

## The Structure of Triphenylphosphorus–Diiodine, $\text{Ph}_3\text{PI}_2$ , the First Crystallographically Characterised Dihalogen Derivative of a Tertiary Phosphine

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Triphenylphosphine reacts with diiodine in dry diethyl ether to produce  $\text{Ph}_3\text{PI}_2$ , shown by X-ray crystallography to be a molecular four-coordinate compound  $\text{Ph}_3\text{P}-\text{I}-\text{I}$ , and not the five-coordinate  $\text{Ph}_3\text{PI}_2$  or the ionic  $[\text{Ph}_3\text{P}]^+\text{I}^-$ , previously thought to be the only possible solid-state structures for such a compound.

Organophosphorus halogen compounds have interested chemists for decades. The delicate balance between ionic and covalent forms is influenced not only by the aggregation (solid, liquid, gas) or the nature of the solvent, but also by the effect of substituents. Thus, for example,  $\text{PhPCl}_4$  is molecular, whereas the corresponding methyl derivative is ionic,  $[\text{MePCl}_3]^+\text{Cl}^-$ .<sup>1</sup>

Investigations into the nature of the products of the reactions between triphenyl derivatives of phosphorus, arsenic, antimony and bismuth began at the beginning of the century<sup>2,3</sup> and continue apace.<sup>4</sup> The so-called dihalides or tetrahalides have been most studied but more complex stoichiometries have also been identified, *e.g.*  $\text{Ph}_3\text{AsCl}_5\text{I}$ .<sup>5</sup>

The nature of these compounds has been studied in the solid state mainly by vibrational,<sup>6</sup> electronic<sup>7</sup> and <sup>31</sup>P NMR<sup>8,9</sup> spectroscopy, and by conductometric titrations, principally by Harris and coworkers,<sup>10</sup> in solution. Very few compounds have been characterised by single crystal X-ray techniques; these include the ionic  $[\text{Bu}^t_3\text{PI}]^+\text{I}^-$  and  $[(\text{Ph}_3\text{PI})_2\text{I}_3]\text{I}_3$ <sup>4</sup> and the covalent  $(\text{PPh}_3\text{I})\text{I}_3$ <sup>4</sup> and  $\text{Ph}_3\text{BiCl}_2$ ,<sup>12</sup> the last of which is trigonal bipyramidal.

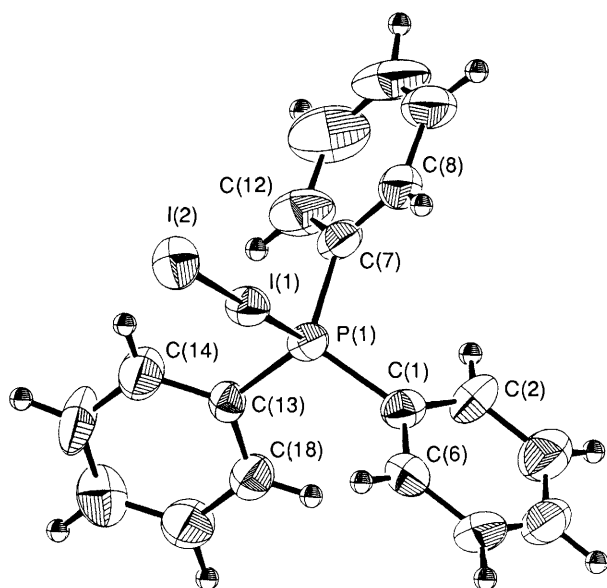
Cotton and Kibala<sup>4</sup> could not isolate a compound of empirical formula  $\text{Ph}_3\text{PI}_2$ , but did isolate two isomeric forms of  $\text{Ph}_3\text{PI}_4$ . However, although  $\text{Ph}_3\text{PI}_2$  has been isolated from MeCN by Harris and coworkers,<sup>10</sup> there has been no crystal structure identification of a compound of this stoichiometry.

We here report the X-ray crystal structure<sup>†</sup> of triphenylphosphorus–diiodine **1**, a yellow crystalline substance isolated from the stoichiometric reaction of  $\text{Ph}_3\text{P}$  and  $\text{I}_2$  in dry diethyl ether.

