# DEDUCTION OF THE STRUCTURES OF THE $R_n PCl_{5-n}$ CHLOROPHOSPHORANES FROM THEIR <sup>31</sup>P NMR SPECTRA IN SOLUTION

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The structure of  $PCl_5$  has been thoroughly studied, both in the solid state and in solution [1]. There is, however, only a limited amount of information on the structures of the organylchlorophosphoranes [2-7].

The molecules of  $PF_5$  and many of the fluorophosphoranes have trigonal bipyramidal form [8, 9]. The situation with respect to the chlorides is somewhat ambiguous. It has been suggested that these compounds are unstable, passage from one P coordination state to another occurring spontaneously under certain conditions. There is an indication that certain phosphoranes break down in solution to establish a

$$R_3PCl_2 \rightleftharpoons R_3PCl + Cl^-$$

type equilibrium [2, 3].

Since the <sup>31</sup>P chemical shift (CS) is closely dependent on the state of the phosphorus, <sup>31</sup>P NMR spectroscopy offers the most direct approach to the study of coordination in phosphorus compounds. For example, the chemical shifts of  $PCl_4^+$ ,  $PCl_5$ , and  $PCl_6^-$  are -91, +80, and +281 ppm, respectively [9]. We have, therefore, followed this method in studying the behavior of certain organylchlorophosphoranes in polar and nonpolar solvents (Table 1).

All of the <sup>31</sup>P NMR spectra were obtained with complete decoupling of the spin – spin proton interaction; each showed isolated signals, the position of which varied from case to case. One could have anticipated a widening of the signal, or even the appearance of two signals, one for the molecular, and one for the ionic, form

	Solvent			
Compound	CH₃CN	CH₃NO₂	C <sub>6</sub> H <sub>6</sub>	
$\begin{array}{c} C_{2}H_{3}PCl_{4} \\ C_{6}H_{41}PCl_{4} \\ (C_{4}H_{3})_{3}NPCl_{4} \\ C_{6}H_{4}PCl_{4} \\ P-CH_{3}C_{6}H_{4}PCl_{4} \\ P-CH_{3}C_{6}H_{4}PCl_{4} \\ P-CH_{3}C_{6}H_{4}PCl_{4} \\ P-Clc_{6}H_{4}PCl_{4} \\ (C_{2}H_{3})_{2}PCl_{3} \\ (t-C_{4}H_{3})_{2}PCl_{3} \\ (t-C_{4}H_{3})_{2}PCl_{3} \\ (C_{6}H_{3})_{2}PCl_{2} \\ (t-C_{4}H_{3})_{3}PCl_{2} \\ (t-C_{4}H_{3})_{3}PCl_{2} \\ (t-C_{4}H_{3})_{3}PCl_{2} \\ (c_{6}H_{3})_{4}PCl_{2} \\ (C_{6}H_{3})_{2}PCl_{2} \\ (C_{6}H_{3})_{2}C-Cl_{2} \\ (C_{6}H_{3})_{2}C-Cl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C_{4}H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C_{4}H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C_{4}H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}C-H_{3}PCl_{2} \\ (C_{6}H_{3})_{2}P-Cl_{2} \\ (C_{6}H_{3})_{2}P-Cl_{3} \\ (C_{6}H_{3})_{3}P-Cl_{3} \\ (C_{6}H_{3})_{3}P-Cl_{3}$	$\begin{array}{r} -24,4\\ -124,3\\ -52,6\\ +36,8\\ +10,6\\ +28,0\\ +36,3\\ -137,3\\ -158,0\\ -138,4\\ -52,4\\ -112,1\\ -118,4\\ -52,4\\ -112,1\\ -104,2\\ -63,7\\ -91,0\\ -75,2\\ -85,7\\ -63,6\\ -90,2\\ \end{array}$	$\begin{array}{r} -26,7\\ -127,9\\ -56,4\\ +44,0\\ +16,3\\ +15,7\\ +25,0\\ -137,9\\ -157,7\\ -137,7\\ -64,5\\ -111,4\\ -117,4\\ -103,2\\ -56,3\\ -90,3\\ -75,4\\ -85,3\\ -63,6\\ -89,7\end{array}$	+25,7 +71,9 +45,4 $\ddagger$ +44,8 +47,2 +47,0 -18,5	

TABLE 1. <sup>31</sup> P Chemical Shifts in the Chlorophosphoranes ( $\delta$ , ppm; relative to 85% H<sub>2</sub>PO<sub>4</sub>)\*

\*Spectra obtained immediately after dissolution.

†In dichloroethane - 37.4.

fin solid state + 37.6.

