An X-ray crystallographic study of the reagent Ph_3PCl_2; not charge-transfer, $R_3P–Cl–Cl$, trigonal bipyramidal or $[R_3PCl]Cl$ but an unusual dinuclear ionic species, $[Ph_3PCl^{+}\cdots Cl^{-}\cdots{}^{+}ClPPh_3]Cl$ containing long Cl–Cl contacts

Stephen M. Godfrey, Charles A. McAuliffe, Robin G. Pritchard and Joanne M. Sheffield

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, UK M60 1QD

An X-ray crystallographic study of the reagent Ph_3PCl_2 reveals it to be $[Ph_3PCl^{+}\cdots Cl^{-}\cdots{}^{+}ClPPh_3]Cl$ and not trigonal bipyramidal, molecular charge-transfer $Ph_3P–Cl–Cl$ or the simple ionic species $[Ph_3PCl]Cl$; this contrasts with the conclusions from all previous spectroscopic data recorded on compounds of stoichiometry R_3PCl_2 by earlier workers, and represents the first compound of this formula to be crystallographically characterised.

Despite the fact that compounds of stoichiometry R_3PCl_2 have been known for over 100 years,[1] their solid-state structural nature remains largely unexplored. This is despite the fact that Ph_3PCl_2 is a widely used chlorinating agent in organic reactions and is commercially available.

Previous studies on compounds of stoichiometry R_3PCl_2 have been predominantly focused on the nature of such species in solution. Extensive $^{31}P\{H\}$ NMR studies[2–10] have concluded that all such species are ionic, $[R_3PCl]Cl$, in CH_2Cl_2 solution, although the presence of a small quantity of molecular species in equilibrium with the ionic form was also considered. This is in agreement with conductivity studies on Ph_3PCl_2 in MeCN solution by Harris and coworkers,[11,12] who also proposed an ionic formulation, $[Ph_3PCl]Cl$. By contrast, cryostatic and vibrational spectroscopic studies[13] of Ph_3PCl_2 in haloform solvents led to the suggestion that 1 : 1 $Ph_3PCl_2{\cdot}YCX_3$ (Y = H, D; X = Cl, Br) adducts were formed which are dimeric molecular species containing six-coordinate phosphorus atoms.

Solid-state studies of R_3PCl_2 are scarce. Dillon and Waddington[14] used high-resolution solid-state $^{31}P\{H\}$ NMR and NQR spectroscopy to study Ph_3PCl_2 and its 1 : 1 adducts with some Lewis acids. Both Ph_3PCl_2 and the adducts exhibited a single resonance at δ 62 ± 8, leading these workers to conclude that Ph_3PCl_2 possesses the ionic $[Ph_3PCl]Cl$ structure in the solid state; similarly, NQR results gave a single $P–{}^{35}Cl$ resonance compatible with a structure containing $[Ph_3PCl]^+$ cations. The solid-state structure of Me_3PCl_2 has also been investigated by Raman[15] and IR spectroscopy,[16] and again an ionic formulation, $[Me_3PCl]Cl$, was proposed.

There is considerable new interest in the structural nature of compounds of stoichiometry R_3EX_2 (E = P, As, Sb). We have established the solid-state molecular charge-transfer 'spoke' structure for Ph_3EX_2 (E = P; X_2 = Br_2,[17] I_2,[18–20] IBr[21]), Fig. 1; on the other hand, other workers have established that Ph_3PF_2[22,23] is trigonal bipyramidal in the solid state. Clearly, knowledge of the solid-state structure of Ph_3PCl_2 is of great importance, since it could adopt either of these structures or even the ionic structure $[Ph_3PCl]Cl$, proposed by Gates and coworkers[24] from solid-state Raman spectroscopic studies. It is also noteworthy that these same workers also claimed to have isolated a trigonal-bipyramidal form of Ph_3PCl_2.[24]

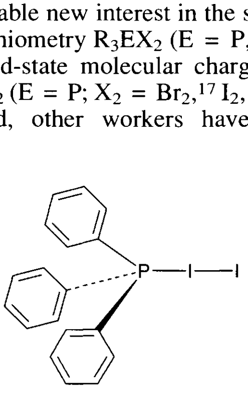

Fig. 1 The molecular structure of the charge-transfer 'spoke' structure Ph_3PI_2[18,19]

Considering these involved, and occasionally contradictory, spectroscopic studies, it seems remarkable that no compound of formula R_3PCl_2 has ever been studied by single-crystal X-ray diffraction, especially since Ph_3PCl_2 is a commonly used reagent in chlorination reactions.

