

# Structural dependence of the reagent $\text{Ph}_3\text{PCl}_2$ on the nature of the solvent, both in the solid state and in solution; X-ray crystal structure of trigonal bipyramidal $\text{Ph}_3\text{PCl}_2$ , the first structurally characterised five-coordinate $\text{R}_3\text{PCl}_2$ compound

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The very delicate structural balance of  $\text{Ph}_3\text{PCl}_2$  when prepared in diethyl ether solution is illustrated by its X-ray crystallographic study; unlike the ionic species,  $[\text{Ph}_3\text{PCl}^+\cdots\text{Cl}^-\cdots\text{ClPPh}_3]\text{Cl}$ , which prevails in dichloromethane solution, the non-solvated molecular species  $\text{Ph}_3\text{PCl}_2$  is formed in diethyl ether which is the first example of a trigonal bipyramidal  $\text{R}_3\text{PCl}_2$  compound to be structurally characterised, and this may have an effect on the chlorinating ability of the reagent.

Although there are a number of previous reports concerning compounds of stoichiometry  $\text{R}_3\text{PCl}_2$ , which are mainly focused on  $\text{Ph}_3\text{PCl}_2$ , they are predominantly concerned with the nature of such species in solution, using  $^{31}\text{P}$  NMR spectroscopy.<sup>1–9</sup> All such studies, performed in acetonitrile or dichloromethane solution, concluded that the compounds are ionic,  $[\text{R}_3\text{PCl}]\text{Cl}$ . Similarly, conductivity studies of  $\text{Ph}_3\text{PCl}_2$  in acetonitrile solution led Harris and coworkers<sup>10,11</sup> to conclude that the compound is ionic,  $[\text{Ph}_3\text{PCl}]\text{Cl}$ , since values close to those expected for a 1:1 electrolyte were recorded. However, Arzoumandis<sup>13</sup> investigated the structural nature of  $\text{Ph}_3\text{PCl}_2$  in haloform solvents and concluded, from cryostatic and vibrational spectroscopic studies, that 1:1  $\text{Ph}_3\text{PCl}_2\cdot\text{YCX}_3$  ( $\text{Y} = \text{H}, \text{D}; \text{X} = \text{Cl}, \text{Br}$ ) adducts were formed. It was reasoned that these species were molecular dimeric entities which contain six-coordinate phosphorus atoms.

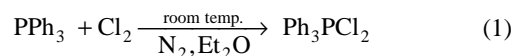
Studies concerning the solid-state structure of  $\text{R}_3\text{PCl}_2$  compounds are rare, and studies concerning  $\text{R}_3\text{PCl}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) again concluded an ionic structure,  $[\text{R}_3\text{PCl}]\text{Cl}$ .<sup>13–15</sup>

There is renewed interest in the structural nature of compounds of stoichiometry,  $\text{R}_3\text{EX}_2$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ). We have established the solid-state molecular charge transfer 'spoke' structure for  $\text{Ph}_3\text{PX}_2$ , viz.  $\text{Ph}_3\text{P}-\text{X}-\text{X}$ , ( $\text{X}_2 = \text{Br}_2$ ,<sup>16</sup>  $\text{I}_2$ ,<sup>17–19</sup>  $\text{IBr}^{20}$ ), whereas other workers have shown that  $\text{Ph}_3\text{PF}_2$  is trigonal bipyramidal.<sup>21,22</sup> A Raman spectroscopic study<sup>23</sup> of  $\text{Ph}_3\text{PCl}_2$  prepared in toluene solution suggested that two structural modifications could exist, an ionic form,  $[\text{Ph}_3\text{PCl}]\text{Cl}$ , prepared by bubbling dichlorine gas through a toluene solution of  $\text{PPh}_3$  and, possibly, a trigonal bipyramidal form, prepared by passing a stream of dichlorine over the surface of a toluene solution of  $\text{PPh}_3$ .

