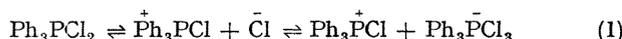


## Evidence for a Novel, Haloform-solvated Triphenylphosphine Dichloride Dimer

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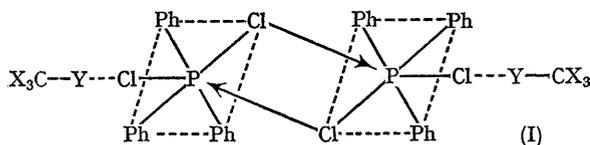
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FROM behaviour of  $\text{Ph}_3\text{PCl}_2$  in solution<sup>1</sup> the position of the equilibrium (I) has been shown to depend on the solvent used; the presence of Lewis acids also affects it.



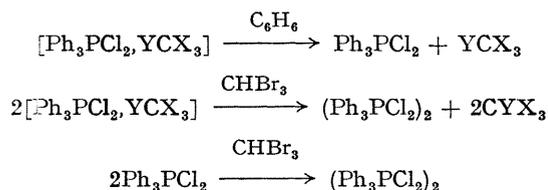
We report that  $\text{Ph}_3\text{PCl}_2$  in haloform solutions forms H- or D-bonded solvates of the nonionic dimeric structure (I) in which the two moieties are linked by chlorine bridges between the phosphorus atoms.

Thus,  $\text{Ph}_3\text{PCl}_2$  was mechanically stirred (1 hr., room temp.) in pure, alcohol-free haloform under nitrogen; removal of solvent under reduced pressure gave the crystalline 1:1 adduct  $\text{Ph}_3\text{PCl}_2 \cdot \text{YCX}_3$  (Y = H or D, X = Cl or Br) (quantitative yield). Elemental analysis was satisfactory.



The compounds are stable under anhydrous conditions and  $\text{Ph}_3\text{PCl}_2 \cdot \text{CHBr}_3$  crystallizes from aromatic hydrocarbons that boil lower than  $\text{CHBr}_3$  (e.g. toluene);  $\text{Ph}_3\text{PCl}_2 \cdot \text{CHCl}_3$  yields only  $\text{Ph}_3\text{PCl}_2$ .

Cryoscopic molecular-weight determinations provide evidence for the following schemes, at the freezing point of the indicated solvent:



The n.m.r. spectra of saturated solutions (ca. 3%) of  $\text{Ph}_3\text{PCl}_2 \cdot \text{CHX}_3$  in  $\text{CDCl}_3$  ( $\text{Me}_4\text{Si}$  as internal standard) show no shift of the  $\text{CHX}_3$  resonance, due to the low solubility of the complexes. The solvation of the species  $(\text{Ph}_3\text{PCl}_2)_2$  in a

mixture of haloforms is an equilibrium reaction, as indicated by the i.r. spectra of  $\text{Ph}_3\text{PCl}_2 \cdot \text{YCX}_3$  in  $\text{Y}'\text{CX}'_3$  solutions (e.g.  $\text{Ph}_3\text{PCl}_2 \cdot \text{CHCl}_3$  in  $\text{CDCl}_3$  or  $\text{CHBr}_3$ ).

In each spectrum a new, relatively intense band appears at a frequency lower than the CY stretching vibration of the solvent.

$$\Delta\nu(\text{CHCl}_3) = 58 \text{ cm.}^{-1}, \Delta\nu(\text{CDCl}_3) = 37 \text{ cm.}^{-1}$$

$$\Delta\nu(\text{CHBr}_3) = 48 \text{ cm.}^{-1}$$

In the i.r. spectrum of  $\text{Ph}_3\text{PCl}_2$  in  $\text{CHCl}_3\text{-CDCl}_3$  (1:1) there are two new bands resulting from H- and D-bonding to the chlorine of the phosphorus moiety ( $\pi$ -interactions with aromatic systems are generally accompanied by an increase in intensity with no resolution of a new band).<sup>2</sup>

In the i.r. spectra in the solid state (Nujol and KEL-F Oil mulls), co-ordinated haloform bands were found by comparison of the  $\text{Ph}_3\text{PCl}_2$  and  $\text{Ph}_3\text{PCl}_2 \cdot \text{YCX}_3$  spectra.

The bathochromic  $\nu(\text{CY})$  shift [ $\Delta\nu(\text{CHCl}_3) = 143 \text{ cm.}^{-1}$ ,  $\Delta\nu(\text{CDCl}_3) = 105 \text{ cm.}^{-1}$ ,  $\Delta\nu(\text{CHBr}_3) = 143 \text{ cm.}^{-1}$ ], accompanied by intensity increase is again strong evidence for H- or D-bonding to the chlorine of the phosphorus moiety.

A new band-assignment pattern, common to all co-ordinated haloforms, is indicative of a lowering of their symmetry from  $C_{3v}$  to  $C_s$  point group, due to crystal-lattice effects.

The strong and sharp P-Cl stretch of the complexes at  $517 \text{ cm.}^{-1}$  is accompanied by a medium shoulder at  $498 \text{ cm.}^{-1}$  (P-Cl  $\rightarrow$  P vibration). In the  $\text{Ph}_3\text{PCl}_2$  spectrum there is only one strong band at  $517 \text{ cm.}^{-1}$ ; no strong band appears at  $772 \text{ cm.}^{-1}$   $\nu_{\text{as}}(\text{PC})$  in the adducts. There are marked changes in intensities and number of bands in the regions  $690\text{--}700$ ,  $430\text{--}470$  [ $\nu(\text{CP})$  modes] and  $540\text{--}550 \text{ cm.}^{-1}$  [ $\gamma(\text{PC})$  modes]. Since the P-C vibration frequencies depend on the nature and number of the substituents of the phosphorus centre,<sup>3</sup> the above differences can be interpreted as a result of a change in the co-ordination number of this atom in the complexes. For a symmetrical,<sup>†</sup> nonionic  $\text{Ph}_3\text{PCl}_2$  dimer the co-ordination number of phosphorus is six.

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<sup>†</sup> A nonsymmetrical  $\text{Ph}_3\text{PCl}_2$  "dimer" would lead to the ionic form  $\text{Ph}_3\text{PCl}^+\text{Ph}_3\text{PCl}_3^-$ .

<sup>1</sup> D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, 1968, **90**, 6332, and references therein.

<sup>2</sup> M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 2966.

<sup>3</sup> T. Goubeau and G. Wenzel, *Z. phys. Chem. (Frankfurt)* 1965, **45**, 31.