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Spectrophotometric and Conductometric Studies on the Interaction between Trivalent Phosphines and 2,2′-Bipyridyl in Solution

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Received December 16, 1971

Complex formation of PCl_3, $C_6H_5PCl_2$, $(C_6H_5)_2PCl$, $(C_5H_5)_3P$, (m-tolyl)$_3$P, (p-tolyl)$_3$P, $P(OCH_3)_3$, $C_6H_5P(OCH_3)_2$, and $(C_6H_5)_2POCH_3$ with 2,2′-bipyridyl have been examined in 1,2-dichloroethane and/or acetonitrile. The continuous variation method or the mole ratio method in the ultraviolet absorption spectra shows that these phosphines form the 1:1 complexes with 2,2′-bipyridyl in solution, except for $P(OCH_3)_3$, $C_6H_5P(OCH_3)_2$, and $(C_6H_5)_2POCH_3$. The measurements of electric conductivity and infrared spectra indicate that the complexes of PCl_3, $C_6H_5PCl_2$, $(C_6H_5)_2PCl$ dissociate more or less into ionic species in acetonitrile, while those of R_3P (R = phenyl, m– and p-tolyl) exist as simple addition compounds in 1,2-dichloroethane. The stability constants of these complexes estimated spectrophotometrically are the order of; $PCl_3 > C_5H_5PCl_2 > (C_6H_5)_2PCl > (C_6H_5)_3P >$ (m-tolyl)$_3$P $>$ (p-tolyl)$_3$P $\gg (C_5H_5)_2POCH_3 \sim C_6H_5P(OCH_3)_2 \sim P(OCH_3)_3$. This trend suggests that the phosphines act as Lewis acids toward 2,2′-bipyridyl and they interact mainly through σ electronic system.

Introduction

The properties of σ electron donor and π electron acceptor of trivalent phosphines to transition metals have widely been studied on the basis of infrared spectra.[1] In the $Ni(PCl_3)_4$ complex,[2] PCl_3 is thought to act as both σ donor and π acceptor to the nickel atom, while PCl_3 may be considered to be a σ electron acceptor in the 1:1 addition compounds with trimethylamine[3] and with pyridine.[4] Triphenylphosphine has recently been reported to form the 1:1 adduct with hexamethylbenzene which is a strong π electron donor.[5] Thus trivalent phosphines could be Lewis acid or base, which depends on the nature of interacting molecules or ions. The purpose of the present work is to elucidate the nature of intermolecular interaction of several trivalent phosphines with 2,2′-bipyridyl in solution, the latter of which may also have both characters of σ donor and π acceptor,[6] on the basis of the electronic and infrared spectra, and conductivity measurement.

Experimental Section

Materials. Triphenylphosphine and 2,2′-bipyridyl obtained commercially were purified by recrystallization from benzene-methanol mixture and ligroin, m. p. 80° and 72°, respectively. Trichlorophosphine and trimethylphosphite were distilled under dry nitrogen, b.p. 76° and 112°, respectively.

Phenyldichlorophosphine was prepared from PCl_3 and benzene by Friedel-Craft reaction,[7] b.p. 68-70°/1mmHg. *Anal.* Found: C, 40.35; H, 2.72%. Calcd for $C_6H_5Cl_2P$: C, 40.26; H, 2.82%. Diphenylchlorophosphine was obtained by the disproportionation reaction of $C_6H_5PCl_2$ according to the literature,[8] b.p. 170-171°/10 mmHg. *Anal.* Found: C, 65.26; H, 4.57% Calcd for $C_{12}H_{10}ClP$: C, 65.36; H, 4.57%.

Dimethyl phenylphosphonite and methyl diphenylphosphinite were synthesized by the reaction of $C_5H_5PCl_2$ or $(C_6H_5)_2PCl$ with dry methanol in the presence of dry pyridine in n-hexane,[9] b.p. 98°/17 mmHg and 151-152°/10 mmHg, respectively. *Anal.* Found: C, 56.48; H, 6.63%. Calcd for $C_8H_{11}O_2P$: C, 56.47; H, 6.52%. Found: C, 71.89; H, 6.63%. Calcd for $C_{13}H_{13}OP$: C, 72.22; H, 6.06%.