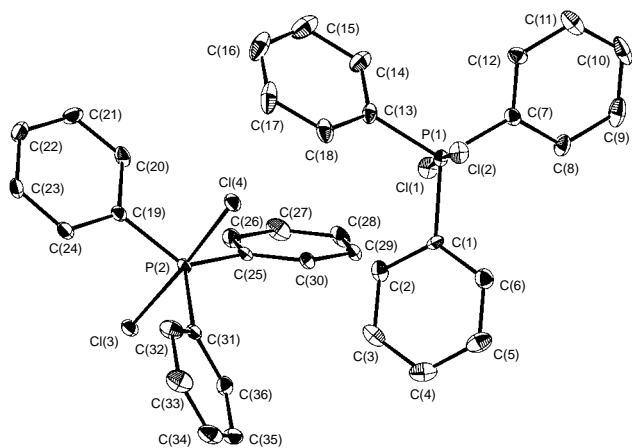
Until very recently, no single crystal X-ray crystallographic data was available for any compound of stoichiometry  $\text{R}_3\text{PCl}_2$ . However, a crystallographic study<sup>24</sup> of the compound prepared from the reaction of  $\text{PPh}_3$  and dichlorine in dichloromethane solution revealed an unusual dinuclear ionic compound,  $[\text{Ph}_3\text{PCl}^+\cdots\text{Cl}^-\cdots\text{ClPPh}_3]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$ . The long  $\text{Cl}\cdots\text{Cl}$  contacts are 3.279(6) Å (van der Waals radius for dichlorine is 3.6 Å). The solution  $^{31}\text{P}\{\text{H}\}$  NMR of this species, recorded in  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  gave single resonances at  $\delta$  65.5 and 66.5, respectively, these values being very similar to the values quoted by previous workers and indicating that the simple ionic species  $[\text{Ph}_3\text{PCl}]\text{Cl}$  prevails in solution for these solvents, and the long range  $\text{Cl}\cdots\text{Cl}$  contacts are broken, as expected.

It therefore occurred to us that a different structural modification of  $\text{Ph}_3\text{PCl}_2$  could be exhibited in solvents of low relative permittivity (low polarity). One reason for this was the fact that  $[\text{Ph}_3\text{PCl}^+\cdots\text{Cl}^-\cdots\text{ClPPh}_3]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$  contains a dichloromethane solvent molecule in the structure,<sup>24</sup> suggesting non-innocent behaviour, and although no bonding interactions between the solvent and the compound are observed, there nevertheless remains the fact that  $\delta^+$  hydrogens on the dichloromethane point towards the  $\text{Cl}^-$  ions giving a suspicion of long range electrostatic interaction, and, therefore, an implied influence on the structure adopted. Considering the widespread use of  $\text{Ph}_3\text{PCl}_2$  as a chlorinating agent, the structural nature of the reagent is of great importance since the structure may influence its efficacy as a chlorinating agent and, possibly, the mechanism of chlorination. Consequently, the choice of solvent employed for a given chlorination reaction utilising  $\text{Ph}_3\text{PCl}_2$  may be of fundamental importance.

Triphenylphosphine dichloride was prepared by us from the direct reaction of triphenylphosphine with dichlorine in diethyl ether in a 1:1 stoichiometric ratio [eqn. (1)].



