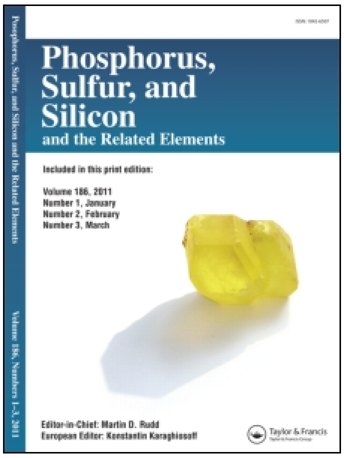

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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**To cite this Article** Wu, T. R. , Chen, W. Y. , Chiu, Y. S. and Chang, T. C.(1997) '$^{31}$P-NMR STUDY OF INTERMEDIATES IN PREPARATION OF PHENYLDICHLOROPHOSPHNE', Phosphorus, Sulfur, and Silicon and the Related Elements, 122: 1, 197 — 203

**To link to this Article: DOI:** 10.1080/10426509708043508
**URL:** http://dx.doi.org/10.1080/10426509708043508

*Phosphorus, Sulfur, and Silicon*, 1997, Vol. 122, pp. 197-203
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# $^{31}$P-NMR STUDY OF INTERMEDIATES IN PREPARATION OF PHENYLDICHLOROPHOSPHINE

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*(Received 26 November 1996; In final form 12 December 1996)*

Phenyldichlorophosphine was prepared via the $AlCl_3$-$PCl_3$ complex method, wherein benzene was caused to react with phosphorus tricholoride ($PCl_3$) in the presence of aluminum chloride ($AlCl_3$) followed by the separation of $AlCl_3$ with tris(2-chloroethyl)-phosphate. The intermediates and mechanism of the reaction were investigated by $^{31}$P nuclear magnetic resonance (NMR) spectroscopy. The results revealed three kinds of intermediates in NMR time scale in the reaction. A reaction mechanism was proposed.

*Keywords:* Phenyldichlorophosphine; $^{31}$P nuclear magnetic resonance; intermediate; mechanism

## INTRODUCTION

Phenyldichlorophosphine (PDC) is a very useful organophosphorus intermediate[1]. It may be used in the manufacture of the insecticides, polymers high temperature stabilizers and fire retardants[2-4]. $PhPCl_2$ is easily obtained from $C_6H_6$ + $PCl_3$ at high temperature. Various processes for the preparation of PDC are known in the art[5-10]. The laboratory method for the preparation of PDC is the $AlCl_3$-$PCl_3$ complex method, in which phosphorus trichloride reacts with benzene in the presence of aluminum chloride as catalyst[11]. The products of this method have been separated with various binding agents. However, the characterization of the intermediates in situ reaction is limited. The advantages of

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*Corresponding author.

nuclear magnetic resonance (NMR) spectroscopy is that they are quick, nondestructive and accurate. In this paper, $^{31}$P-NMR is used to investigate the intermediates and then to propose the reaction mechanism.

## EXPERIMENTAL

### Materials

All reagents are Merck c.p. quality. Phosphorus trichloride and aluminum chloride were used without further purification. Benzene was dried over phosphorus pentaoxide. Tri(2-chloroethyl)phosphate was used as received.

### Reactions

In all experiments, various molar portions of phosphorus trichloride, aluminum chloride and benzene were refluxed under nitrogen in a three-necks flask (500 mL) equipped with a long-stem thermometer, and a Allihn condenser (jacket length 30 cm). The solution was refluxed (≈90°C) with vigorous stirring (500 rpm). During the reaction, a sample was drawn out (0.5 mL) by long dropper from the top of the condenser for NMR experiment.

### Instruments

The $^{31}$P-NMR spectra were determined on a JEOL FX-90Q spectrometer operating at 36.23 MHz, and were referenced to 85% $H_3PO_4$ as an external standard. Two-dimensional $^{31}$P-$^{31}$P COSY was recorded on a Bruker MSL-300 spectrometer.