Triphenylphosphine dichloride was prepared by us by the direct 1 : 1 stoichiometric reaction of triphenylphosphine with dichlorine in dichloromethane [eqn. (1)].

$$\mathrm{PPh_3 + Cl_2} \xrightarrow[\mathrm{N_2}]{\text{room temp., }\mathrm{CH_2Cl_2}} [\mathrm{Ph_3PCl\cdots Cl\cdots ClPPh_3}]\mathrm{Cl} \tag{1}$$

Chlorination of the tertiary phosphine occurred almost immediately and the reaction was exothermic, a noticeable temperature rise (*ca.* 20 °C) of the dichloromethane was observed during addition of the dichlorine. Recrystallisation of the Ph_3PCl_2 from dichloromethane–diethyl ether (1 : 1) produced a large quantity of colourless crystals with a melting point of 160–161° on standing at room temperature for *ca.* 24 h. A crystal was chosen for analysis by single-crystal X-ray diffraction. Surprisingly, the structure of Ph_3PCl_2 is revealed to be not the charge-transfer species, $Ph_3P–Cl–Cl$, previously established for $Ph_3E–X–X$ (E = P; X_2 = Br_2,[17] I_2,[18] IBr;[21]

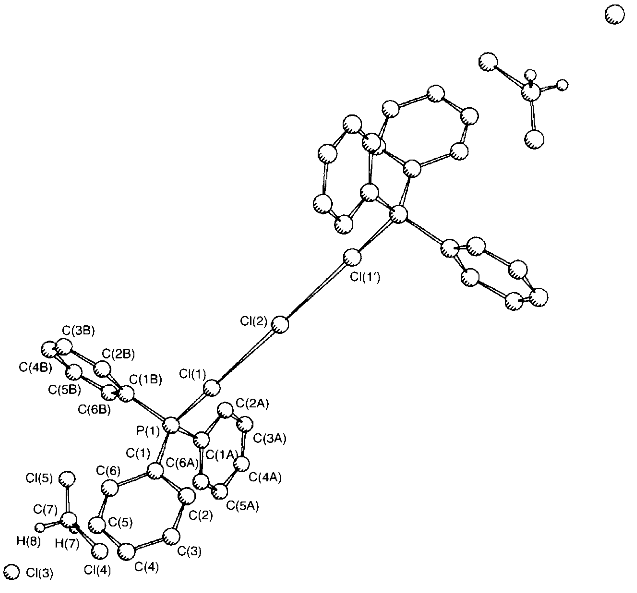

Fig. 2 Selected bond lengths (Å) and angles (°) for $[Ph_3PCl\cdots Cl\cdots ClPPh_3]Cl{\cdot}2CH_2Cl_2$: Cl(1)–P(1) 2.015(9), Cl(1)–Cl(2) 3.279(6); Cl(1)–P(1)–C(1) 107.2(5) C(1)–P(1)–C(1) 111.7(5), P(1)–C(1)–C(2) 121(1); P(1)–C(1)–C(6) 123(1); Cl(1)–Cl(2)–Cl(1) 180.00

E = As; X_2 = I_2,[25] IBr[26]), or the trigonal-bipyramidal species, Ph_3PCl_2 established for Ph_3EX_2 (E = P; X = F;[22,23] E = As; X = Br,[26] F[27]), or the simple ionic species $[Ph_3PCl]Cl$ which has not been crystallographically characterised but strongly suggested from a variety of spectroscopic studies; rather, an unusual dinuclear ionic species† which contains long Cl–Cl contacts, $[Ph_3P–Cl\cdots Cl\cdots Cl–PPh_3]$ Cl **1**, Fig. 2. The Cl–Cl contacts are 3.279(6) Å which can be compared to the dichlorine van der Waals radius of 3.6 Å. The distances therefore represent long but significant interactions in the solid state. The solution $^{31}P\{H\}$ NMR spectrum of **1** in $CDCl_3$ and CD_3CN solutions revealed a single peak at δ 65.5 and 66.5, respectively, relative to 85% H_3PO_4, *i.e.* similar to shifts reported by earlier workers.

In conclusion, not only is **1** the first crystallographically characterised compound of stoichiometry R_3PCl_2, it also exhibits a previously unconsidered structure for any compound of formula R_3EX_2 (E = P, As, Sb; X_2 = F_2, Cl_2, Br_2, I_2, IBr). It may be suggested that this structure represents an intermediate between the two bonding extremes, *viz.* the covalent $Ph_3P–X–X$ and the ionic $[Ph_3PX]X$. The former structure is stable for X = Br, I, but for X = Cl a new structural motif assembles.

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Footnote

† The complex crystallises as $[Ph_3PCl\cdots Cl\cdots ClPPh_3]Cl\cdot 2CH_2Cl_2$; there is no bonding interaction between **1** and the dichloromethane solvent of crystallisation molecules: *Crystal data*: cubic, space group $Pa\bar{3}$ (no. 205), a = 15.994(5) Å, U = 4091(1) Å^3, Z = 4, D_c = 1.358 g cm^{-3}, μ = 6.57 cm^{-1}, $F(000)$ = 1712. The structure analysis is based on 782 reflections (Mo–Kα, $2\theta_{max}$ = 49.9°), 265 observed [$I > 1.75\sigma(I)$], 82 parameters. Absorption correction (min., max. transmission 0.82, 1.00). The structure was solved by direct methods and refined by full-matrix least-squares. Final residuals R = 0.057, R_w = 0.054. The dichloromethane solvent of crystallisation was disordered. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/252.

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