Tri-*m*-tolylphosphine and tri-*p*-tolylphosphine were obtained by the reaction of $(C_5H_5O)_3P$ with *m*- or *p*-tolylmagnesium bromide,[10] m.p. 99-100° and 145° (lit.:[11] 100° and 146°), respectively. Ethylene bis(triphenylphosphonium chloride) was prepared by the reaction of $(C_5H_5)_3P$ with 1,2-dichloroethane,[12] m.p. 287-289°. *Anal.* Found: C, 72.66; H, 5.50%. Calcd for $C_{38}H_{34}Cl_2P_2$: C, 73.19; H, 5.50%.

1,2-Dichloroethane used for spectrophotometric and

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conductometric measurements was purified according to the conventional method.[13] Acetonitrile used for the same purpose was distilled five times with P_2O_5, specific conductivity of 2×10^{-7} mho · cm^{-1} at 25°.

Apparatus and Procedure. The ultraviolet absorption spectra were measured for 2,2′-bipyridyl in 1,2-dichloroethane or acetonitrile with varying amounts of the phosphine, using a Hitachi 124 Spectrophotometer with 1 cm or 1 mm quarz cells at 25°±2°. The electric conductivities were measured for acetonitrile or 1,2-dichloroethane solution containing a definite amount of phosphine and varying amounts of 2,2′-bipyridyl, using a Yokogawa F-225A Universal Bridge at 25°±0.5°. The infrared spectra were recorded on a Hitachi EPI-L Spectrophotometer.

Stability constants were determined spectrophotometrically using the following equation,

$$\frac{1}{K}=\frac{d-d_o}{\varepsilon_{ab}-\varepsilon_b}-(a+b)+\frac{ab(\varepsilon_{ab}-\varepsilon_b)}{d-d_o} \qquad (1)$$

where d_o is the absorbance of 1,2-dichloethane solutions containing only 2,2′-bipyridyl, d is the observed absorbance of the phosphine-2,2′-bipyridyl mixtures, a is the concentration of the phosphines, b is the constant concentration of 2,2′-bipyridyl, and ε_b and ε_{ab} are the molar extinction coefficients of 2,2′-bipyridyl and of its complex, respectively.

Results and Discussion

Figure 1 shows the u.v. spectra of 2,2′-bipyridyl in the presence of varying amounts of $(C_6H_5)_2PCl$ or $C(_6H_5)_3P$ in 1,2-dichloroethane. The absorption maximum of 2,2′-bipyridyl at 280 mμ shifts to longer wave length with increasing amounts of the phosphines added. Similar spectra are observed in the Bipy-$C_6H_5PCl_2$, –(*m*-tolyl)$_3$P, and –(*p*-tolyl)$_3$P mixtures (where Bipy = 2,2′-bipyridyl) in 1,2-dichloroethane. The maximum absorbance at 303 mμ may be due to the *cis*-configuration of 2,2′-bipyridyl;[14] the both nitrogen atoms coordinate to the phosphine atom.

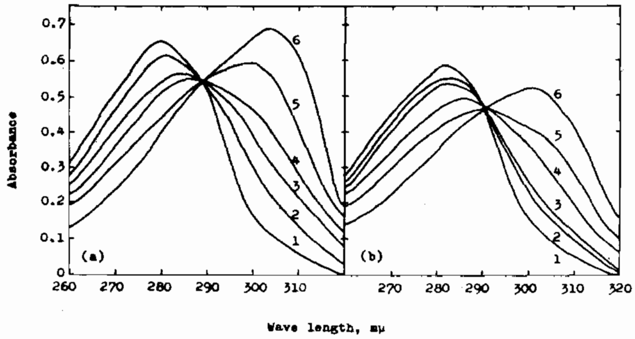

Figure 1. Absorption spectra of (a) 2,2′-bipyridyl (4.35×10^{-4} *M*) in 1,2-dichloroethane, with varying amounts of $(C_6H_5)_2PCl$: (1) 0, (2) 0.96, (3) 1.92, (4) 2.40, (5) 4.35, (6) 9.61×10^{-4} *M*; cell length 1 mm, and (b) 2,2′-bipyridyl 4.00 $\times10^{-5}$ *M*) in 1,2-dichloroethane, with $(C_6H_5)_3P$: (1) 0, (2) 1.62, (3) 3.24, (4) 8.10, (5) 12.2, (6) 16.2×10^{-5} *M*; cell length 10 mm.

Plots of the absorbance at 305 and 318 mμ to the mole ratios of $(C_6H_5)_2PCl$/Bipy are given in Figure 2, which indicates the formation of the 1:1 complex between these molecules. The same is true of the $C_6H_5PCl_2$–Bipy mixture in 1,2-dichloroethane, and also of the both $(C_6H_5)_2PCl$– and $C_6H_5PCl_2$-Bipy systems in acetonitrile. For the $(C_6H_5)_3P$-Bipy system, the mole ratio method could not elucidate the composition, but the continuous variation method apparently shows the existence of the 1:1 adduct in 1,2-dichloroethane, as is found in Figure 3.