## RESULTS AND DISCUSSION

### Mechanism of Reaction

The $^{31}$P-NMR spectra of reaction mixture (molar ratio of $C_6H_6 : PCl_3 : ACl_3$ = 1 : 3 : 1.05) as a function of time elapsed are shown in Fig. 1. Initially we find only one peak (Fig. 1A) for the reactant $PCl_3$ at 218 ppm. However, several new signals are observed at 110, 83, 79 and 59 ppm after reaction at 90°C for 15 min (Fig. 1B). The intensities of the peaks at 110 and 83 ppm increase as the reaction proceeds, whereas that at 79 and 59 ppm decrease. On the other hand, only the five signals are observed in the evolution of the reaction (Fig. 1A to 1E), suggesting that the reaction proceeds with no other side-reactions.

The chemical shift at 218 ppm ($PCl_3$) is independent on the extent of the reaction. The $AlCl_4^-PCl_2^+$ complex formed in the Friedel-Crafts alkylation is not found in the NMR spectra, therefore the transient complex $[Cl_2P...Cl...AlCl_3]$ may be proposed. After $^{31}P$-$\{^1H\}$ decoupling, the upfield doublet (79 and 59 ppm) in Fig. 1E changes into a singlet (69 ppm; $J_{PH}$ 711 Hz), but other peaks are not changed (Fig. 1F). It means that there is an intermediate **X** which contains a phosphorus atom which directly connects to hydrogen. Therefore, according to Figs. 1 and 2 there exist four kinds of phosphorus with markedly different electronic environments. The peaks at 69, 83 and 110 ppm can be referred to the species **X**, **Y**, and **Z**, respectively. The integrated intensities of the $^{31}P$ spectra for peaks 110, 83 and 69 ppm are markly different between two reaction systems. The P-H bond dissociation, i.e. given off HCl, may be accelerated in the $C_6H_6:PCl_3:AlCl_3 = 1:3:1.05$ system, while it can be stabilized in the $C_6H_6:PCl_3:AlCl_3 = 1:1:1:1.05$ system by agglomeration due to chain structure[12]. The results indicate that the molar ratio of the intermediates is influenced by the amount of $PCl_3$.

## Identification of the Intermediates

Investigation of the $^{31}P$-NMR spectrum's dependence of the reagent $AlCl_3$ is showed in Fig. 2. It is indicated that the structure and composition of the intermediates are determined by the molar ratio of ligand/Lewis acid $AlCl_3$. Obviously, only two singlets (218 and 160 ppm) are observed in the mixture of PDC and $PCl_3$ (Fig. 2A). After $AlCl_3$ is added (Fig. 2B), the reaction of PDC with $AlCl_3$ gives a complex. Shagvaleev *et al.*[13] reported that the value of the chemical shift for 3-coordinate phosphorus atom in phosphinophosphonium aluminate depends on the amount of $AlCl_3$ introduced. However, the 2D $^{31}P$-$^{31}P\{H\}$ COSY plot (Fig. 3) shows that indeed the phosphorus in intermediate **Z** (110 ppm) is expected to be uncorrelated with phosphorus in intermediate **Y** (83 ppm). Therefore, the intermediate phosphinophosphonium aluminate is not present, while the intermediates $C_6H_5PCl_2{\cdot}AlCl_3$ (**Y**) and $(C_6H_5PCl_2)_2{\cdot}AlCl_3$ (**Z**), are postulated[12-14].

Under the action of dry HCl, the reverse reaction for intermediates (**Y** and **Z**) occurs with the formation of P-H containing dichlorophenylphosphonium tetrachloroaluminate **X** (59 and 79 ppm), as shown in Fig. 2C. After heating at 90°C for 10 min, the **Y** and **Z** intermediates, which are transformed by **X**, appear (Fig.