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(1)

TABLE 2. Change in the Chlorophosphorane <sup>31</sup>P CS Resulting from Dissolution in CH<sub>3</sub>NO<sub>2</sub> ( $\delta$ , ppm; relative to 85% H<sub>3</sub>PO<sub>4</sub>)

	Chemical shift after			
Compound	'ı min	9 h	48h	
$\begin{array}{c} C_{2}H_{5}PCl_{4}\\ C_{2}H_{5}PCl_{4}\\ p-CH_{2}C_{6}H_{4}PCl_{4}\\ p-CH_{3}OC_{6}H_{4}PCl_{4}\\ p-ClC_{6}H_{4}PCl_{4}\\ (C_{6}H_{5})_{2}PCl_{3}\\ (C_{6}H_{5})_{3}PCl_{2} \end{array}$	$\begin{array}{c c} -26,6 \\ +41,0 \\ +16,3 \\ +15,7 \\ +25,0 \\ -64,5 \\ -5,63 \end{array}$	+9,9 +2,3 +10,6	-114,7 -87,9 -96,6 -96,9 -77,6 -92,7 -64,0	

in the spectra of solutions in which a type (1) equilibrium hadbeen established. The absence of such effects was probably due to the fact that exchange is rapid on the NMR time scale [10]. Attempts to reduce the exchange rate by cooling the solution led to precipitation of the sparingly soluble chlorophosphoranes. Certain facts, suggest, however, that this equilibrium was indeed established in our solutions. It can be seen from Table 1 that the solvent itself has a marked effect on the <sup>31</sup>P CS in the chlorophosphoranes. For EtPCl<sub>4</sub>, Et<sub>2</sub>PCl<sub>3</sub>,  $Et_2NPCl_4$ , and the arylchlorophosphoranes in  $C_6H_6$ , the <sup>31</sup> P CS fell in the region characteristic of pentacoordinated phosphorus compounds. For solutions in the ionizing MeCN and MeNO<sub>2</sub>, the signal was shifted into the region characteristic of tetracoordinated phosphorus compounds. The shift in Et<sub>2</sub>NPCl<sub>4</sub> paralleled the change in the solvent dielectric constant ( $C_6H_6$ ,  $\varepsilon = 2.28$ ,  $\delta^{31}P = 71.9$ ;  $Cl(CH_2)_2Cl$ ,  $\varepsilon = 10$ ,  $\delta^{31}P = -37.4$ ; MeCN,  $\varepsilon = 36.2$ ,  $\delta^{31}P = -52.6$ ; MeNO<sub>2</sub>,  $\varepsilon = 38.6$ ,  $\delta^{31}P = 56.4$ ). This is in line with the known solvent effect in chemical equilibrium, solvents with high dielectric constant shifting the point of equilibrium toward the ionic form [11, 12].

The resonance signal of certain of the chlorophosphoranes in MeNO<sub>2</sub> solution was found to drift downfield with the passage of time (Table 2). This drift did not, however, alter the signal strength. It can be seen from the table that a 2-day drift carried the CS into the region characteristic of compounds with ionic, tetracoordinated structures. It can be assumed that one has here to deal with the gradual establishment of a stable equilibrium between ionic and molecular forms, the exchange rate remaining at its original high value. It is obvious that care must be used in working with CS's reported for chlorophosphoranes in polar solvents.

It can therefore be concluded that the position of the <sup>31</sup> P NMR signal in chlorophosphorane solutions will be determined by additive contributions from the molecular and ionic forms, the situation here being reminiscent of that observed in exchange reactions [10]

$$=\delta_{i0} \cdot N + \delta_{i0} \cdot N_{i0} + \delta_{i0} \cdot N_{i0}$$
(2)

 $\delta = \delta_{ion} \cdot N + \delta_{mol} \cdot N_{ion} + \delta_{mol} \cdot N_{mol}$  $\delta_{ion}$  and  $\delta_{mol}$  being the chemical shifts, and  $N_{ion}$  and  $N_{mol}$  the mole fractions, of the respective states.

A knowledge of the CS's of the molecular and ionic forms is required in order to determine the position. of the point of equilibrium. It can be assumed that the CS shift observed in nonpolar solvents such as  $C_{g}H_{g}$  is that corresponding to the molecular form. We have found, for example, that the CS's for the solid state and for the compound in  $C_{6}H_{6}$  solution are almost identical in the case of PhPCl<sub>4</sub>. It has been reported [13] that the molecule of this last compound has trigonal bipyramidal form in the crystalline state. Information concerning the ionic forms of the phosphoranes can be obtained from a study of the  ${}^{31}PCS$ 's in the corresponding organylchlorophos-phonium hexachlorophosphates, compounds with fixed  $R_nPCl_{4-n}$  cation (Table 3).

There have been relatively few <sup>31</sup>P NMR studies of compounds of this type [5, 14]. In solution, the spectra of each of the compounds studied here showed two resonance signals, corresponding to two phosphorus atoms in different coordination. The position of the  $PCl_6^-$  anion signal,  $298 \pm 0.6$  ppm, varied only slightly, change in the counter-ion having only a slight effect on the shielding. In distinction, the CS for the chlorophosphonium cation varied over rather wide limits.