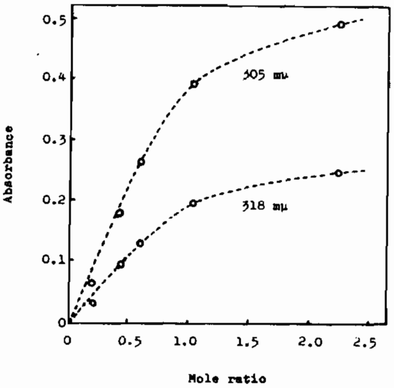

Figure 2. Plots of the absorbance to the mole ratios of $[(C_6H_5)_2PCl]/[\text{Bipy}]$; [Bipy], 4.35×10^{-4} *M*; cell length, 1 mm.

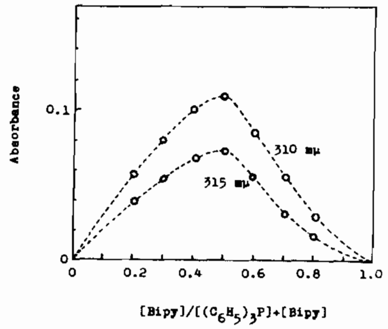

Figure 3. Plots of the absorbance to the ratios of [Bipy]/ $[(C_6H_5)_3P]+[\text{Bipy}]$; $[(C_6H_5)_3P]+[\text{Bipy}]$, 5.12×10^{-5} *M*; cell length, 10 mm.

On the other hand, it was difficult to determine the composition of the complex formed between PCl_3 and 2,2′-bipyridyl in 1,2-dichloroethane, because of low solubility. However, the continuous variation method in acetonitrile also indicates that PCl_3 forms 1:1 complex with 2,2′-bipyridyl.

Judging from spectrophotometric results, $(C_6H_5)_3P$ can interact with 2,2′-bipyridyl to form 1:1 adduct in 1,2-dichloroethane, but not in solvents of much greater or lower polarity, such as carbon tetrachloride, cyclohexane, benzene, ethanol, acetonitrile, and

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tetrahydrofurane. This anomalous behavior might lead to the idea that $(C_6H_5)_3P$ reacts with 1,2-dichloroethane to produce a compound containing a phosphine atom which is able to interact with 2,2′-bipyridyl in solution. However, the following observations make such a hypothesis very unlikely.

When 1,2-dichloroethane solutions of 2,2′-bipyridyl (3.0×10^{-4} and 5.1×10^{-5} *M*) containing excess amounts of $(C_6H_5)_3P$ (1.5×10^{-3} and 2.5×10^{-4} *M*, respectively) is irradiated with a Deuterium lamp (200-370 mμ) of the spectrophotometer for several hours, the absorption maximum at 303 mμ originally appeared loses intensity slowly with irradiation time, and at the same time the absorbance gradually increases at 280 mμ, which corresponds to the *trans*-form of 2,2′-bipyridyl.[14] On the other hand, keeping the solutions for a few days without exposure to the u.v. source did not produce any change in appearance of the absorption spectra. It is therefore assumed that the $(C_6H_5)_3P \cdot$ Bipy complex in 1,2-dichloroethane reacts with the solvent molecules upon irradiation of the u.v. source to liberate *trans*-2,2′-bipyridyl. We have not characterized the reaction product, since the solutions used for measuring the u.v. spectra are too dilute to do it. Alternatively, $(C_6H_5)_3P$ was refluxed in 1,2-dichloroethane for 15-20 hours to give ethylene bis(triphenylphosphonium chloride), which can not interact with 2,2′-bipyridyl in solution on the basis of the u.v. measurements. It is therefore evident that in 1,2-dichloroethane 2,2′-bipyridyl forms the complex with $(C_6H_5)_3P$, but not with the product derived from $(C_6H_5)_3P$.

Nature of the complexes. Molar conductances obtained are listed in Table I. It is more desirable to measure conductivity of the 1,2-dichloroethane solutions for most of the mixtures in ordre to compare with the results of the u.v. measurements. Some of the mixtures shown in Table I are, however, too insoluble to obtain any reliable conductivity at the concentration of 10^{-3} *M* in 1,2-dichloroethane.