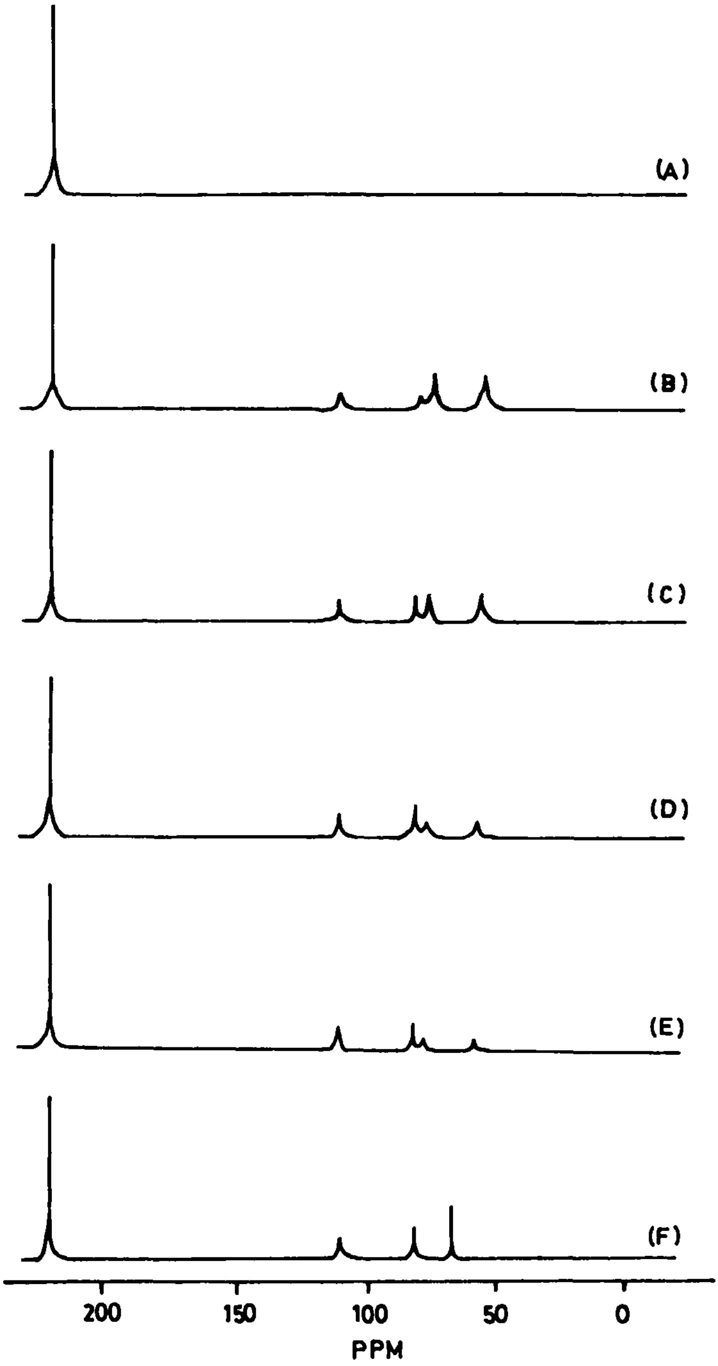


FIGURE 1 $^{31}$P-NMR spectra for $C_6H_6:PCl_3:AlCl_3 = 1:3:1.05$ system at 90°C (A) 0, (B) 15, (C) 30, (D) 45, (E) 60 min, and (F) P{H} decoupling of (E) spectrum.

