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Metal Phosphinylides and Phosphinothioylides. VI.[1] Some Observations in Reactions of Diphenylphosphinic Chloride with Tetrahydrofuran in the Presence of Metal Chlorides

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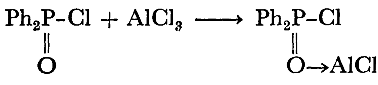
Synopsis. ^{31}P-NMR data showed a formation of a stable *1 : 1* complex between diphenylphosphinic chloride (**1**) and aluminum chloride. The effect of common chloride ion on the reaction of **1** with tetrahydrofuran in the presence of zinc or cuprous chloride supported a cationic mechanism in the former case, and no free radical but homolytic mechanism in the latter.

We reported in a previous paper[2] that diphenylphosphinic chloride (**1**) reacted with tetrahydrofuran (THF) in the presence of cuprous, cupric, zinc, aluminum or ferric chloride to give *O*-4-chlorobutyl diphenylphosphinate (**2**) in all cases, and it was suggested that **2** was formed through no free radical but homolytic mechanism in the case of cuprous chloride. This note describes on further observation in the above reactions.

Though zinc, aluminum, and ferric chlorides are typical Lewis acids, the latter two chlorides give **2** in a moderate yield.[2]

^{31}P-NMR data showed that **1** formed a stable 1 : 1 complex (**3**) with aluminum chloride (see Table 1) as reported in analogous systems,[3] but that, in the case of zinc chloride, ^{31}P chemical shift of **1** did not change within the experimental error. Therefore, it is considered that the reactivity of **1** becomes very low in the presence of aluminum chloride, because of the formation of the stable complex (**3**). Thus, zinc chloride becomes more effective as a catalyst than aluminum chloride.



$$\underset{\mathbf{1}}{Ph_2P(=O)\text{-}Cl} + AlCl_3 \longrightarrow \underset{\mathbf{3}}{Ph_2P(=O{\rightarrow}AlCl_3)\text{-}Cl}$$

1 3

TABLE 1. CHANGES IN ^{31}P CHEMICAL SHIFT OF **1** IN THE PRESENCE OF ALUMINUM CHLORIDE IN NITROBENZENE

$AlCl_3$/**1** (mol/mol)	0	0.28	0.56	0.62	0.83	1.05	1.38	2.06
$-\delta^{31}P$ (ppm)	42.8	44.1	46.5	49.6	55.9	60.6	60.5	60.6

Similarly, ^{31}P-NMR data also showed that **1** did not form a complex with cuprous chloride in acetonitrile. These tendency were also similar in the case of diphenylphosphinothioic chloride.

In order to make clear a difference in mechanisms in the presence of zinc or cuprous chloride, effects of addition of lithium chloride on the yields of **2** were scrutinized. The results are shown in Table 2.

$$\underset{\mathbf{1}}{Ph_2P(O)Cl} + THF \xrightarrow[\text{or CuCl}]{ZnCl_2} \underset{\mathbf{2}}{Ph_2P(O)O(CH_2)_4Cl}$$

TABLE 2. EFFECT OF ADDITION OF LITHIUM CHLORIDE ON YIELDS OF **2** (AT 120 °C FOR 6 h)

a) In the case of zinc chloride

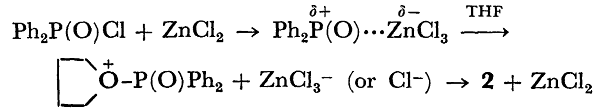
[LiCl]/**1** (mol/mol)	[LiCl]/[$ZnCl_2$]	Yield of **2** (%)
0	0	36
2.4×10^{-2}	1.3	62
9.2×10^{-2}	5.2	61
16×10^{-2}	10.1	58
34×10^{-2}	18.6	55

b) In the case of cuprous chloride

[LiCl]/**1** (mol/mol)	[LiCl]/[CuCl]	Yield of **2** (%)
0	0	38
1.9×10^{-2}	1.1	7
8.1×10^{-2}	4.6	9
17×10^{-2}	9.0	12
31×10^{-2}	17.0	12
98×10^{-2}	∞[a]	13

a) In the absence of cuprous chloride.