The resultant white powder, which formed almost immediately upon addition of the dichlorine, was recrystallised from diethyl ether solution to produce a large quantity of colourless crystals on standing at room temperature for ca. 1 week. The melting point of the crystals was determined to be 118–119 °C {cf. 160–161 °C for  $[\text{Ph}_3\text{PCl}^+\cdots\text{Cl}^-\cdots\text{ClPPh}_3]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$ }. A crystal was chosen for analysis by single crystal X-ray diffraction. Interestingly, the structure<sup>‡</sup> of  $\text{Ph}_3\text{PCl}_2$  is shown to be the sole example of a molecular trigonal bipyramidal  $\text{R}_3\text{PCl}_2$  compound, Fig. 1, and not the ionic structure,  $[\text{Ph}_3\text{PCl}^+\cdots\text{Cl}^-\cdots\text{ClPPh}_3]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$  which prevails in dichloromethane solution. This result is important for two reasons: firstly, the very delicate balance between ionic and covalent forms for  $\text{Ph}_3\text{PCl}_2$  is clearly illustrated, in the more polar  $\text{CH}_2\text{Cl}_2$  an ionic structure is adopted whereas in diethyl ether a molecular form is revealed. Secondly, the acute solvent dependency of the structure of this reagent is clearly shown, and other workers utilising the reagent for chlorination reactions may find different rates and/or products which are dependent solely on the polarity of the solvent chosen. The structure of  $\text{Ph}_3\text{PCl}_2$  contains two crystallographically independent molecules in the asymmetric unit which exhibit quite different P–Cl bond lengths. In one molecule,  $d(\text{P}-\text{Cl})$  are quite similar, being 2.252(2) and 2.262(2) Å, however differences are observed in the other, 2.280(2) and 2.225(1) Å. Both molecules also exhibit slight distortions from regular trigonal bipyramidal geometry. These distortions and the asymmetry of the  $d(\text{P}-\text{Cl})$  may arise from the ease of ionisation of the molecule. However, asymmetric bonds in multiple halide systems are not un-



**Fig. 1** X-Ray crystal structure of trigonal bipyramidal  $\text{Ph}_3\text{PCl}_2$  (two crystallographically independent molecules are present in the asymmetric unit). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): P(1)–Cl(1) 2.280(2), P(1)–Cl(2) 2.225(1), P(2)–Cl(3) 2.262(2), P(2)–Cl(4) 2.252(2), C(7)–P(1)–C(1) 123.5(2), C(7)–P(1)–C(13) 118.2(2), C(1)–P(1)–C(13) 118.2(2) C(12)–P(1)–Cl(1) 176.09(6), C(19)–C(25) 120.0(2), C(19)–P(1)–C(31) 123.6(2), C(25)–P(2)–C(31) 116.42, Cl(4)–P(2)–Cl(3) 176.20(6).

common. The classic example is  $\text{I}_3^-$ , where asymmetric I–I bonds are ascribed to the influence of surrounding molecules or ions. Our recent work has shown even more dramatic examples of autosolvation in  $\text{R}_3\text{PCl}_2$  systems.<sup>25</sup> In the case of  $\text{Ph}_3\text{PCl}_2$  described here, comparison of the four Cl environments shows that the closest approaches between Cl and H in adjacent molecules are 2.92, 3.05, 2.83 and 2.82 for Cl(1), Cl(2), Cl(3) and Cl(4), respectively. As P–Cl(4) is the shortest P–Cl bond, it would appear that phenyl rings are exerting their influence on  $d(\text{P}–\text{Cl})$ . We have previously observed this phenomenon with interaction of Cl with  $\delta^+$  hydrogens on propyl chains.<sup>25</sup> Caution must be exercised when discussing E–X (E = P, As, Sb, Bi; X = Br, Cl) bond lengths however, since considerable asymmetry has already been illustrated from crystallographic studies *e.g.*  $\text{Ph}_3\text{BiCl}_2$ <sup>26</sup> [ $d(\text{Bi}–\text{Cl})$  2.529–2.615  $\text{\AA}$ ],  $[\text{Me}_3\text{CH}–\text{CH}_2]_3\text{AsBr}_2$ ,<sup>27</sup> [ $d(\text{As}–\text{Br})$  2.530–2.596  $\text{\AA}$ ],  $\text{Ph}_3\text{SbCl}_2$  [ $d(\text{Sb}–\text{Cl})$  2.382–2.490  $\text{\AA}$ ].<sup>28</sup>

