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STUDIES IN ORGANOPHOSPHORUS CHEMISTRY

III.(1) STRUCTURES OF TERTIARY PHOSPHINE DIHALIDES IN SOLUTION

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Tertiary phosphine dihalides (R_3PX_2) are efficient reagents for alkyl halide synthesis by virtue of having only two replaceable groups on "pentavalent" phosphorus(3). Previous attempts at determining the structures of these substances have had limited success(4). We report here the solution to this problem.

Analogy with the phosphorus pentahalides suggests the structural possibilities shown in Equation 1(5a, b):

$$\underset{\text{I}}{R_3PX_2} \rightleftarrows \underset{\text{II}}{R_3PX^+\ X^-} \rightleftarrows \underset{\text{III}}{R_3PX^+\ R_3PX_3^-} \qquad (1)$$

$$R = \underline{n}\text{-}C_4H_9 \text{ or } C_6H_5;\quad X = Cl,\ Br,\ \text{or } I$$

Our method is based on the premise that in the presence of a strong Lewis acid all of the phosphorus species in Equation 1 will convert completely to phosphonium salt ($R_3PX^+\ LX^-$; where L is the Lewis acid)(4a, 5b, c). This permits the spectroscopic properties of R_3PX^+ to be unambiguously defined.

Results:

A. Triphenylphosphine Dichloride

TABLE I

P^{31} N.M.R. Data for Triphenylphosphine Dichloride

Compound	Solvent	Chemical* Shift (p.p.m.)
Ph_3PCl_2**	CH_3CN	-62

Compound	Solvent	Chemical* Shift (p. p. m.)
$Ph_3PCl^+SbCl_6^-$	CH_3CN	-66
Ph_3PCl_2	$PhNO_2$	- 8
$Ph_3PCl^+AlCl_4^-$	$PhNO_2$	-65

*85% H_3PO_4 used as reference

**Spectra of hydrolysis products were run throughout to check for possible decomposition. Varying amounts of hydrolysis products were detected.

The similarity of the P^{31} n.m.r. chemical shift(6) for Ph_3Cl_2 in acetonitrile to those of its 1:1 adducts with $AlCl_3$ or $SbCl_5$ provides strong evidence that in each case the resonance observed is that of the chlorotriphenylphosphonium ion (Ph_3PCl^+) and that triphenylphosphine dichloride exists as the phosphonium chloride structure in acetonitrile (Type II in Equation 1). The considerably more positive shift for Ph_3PCl_2 in nitrobenzene suggests that in this solvent it exists as a pentavalent species or as $R_3PX^+R_3PX_3^-$.

These conclusions are fully supported by infrared spectra(7) in the 800-250 cm^{-1} region The spectrum of Ph_3PCl_2 in acetonitrile underwent no change upon addition of one equivalent of $SbCl_5$ except for the appearance of an intense band at 335 cm^{-1} attributable to the $SbCl_6^-$ ion.(5b) Triphenylphosphine dichloride in nitrobenzene exhibits a band at 310 cm^{-1} which is absent in its spectrum in acetonitrile as well as in the spectra of its Lewis acid adducts.

The work of Moedritzer and Van Wazer(9) combined with the assumption that the difference in chemical shifts between Ph_3PCl^+ and $Ph_3PCl_6^-$ would be greater than 150 p.p.m. permits us to rule out rapid equilibration of these species to account for the single band found for Ph_3PCl_2 in nitrobenzene. One would expect that the necessary lifetime to allow appearance of the separated peaks is approximately 10^{-7} sec. The exchange rate is likely smaller than that(10) so that a separate band should appear for each ion if present. We thus conclude that the pentavalent form prevails in nitrobenzene.

B. Tri-n-butylphosphine Dichloride

TABLE II

P^{31} N.M.R. Data for Tributylphosphine Dichloride

Compound	Solvent	Chemical Shift (p. p. m.)
$(\underline{n}\text{-}C_4H_9)_3PCl_2$	CH_3CN	-106
$(\underline{n}\text{-}C_4H_9)_3PCl^+SbCl_6^-$	CH_3CN	-102
$(\underline{n}\text{-}C_4H_9)_3PCl_2$	$PhNO_2$	-104

The P^{31} n.m.r. data for this substance are given in Table II. The similarity of the chemical shifts for this substance in either acetonitrile or nitrobenzene to that of its 1:1 adduct with $SbCl_5$ in acetonitrile causes us to assign the phosphonium chloride structure (Type II in Equation 1) to it in both of these solvents. The infrared and proton n.m.r. data for these substances are more ambiguous but are more easily rationalized on the basis of structure II. Table III reproduces the pertinent data. Only minor shifts in infrared absorption frequencies and intensities are observed for the $SbCl_5$ adduct as compared with tributylphosphine dichloride. Major shifts normally accompany changes in coordination number from five to four.(4b, 5b) That no such change has occurred is suggested by the slight upfield shift of the α-CH_2 in the $SbCl_5$ adduct. A large downfield shift might have been expected if five to four coordination changes were occurring.(8) The small changes in these spectra could arise from environmental effects occasioned by changing the counter ion of an ion pair.

TABLE III

Infrared and Proton N.M.R. Spectra of
Tributylphosphine Dichloride in Acetonitrile

Compound	Chemical Shift* for α-CH_2 (p.p.m.)	Infrared Bands (cm^{-1})	
$(\underline{n}\text{-}C_4H_9)_3PCl_2$	-3.14	546	524
$(\underline{n}\text{-}C_4H_9)_3PCl^+SbCl_6^-$	-2.61	555	540

*Tetramethyl silane used as a reference

Similar experiments have been done with tri-n-butylphosphine dibromide using mercuric bromide as the Lewis acid. P^{31} n.m.r. data indicate that the phosphonium salt structure is again present in both acetonitrile and nitrobenzene. In both solvents the dibromide has a chemical shift of 105 p.p.m. which changes only to 102 p.p.m. upon addition of the Lewis acid.

Compounds of the type R_3PF_2 (R = phenyl, methyl, ethyl, or n-butyl) are reported to be "pentavalent" as pure liquids.(4d) All these findings harmonize with the expectation that the tendency toward "pentavalence" follows the patterns: F > Cl > Br > I, Ph > alkyl and non-polar solvents > polar solvents.

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