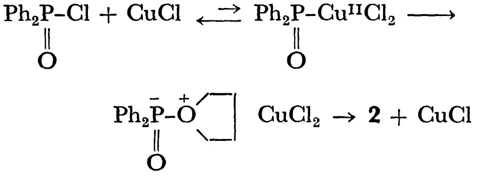
The effect of the common chloride ion showed an extreme contrast in both cases as shown in Table 2, suggesting a different mechanism in each case. Increase in yield of **2** in the case of zinc chloride is in agreement with the following ionic mechanism.



$$Ph_2P(O)Cl + ZnCl_2 \rightarrow Ph_2\overset{\delta+}{P}(O)\cdots\overset{\delta-}{Z}nCl_3 \xrightarrow{THF} \text{(THF-}\overset{+}{O}\text{)-}P(O)Ph_2 + ZnCl_3^- \text{ (or } Cl^-\text{)} \rightarrow \mathbf{2} + ZnCl_2$$

Furthermore, in the case of cuprous chloride, ten times molar amounts (based on cuprous chloride) of cupric acetate were added in place of lithium chloride under the same condition, but 4-acetoxybutyl diphenylphosphinate could not be detected. The product was only **2** (45%). This result ruled out a cationic mechanism.

The **1**-CuCl system did not result in isomerization of *cis*-stilbene in acetonitrile at 120 °C for 24 h, indicating the absence of free $Ph_2\dot{P}O$ radical. Therefore, a mechanism containing an inner-sphere electron transfer as shown in the following scheme might be more reasonable.



$$Ph_2P(=O)\text{-}Cl + CuCl \rightleftarrows Ph_2\dot{P}(=O)\text{-}Cu^{II}Cl_2 \xrightarrow{THF} Ph_2P(=O)\text{-}\overset{-\;+}{O}\text{(THF)}\; CuCl_2 \rightarrow \mathbf{2} + CuCl$$

The remarkable decrease in the yield of **2** in the presence of chloride ion is understandable, assuming that chloride ion coordinates with cuprous chloride and the electron transfer becomes difficult. A similar effect of lithium chloride has been reported in a carbon tetrachloride–cuprous chloride–olefin system.[4]

The yield of **2** is expected to decrease by addition of acetonitrile which can coordinate to cuprous chloride. In fact, addition of 3.5 times amounts of acetonitrile decreased the yield of **2** from 38% to 29%.

Moreover, the yield of **2** was better in the presence of cupric chloride than in the presence of cuprous chloride.[2] In order to make this point clear, cupric chloride was heated in THF at 120 °C for 24 h, and 12% of cuprous chloride was formed. Thus, the previous result is explained by the formation of more reactive cuprous chloride *in situ*.

Experimental

The ^{31}P-NMR spectra were measured with a Hitachi R-20 B-R-204-PB spectrometer using 85% phosphoric acid as an external standard. All reactions were carried out under nitrogen in a sealed tube.

*Reaction of Diphenylphosphinic Chloride (**1**) with THF in the Presence of Metal Chloride.* *1) Zinc Chloride*: A mixture of **1**[5] (6.2—6.8 mmol) and zinc chloride (0.11—0.12 mmol) in 8 ml of THF was heated in the presence of an appropriate amount of lithium chloride for 6 h at 120 °C. The reaction mixture was treated with methanol, concentrated, and determined by gas chromatography (column: H 523 on Diasolid at 210 °C) with methyl diphenylphosphinodithioate as an internal reference.

2) Cuprous Chloride: A mixture of **1** (5.6—5.8 mmol) and cuprous chloride (0.10—0.11 mmol/mmol of Cu atom) in 9 ml of THF was heated in the presence of an appropriate amount of lithium chloride for 6 h at 120 °C. The reaction mixture was treated similarly.

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