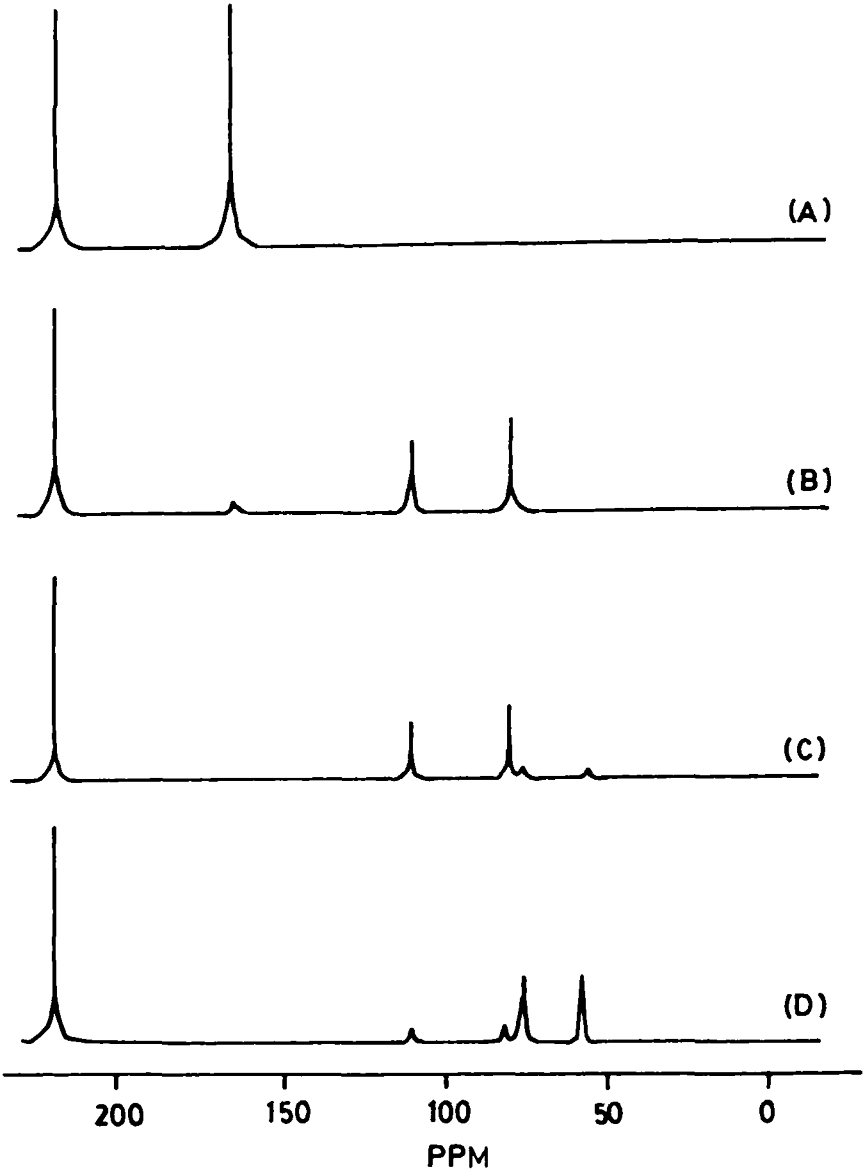


FIGURE 2 $^{31}$P-NMR spectra of the dependence of $AlCl_3$ and HCl on the mixture of PDC and $PCl_3$ (A) PDC/$PCl_3$ mixture, (B) 1.0 equivalent of $AlCl_3$ added, (C) after introduction of HCl into the mixture of (B), and (D) after reflux (C) of the solution for 10 min at 90°C.