The phosphines as well as 2,2′-bipyridyl independently gave non-conducting acetonitrile or 1,2-dichloroethane solution. There is therefore no doubt that large conductances of the chlorophosphine-2,2′-bipyridyl mixtures do not result from their hydrolysis products. Further, solutions containing the chlorophosphines and 2,2′-bipyridyl show increases in conductance when a large excess of the latter is added, although the increases are not large (Table I).

Table I. Molar conductances, Λ [a], of some trivalent phosphines (1.0×10^{-3} *M*) in acetonitrile with varying amounts of 2,2′-bipyridyl at 25° mho . cm^2 . mole^{-1}.

Phosphines	Mole ratios, [Bipyl]/[Phosphine] 1	10
PCl_3	146	151
$C_6H_5PCl_2$	131	132
$(C_6H_5)_2PCl$	58	63
$(C_6H_5)_3P$	0.7	0.9
	0.01 [b]	0.01 [b]

[a] Λ of the acetonitrile solution containing only 2,2′-bipyridyl (1.0×10^{-3} *M*): 0.05 mho . cm^2 . mole^{-1}. [b] 1,2-Dichloroethane solution.

These results indicate the complexes dissociating into ionic species in acetonitrile.

As was previously reported, PCl_3[15] and $(C_6H_5)_2PCl$[16] exhibit two strong P-Cl stretching bands in the region of 507-452 cm^{-1}, while $(C_6H_5)_2PCl$[16] displays one band at 504 cm^{-1}. The equimolar mixture of $(C_6H_5)_2PCl$ and 2,2′-bipyridyl in acetonitrile shows the P-Cl stretching band as a shoulder on the strong band due to the phenyl group, Figure 4a, indicating that P-Cl bond more or less remains without complete dissociation into the chloride and phosphonium ions, even when coordinated by 2,2′-bipyridyl. On the other hand, the 1:1 mixture of $C_6H_5PCl_2$ and 2,2′-bipyridyl in the same solvent exhibits two P-Cl bands, but the low frequency one is extremely weak (Figure 4b).

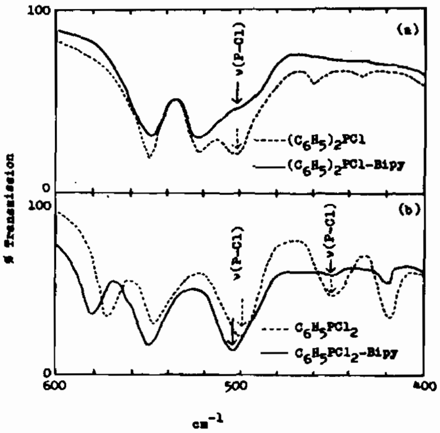

Figure 4. Infrared spectra of $(C_6H_5)_2PCl$, $C_6H_5PCl_2$, and their 1:1 mixtures with 2,2′-bipyridyl in acetonitrile, 3 wt.%.

This result seems to indicate that one of the P-Cl bonds of $C_6H_5PCl_2$ dissociates almost quantitatively into the ions upon coordination of 2,2′-bipyridyl in acetonitrile. In the infrared spectrum of the 1:1 PCl_3-Bipy mixture in acetonitrile, the two P-Cl stretching bands are evidently observed with the symmetric one becoming very broad. In view of the present infrared and conductivity measurements, the PCl_3-Bipy complex is thought to be essentially one to one electrolyte in solution, although the complex may partly dissociate into $[PCl \cdot Bipy]^{2+}$ and $2Cl^-$. This assumption is consistent with the formulation for the 2,2′-bipyridyl complexes of trihalogenoarsine, –stibine, and –bismuth, which have been reported to dissociate in nitrobenzene as follow;[17]

$$MX_3 + Bipy \leftrightarrows [MX_2 . Bipy]^+ + X^- \qquad (2)$$

M = As, Sb, and Bi; X = Cl, Br and I

Table II summerizes the infrared frequencies due to the P-Cl stretching vibrations of the chlorophosphines and their mixtures with 2,2′-bipyridyl in acetonitrile. Thus, the chlrophosphine complexes appear to

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(16) H. Schindlbauer and H. Stenzenberger, *Spectrochim. Acta*, 26A, 1707 (1970).
(17) W. R. Roper and C. J. Wilkins, *Inorg. Chem.*, 3, 500 (1964).

Table II. P-Cl Stretching frequencies of PCl_3, $C_6H_5PCl_2$, $(C_6H_5)_2PCl$, and their complexes with 2,2'-bipyridyl in acetonitrile, cm^{-1}.