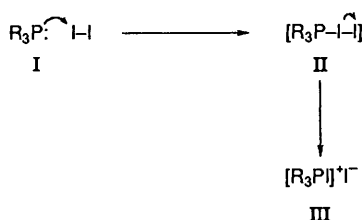
Compound **1**, which was recrystallised from diethyl ether at *ca.* 0 °C, is isostructural with the arsenic analogue **2**,<sup>13</sup> although the I–I distance in the former, 3.161(2) Å, is longer than that in the latter, 3.005(1) Å.

The Raman spectrum as a Nujol mull exhibits a strong band at 160  $\text{cm}^{-1}$ , assignable to  $\nu(\text{I}-\text{I})$ ; this is shifted to lower energy from that observed for molecular iodine, 215  $\text{cm}^{-1}$ ,<sup>14</sup> but within the range found for charge-transfer complexes of diiodine.<sup>15</sup> The electronic spectrum of **1** in 1,2-dichloroethane

<sup>†</sup> Crystal data:  $\text{C}_{18}\text{H}_{15}\text{I}_2\text{P}$ ,  $M = 516.10$ ,  $T = 293$  K, orthorhombic, space group  $P2_12_12_1$  (No. 19),  $a = 10.461(6)$ ,  $b = 12.993(1)$ ,  $c = 13.673(3)$  Å,  $V = 1858.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.844$  Mg m<sup>-3</sup>,  $F(000) = 976$ , Enraf-Nonius CAD4 diffractometer, Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 3.426$  mm<sup>-1</sup>. The heavier atoms were located using Patterson techniques (SHELXS) and refined by full-matrix least-squares analysis (TEXSAN). Anisotropic vibrational parameters for non-hydrogen atoms, hydrogen atoms placed in chemically reasonable positions.  $R = 0.037$ ,  $R_w = 0.037$ ,  $w = 1/(\sigma^2(F_o) + 0.03F_o^2)$  for 1802 unique reflexions with  $F_o \geq 5\sigma(F_o)$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** Molecular structure of  $[\text{Ph}_3\text{P}\cdot\text{I}_2]$ . Selected bond lengths (Å) and angles ( $^\circ$ ): I(1)–I(2) 3.16(2); I(1)–P(1) 2.481(4); I(2)–I(1)–P(1) 178.22(7); torsion angle I(1)–P(1)–C(1)–C(6) 38(1); I(1)–P(1)–C(7)–C(8) 57(1); I(1)–P(1)–C(13)–C(14) 45(1).



**Scheme 1**

exhibits two intense bands at 290 and 360 nm. Whilst **I** is a molecular compound in the solid state, it ionises in 1,2-dichloroethane to form  $[\text{Ph}_3\text{PI}]^+\text{I}^-$ , as evidenced by a single sharp  $^{31}\text{P}$  NMR signal at  $\delta$  44.8. This is identical to the chemical shift obtained from a solution of  $\text{Ph}_3\text{PI}_2 + \text{I}_2$ , which produces  $[\text{Ph}_3\text{PI}]^+\text{I}_3^-$  (electronic absorption bands at 226, 294 and 366 nm being indicative of  $\text{I}_3^-$ ) in the same solvent.

Thus, although compound **I** can adopt an ionic structure in solution, we show here clearly that in the solid state it is a

four-coordinate molecular compound, and in the solid state is neither the molecular five-coordinate  $\text{Ph}_3\text{PI}_2$  nor the ionic  $[\text{Ph}_3\text{PI}]^+\text{I}^-$  previously accepted as the only possible structures for a compound of this formulation.

The fact that compound **I** reported here is isostructural with the analogous  $\text{Ph}_3\text{AsI}_2$  **2**, obtained by the thermal decomposition of  $[\text{Mn}(\text{OAsPh}_3)_3\{\text{OS}(\text{O})\text{I}\}_2]$ ,<sup>14</sup> seems to suggest that four-coordinate  $[\text{Ph}_3\text{EI}_2]$  may be a common structure, and independent of origin.

This type of charge transfer complex may be regarded as a 'frozen' transition state **II** in the reaction sequence in Scheme 1.

Reaction results in **III** when  $\text{R} = \text{Bu}^t$ , but halts at **II** for  $\text{R} = \text{Ph}$  (in ether). There is also a report of an amine diiodine structural analogue, viz.  $\text{Me}_3\text{NI}_2$ ,  $d(\text{I}-\text{I})$  2.829(7) Å.<sup>16</sup>

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