Comparison of the data of Tables 1 and 3 shows that the organyltetrachlorophosphoranes exist largely in molecular form in benzene, but pass into their stabilized ionic forms under the action of polar solvents. As much is indicated by the fact that the <sup>31</sup>P CS's for Et<sub>2</sub>NPCl<sub>4</sub> and Et<sub>2</sub>NPCl<sub>3</sub> are almost identical, as are the CS's, first of the aryltetrachlorophosphoranes in their final ionization stages (cf. Table 2) and then for the corresponding aryltrichlorophosphonium hexachlorophosphates in nitromethane solution. With the assumptions suggested above, Eq. (2) can be drawn to calculate the mole fractions of the molecular and ionized forms present in chlorophosphorane solutions. One minute after dissolution in nitromethane, the respective mole fractions for PhPCl, were 0.97 and 0.03. Similar calculations were carried out for the other compounds.

· · ·	Chemical shift in the solvents			
Compound	CH₃CN	CH₃NO₂		
$C_{8}H_{*}PCl_{3} \cdot PCl_{6}$ $(C_{6}H_{5})_{2}PCl_{2} \cdot PCl_{6}$ $(C_{6}H_{5})_{3}PCl \cdot PCl_{6}$ $p-CH_{3}C_{6}H_{4}PCl_{3} \cdot PCl_{6}$ $p-CH_{3}OC_{6}H_{4}PCl_{3} \cdot PCl_{6}$ $p-Cl_{6}H_{4}PCl_{3} \cdot PCl_{6}$ $(C_{2}H_{3})_{2}PCl_{2} \cdot PCl_{6}$ $(z_{6}H_{4})_{2}PCl_{3} \cdot PCl_{6}$ $(z_{6}H_{4})_{2}PCl_{3} \cdot PCl_{6}$ $(z_{6}H_{4})_{3}PCl_{3} \cdot AlCl_{6}$ $(a-C_{4}H_{3})_{3}PCl_{-}SbCl_{6}$	$\begin{array}{c} -95.5; \ +298.0\\ -92.5; \ +298.1\\ -65.4; \ +297.9\\ -94.3; \ +297.8\\ -89.8; \ +297.4\\ -73.1; \ +298.0\\ -57.6; \ +298.0\\ -158.0; \ +296.6\\ -128.6 \ [15] \ +\\ -102 \ [3] \end{array}$	-101,0; +298,0 -92,0; +298,1 + -65,1; +298,4 + -101,1; +298,0 -97,1; +298,1 -99,6; +297,4 -58,6; +298,7 -158,3; +296,6		
In dichloroethane	e —73; +295 pp	m [5].		
Innitrobenzene -	-64.7; +298.0	[14].		
T				

TABLE 3. <sup>31</sup>P Chemical Shifts in the  $R_nPCl_{4-n}^+PCl_6^-$ Organylchlorophosphonium Hexachlorophosphates ( $\delta$ , ppm, relative to 85%  $H_3PO_4$ )

1 In tetrachloroethane [15].

It is clear that the triorganylchlorophosphoranes exist almost entirely in the ionized form, both in the crystalline state and insolution. The possibility that these compounds have saltlike structures is suggested by the fact that they are all insoluble in benzene. In addition, the CS's of  $Ph_3PCl_2$  and  $Bu_3PCl_2$  in polar solvents are close to those for the corresponding chlorophosphonium cations. It is also known that  $Ph_3PCl_2$  exists in ionic form in the solid state [16].

On the basis of the data presently available, it is difficult to identify the factors which determine the chlorophosphorane structures. It can, however, be suggested that the trigonal bipyramidal structure tends to pass over into the chlorophosphonium form under the action of electronic, and possibly steric, effects from the organic radicals at the phosphorus atom. These two forms exist simultaneously in solution, being in equilibrium, with the point of equilibrium displaced to the one side or the other.\*

#### EXPERIMENTAL

The <sup>31</sup>P NMR spectra were obtained with a Varian XL-100/12 spectrometer. Chemical shifts were measured relative to 85% H<sub>3</sub>PO<sub>4</sub> under complete decoupling of the spin – spin proton interaction. All the operations involved in synthesizing the various compounds and preparing their solutions for measurement were carried out in an atmosphere of dry argon, using absolute solvents.

The organyltetrachloro- and diorganyltrichlorophosphoranes were prepared by reacting the respective chlorophosphines with equimolar quantities of dry chlorine in  $CCl_4$  at low temperature. The triorganyldichlorophosphoranes were prepared by a modification of the procedure of [18], working at -30 °C and using etheral phosgene solutions as chlorinating agents. The organylchlorophosphonium hexachlorophosphates were synthesized by reacting PCl<sub>5</sub> with an equimolar quantity of the phosphorane in benzene.

### CONCLUSIONS

The methods of <sup>31</sup>P NMR spectroscopy have been used to show that the organylchlorophosphoranes exist as mixtures of ionic and molecular forms in solution. The position of the equilibrium point in these systems is determined by the solvent and the nature of the substituents in the chlorophosphorane.

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\* For additional data cf. [17].

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