The solution structure of  $\text{Ph}_3\text{PCl}_2$  in low-polarity solvents is also of importance since the trigonal bipyramidal structure of  $\text{Ph}_3\text{PCl}_2$  could simply be a solid-state phenomenon, *i.e.* the molecule could auto-ionise in any given solvent, which has already been illustrated<sup>25</sup> when  $\text{Ph}_3\text{PCl}_2$  is dissolved in  $\text{CH}_2\text{Cl}_2$ . Deuterated ether,  $\text{C}_2\text{D}_6\text{O}$  is not really available; however, we dissolved a sample of crystalline  $\text{Ph}_3\text{PCl}_2$  prepared in  $\text{Et}_2\text{O}$  in deuterated benzene,  $\text{C}_6\text{D}_6$ , *i.e.* a non-polar solvent. A single resonance was observed in the NMR spectrum at  $\delta -47$ , very different to that observed for the ionic  $[\text{Ph}_3\text{PCl}\cdots\text{Cl}\cdots\text{ClPPh}_3]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$  which exhibited resonances at  $\delta$  65.5 or 66.5 (recorded in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ , respectively). This value of  $\delta -47$  is also completely different to any previously reported value for a sample of  $\text{Ph}_3\text{PCl}_2$  which, prior to this work, has only been studied by  $^{31}\text{P}\{\text{H}\}$  NMR spectroscopy in solvents of quite high polarity. This value of  $\delta -47$  is however comparable to analogous difluorophosphoranes,  $\text{R}_3\text{PF}_2$ , which are known to retain a molecular five-coordinate geometry in solution, *e.g.*  $\text{MePh}_2\text{PF}_2$  ( $\delta -43.2$ ) and  $\text{Ph}_3\text{PF}_2$  ( $\delta -58.1$ ).

The only  $^{31}\text{P}\{\text{H}\}$  NMR study of a compound of stoichiometry  $\text{R}_3\text{PCl}_2$ ,<sup>27</sup> which was claimed to be trigonal bipyramidal is  $(\text{C}_6\text{F}_5)_3\text{PCl}_2$ , which gave a single resonance at  $\delta -110$ .<sup>29</sup>

Clearly, therefore,  $\text{Ph}_3\text{PCl}_2$  retains a molecular trigonal bipyramidal structure in solvents of low polarity. Addition of  $\text{CH}_2\text{Cl}_2$  to the  $\text{C}_6\text{D}_6$  solution of  $\text{Ph}_3\text{PCl}_2$  ionises the molecule to produce  $[\text{Ph}_3\text{PCl}\cdots\text{Cl}\cdots\text{ClPPh}_3]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$ , since a resonance

at  $\delta$  65.5 is observed and the former resonance at  $\delta -47.0$  disappears.

In conclusion, the solvent of preparation is critical in determining the structure of  $\text{Ph}_3\text{PCl}_2$ . A molecular form persists in solvents of low polarity which is converted into an ionic form in solvents of higher polarity. Which structure is adopted will almost certainly have an effect on the chlorinating ability of the reagent, and, possibly, the nature of any products formed.

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## Notes and References

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‡ *Crystal data*: Triclinic, space group  $P\bar{1}$  (no. 2)  $a = 9.408(2)$ ,  $b = 11.579(6)$ ,  $c = 16.203(2)$   $\text{\AA}$ ,  $\alpha = 95.23(3)$ ,  $\beta = 103.09(2)$ ,  $\gamma = 111.10(3)^\circ$ ,  $U = 1574.7(1)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.405$   $\text{g cm}^{-3}$ ,  $\mu = 5.04$   $\text{cm}^{-1}$ ,  $F(000) = 688$ . The structure analysis is based on 5280 reflections ( $\text{Mo-K}\alpha$   $2\theta_{\text{max}} = 49.9$ ), 5222 observed [ $I > 2\sigma(I)$ ], 379 parameters Absorption correction (min., max. transmission 0.81, 1.00). The structure was solved by direct methods and refined by full-matrix least squares. Final residual  $R_1 = 0.0762$ ,  $wR_2 = 0.2137$ . Final residuals (all data)  $R_1 = 0.0941$ ,  $wR_2 = 0.2681$ . CCDC 182/773.

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