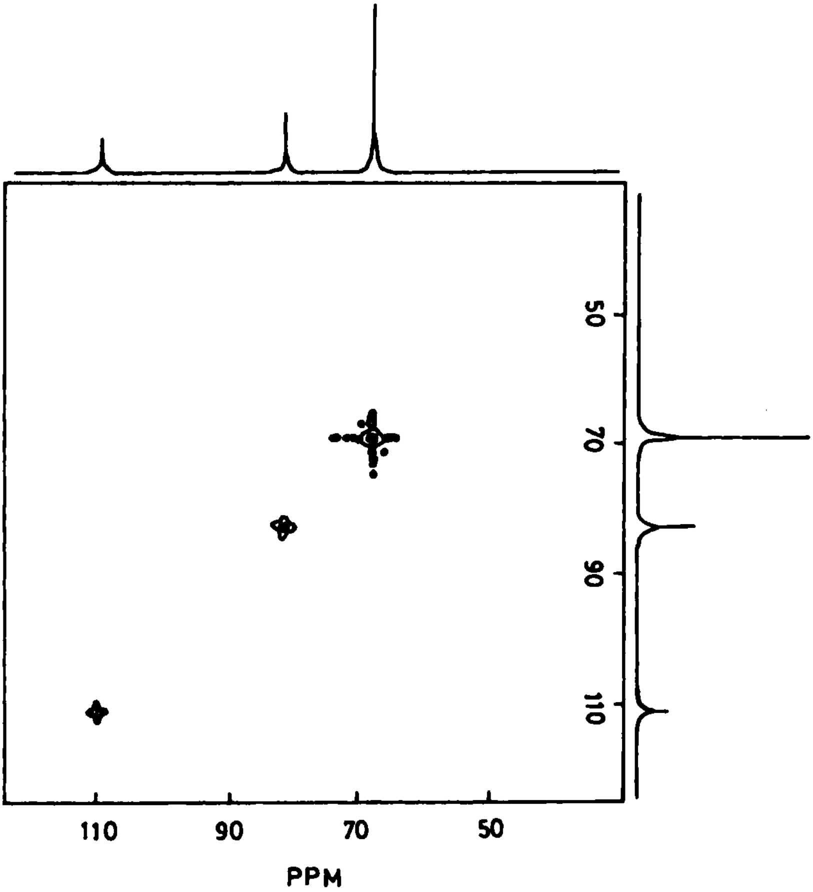
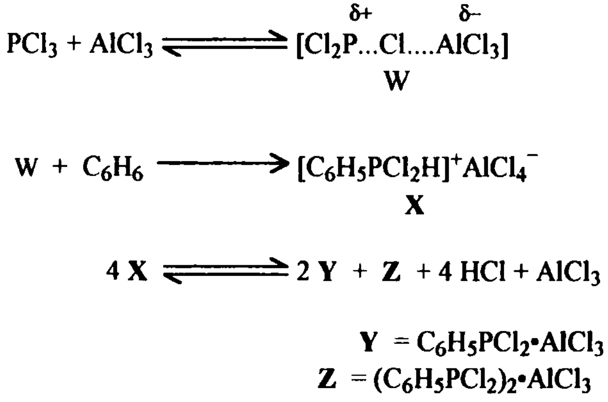


FIGURE 3 Two-dimensional $^{31}P$- $^{31}P\{H\}$ homonuclear COSY spectrum of the intermediates of PDC preparation.

2D). In addition, the intensities of the signals at 110 and 83 ppm are approximately equal. On the other hand, a triplet at 69 ppm ($J_{PD}$ 109 Hz) is observed other than 83 and 110 ppm in $C_6D_6$:$PCl_3$:$AlCl_3$ = 1:3:1.05 system. The multiplicity of the peaks which is attributed to $^{31}P$-$^{2}H$ couplings further indicates the presence of intermediate **X**. Therefore, the mechanism of the reaction of benzene, $PCl_3$ and $AlCl_3$ can be proposed as indicated in SCHEME 1, in which the first step and third step remain at equilibrium.



$$PCl_3 + AlCl_3 \rightleftharpoons \underset{W}{[Cl_2\overset{\delta+}{P}...Cl....\overset{\delta-}{Al}Cl_3]}$$

$$W + C_6H_6 \longrightarrow \underset{X}{[C_6H_5PCl_2H]^+AlCl_4^-}$$

$$4\,X \rightleftharpoons 2\,Y + Z + 4\,HCl + AlCl_3$$

$$Y = C_6H_5PCl_2{\bullet}AlCl_3$$
$$Z = (C_6H_5PCl_2)_2{\bullet}AlCl_3$$

SCHEME 1

## *Acknowledgement*

We thank the National Science Council and the Ministry of Economic Affairs of the Republic of China for financial support.

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