Phosphines	ν(P-Cl) [a] Free [b]		Complex	
PCl_3	507 s	494 s	490 br	520 s
$C_6H_5PCl_2$	498 s	452 m	495 vw	506 s
$(C_6H_5)_2PCl$	504 s	—	—	504 sh

[a] s: strong, m: medium, vw: very weak, br: broad, sh: shoulder. [b] Liquid films, refs. 15 and 16. These wave numbers are in accord wtih those of the acetonitrile solutions within ± 2 cm^{-1}.

undergo the following equilibrium in acetonitrile.

$$\underset{(A)}{XYPCl} + Bipy \leftrightarrows \underset{(B)}{[XYPCl\,.\,Bipy]} \leftrightarrows \underset{(C)}{[XYP\,.\,Bipy]^+ + Cl^-} \qquad (3)$$

$$X,\ Y = C_6H_5 \text{ or } Cl$$

It should be noted that the infrared results can not necessarily be discussed by direct comparison with the conductivity measurements, since the concentrations of the complexes in solution are different between the experiments. In view of the infrared spectra and the molar conductances, however, it is reasonable to assume that the $(C_6H_5)_2PCl$-Bipy system mainly exists in equilibrium between the (B) and (C) species, and the latter species is predominant in the $C_6H_5PCl_2$– and PCl_3-Bipy systems, while the R_3P-Bipy complexes (R = phenyl, *m*-tolyl, and *p*-tolyl) in 1,2-dichloroethane are most likely to be neutral adducts, because there is neither atom or group which easily dissociates into anion nor appreciable conductance. This assumption does not contradict to the values of the stability constants in 1,2-dichloroethane, which will be described below.

Stability constants. The stability constants, K, have been calculated for the formation of the neutral 1:1 adducts in 1,2-dichloroethane;

$$K = \frac{[R_nPCl_{3-n}\,.\,Bipy]}{[R_nPCl_{3-n}][Bipy]} \qquad (4)$$

where n = 3 when R = *m*– or *p*-tolyl, and n = 1-3 when R = phenyl. The results are listed in Table III, which indicates that in the $(C_6H_5)_nPCl_{3-n}$ complexes (n = 1–3) the K value decreases with increasing number of the phenyl group, *i.e.* with decreasing total electronegativity of the substituents on the phosphine atom, although the values in these systems are only approximates. In view of this trend, it may be expected that the stability constant of the PCl_3-Bipy complex is larger than those of any complexes shown in Table III. With triarylphosphine-2,2'-bipyridyl systems, the order of stability constant is $(C_6H_5)_3P$ > (*m*-tolyl)$_3$P > (*p*-tolyl)$_3$P. This order also suggests that more electron donating power of the substituents on the phosphine atom leads to weaker interaction with 2,2'-bipyridyl.

Table III. Stability Constants, K, of some phosphine(III)-2,2'-bipyridyl complexes in 1,2-dichloroethane at 25°.

Phosphines	Log. K
PCl_3	[a]
$C_6H_5PCl_2$	5.3±0.1
$(C_6H_5)_2PCl$	5.1±0.1
$(C_6H_5)_3P$	3.91±0.03
(*m*-tolyl)$_3$P	3.76±0.02
(*p*-tolyl)$_3$P	3.67±0.02

[a] Too insoluble to measure.

In the $(C_6H_5)_2POCH_3$–, $C_6H_5P(OCH_3)_2$–, and $P(OCH_3)_3$–Bipy systems, the absorption band of 2,2'-bipyridyl at 280 mμ does not shift to higher wave length, even when a large excess of the phosphine compounds (mole ratios of 1:300, 1:1000, and 1:10000, respectively) exists in 1,2-dichloroethane or acetonitrile. This is indicative of extremely weak interaction between 2,2'-bipyridyl and these phosphine compounds in solution, possibly because of electron donating power of the methoxy group; there is no appreciable π interaction as well as σ one, although $P(OCH_3)_3$ has been assumed to be rather strong π acceptor than $(C_6H_5)_3P$ in their transition metal complexes.[18]

Thus, it may be concluded that the trivalent phosphines act as Lewis acids toward 2,2'-bipyridyl and they interact mainly through σ electronic system. Moreover, in the chlorophosphine-2,2'-bipyridyl systems excess negative charges on the phosphine atom upon complex formation will partly be canceled off by dissociation of the chlorine atom into the anion.

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