(1) 2.181(3); Br(2)–Br(1)–P(1) 177.16(8); torsion angles Br(1)–P(1)–C(1)–C(6) 43.0(9), Br(1)–P(1)–C(7)–C(8) 57.7(8), Br(1)–P(1)–C(13)–C(14) 49.1(9).

metric, which showed that bromophosphoranes are ionic in acetonitrile.[17] Prior to this communication, no bromophosphorane had been crystallographically characterised.

Our own recent studies on compounds of formula R$_3$EX$_2$ (E = P, As, Sb; X = Br, I) have shown by X-ray crystallography that, whereas Ph$_3$SbBr$_2$ has the expected *trans*-trigonal bipyramidal structure,[18] both Ph$_3$AsI$_2$[19] and Ph$_3$PI$_2$[1] adopt a completely novel four-coordinate molecular structure, Ph$_3$E–I–I, in which the dihalogen is bound to the P or As atom as a linear 'spoke'.

The ability of diiodine to form charge transfer adducts with solvents or molecules containing a lone pair of electrons is well recognised.[20–25] In all such compounds which have been crystallographically characterised the I–I bond considerably lengthens upon adduct formation, as expected, since electron density is put into the σ-antibonding orbitals of the diiodine by the electron donor. However, charge transfer complexes involving dibromine are much less common, and we report here the first X-ray crystal structure of a bromophosphorane.

Triphenylphosphorus–dibromine, 1,† is isolated as a colourless crystalline solid from the reaction of stoichiometric quantities of Ph$_3$P and Br$_2$ in (80:20) dry diethyl ether–dichloroethane. Compound 1 is isostructural with both Ph$_3$PI$_2$[1] and Ph$_3$AsI$_2$.[19] In an analogous manner to these compounds, 1 shows a lengthening of the Br–Br bond with respect to molecular bromine (3.12 compared to 2.28 Å), but

this is still well within bonding distance when compared to the van der Waals radius of dibromine, 3.9 Å.[26]

The solid-state Raman spectrum of 1 exhibits an intense band at 239 cm^{-1}, assignable to ν(P–Br),[15] but unambiguous identification of ν(Br–Br) was not possible. Whilst 1 is a molecular compound in the solid state it ionises in dichloromethane to form [Ph$_3$PBr]$^+$Br$^-$, as evidenced by a single sharp ^{31}P{H} NMR resonance at δ 49.2. This is identical to the chemical shift obtained from the same system after the addition of one equivalent of AlBr$_3$, which is known to produce the ionic species [R$_3$PX]$^+$[AlX$_4$]$^-$.[27–29]

What these new results indicate is that the four-coordinate molecular structure R$_3$E–X–X is quite common for compounds of formula R$_3$EX$_2$; not only for the diiodo species, but, more remarkably, for bromophosphoranes. This contrasts with the rather limited number of previous reports on compounds of this type, all of which pointed to the existence of the ionic [R$_3$PX]$^+$X$^-$ structure.

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