The Ammonolysis of Phenylimino(dialkylamino)phosphorus(V) Dichlorides

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The reactions of a series of phenylimino(dialkylamino)phosphorus(V) dichlorides with ammonia have been carried out and for the first time phosphonium chlorides with primary, secondary, and tertiary amino groups linked to the same phosphorus atom have been obtained. Nmr, infrared, and mass spectra and Λ_0 and K_c values of these compounds have been recorded. The thermal behavior of anilino(diethylamino)(diamino)phosphonium chloride is discussed, as well as its polarogram.

In an earlier communication,[1] the reaction of dimeric N-phenyltrichlorophosphinimine, $(C_6H_5N=PCl_3)_2$, with diethylamine was shown to yield monomeric compounds of the type $C_6H_5N=P(N(C_2H_5)_2)_nCl_{3-n}$ ($n = 1-3$). Ammonolysis of $(C_6H_5N=PCl_3)_2$[2] and $(RN=PCl_3)_2$ (R = alkyl group)[3] produces compounds of the general formula $[(RNHP(NH_2)_2)_2N]^+Cl^-$ in accordance with the equation

$$(RN=PCl_3)_2 + 10NH_3 \longrightarrow$$
$$[RNHP(NH_2)_2=N=P(NH_2)_2NHR]^+Cl^- + 5NH_4Cl$$

Since $C_6H_5N=P(N(C_2H_5)_2)_2Cl$ even under drastic conditions does not react with ammonia,[4] it was of interest to us to study the reaction of $C_6H_5N=P(X)Cl_2$ (X = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(n-C_4H_9)_2$, $N(CH_3)CH_2C_6H_5$) with ammonia in order to obtain more information concerning the reactivity of phenyliminophosphorus(V) chlorides.

This paper reports the results of this investigation. The synthetic procedures and analytical and spectral data are reported.

Experimental Section

Materials.—All solvents were dried by standard methods. Ammonia was dried over solid KOH and distilled from sodium into the reaction vessel. $(C_6H_5N=PCl_3)_2$ was prepared from PCl_5 and $C_6H_5NH_3Cl$ in carbon tetrachloride.[5]

Analyses.—Elemental analyses were carried out by the Mikroanalytisches Universitätslaboratorium, Vienna. Some of the nitrogen, chlorine, and phosphorus analyses were carried out by the authors in this laboratory using standard semimicro methods. Melting points were obtained on a Kofler melting point apparatus and are uncorrected. Analytical and melting (or boiling) point data are given in Table I.

Infrared and ^{1}H and ^{31}P Nmr Spectra.—The infrared spectra were recorded with a Perkin-Elmer Model IR-237 infrared spectrometer. The spectra of liquids were taken as capillary films or in solution (CCl_4-CS_2) and those of the solids were taken as KBr pellets (Table II).

The proton and phosphorus nuclear magnetic resonance spectra were recorded with a RS II spectrometer (Allied Electric Industries) at 60 Mcps (^{1}H) and 25 Mcps (^{31}P), respectively. The liquids and solids were dissolved in deuteriochloroform or in hexadeuteriodimethyl sulfoxide (DMSO-d_6) with TMS or the sodium salt of 3-(trimethylsilyl)propanesulfonic acid as the internal standard for the ^{1}H nmr spectra. The liquids were used

neat and the solids were dissolved in dimethyl sulfoxide with 85% H_3PO_4 as the external standard for the ^{31}P nmr spectra. The chemical shifts were determined by the side-band method. The nuclear magnetic resonance data are summarized in Table III.

Mass Spectra.—The mass spectra were observed by means of a RMU 6E mass spectrometer (Hitachi Perkin-Elmer) at an ionizing voltage of 70 eV.

Conductivity Measurements.—Electric conductivity measurements at $25 \pm 0.05°$ of $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$ were carried out in dry acetonitrile (specific conductance $(1.9-2.1) \times 10^{-7}$ ohm^{-1} cm^{-1}) using a conductance cell described in detail elsewhere[6] and a PR 9501 (Philips) conductivity bridge. Λ_0 values were determined by the method of Fuoss.[7,8] The calculations were carried out on an IBM 1130. A least-squares treatment of the data was applied. Λ_c, Λ_0, and K_c values are listed in Tables IV and VII.

Polarographic Study.—The polarographic measurements of $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$ were made in dry dimethyl sulfoxide with a Polariter PO 4b (Radiometer, Copenhagen). The supporting electrolyte was tetraethylammonium perchlorate.

Phenylimino(dialkylamino)phosphorus(V) Dichlorides. General Procedure.—$(C_6H_5N=PCl_3)_2$ (0.25 mol) was suspended in 500 ml of dry carbon tetrachloride containing 0.7 mol of dry triethylamine. A solution of 0.50 mol of the secondary amine in 100 ml of dry carbon tetrachloride was added over a period of 60 min. After refluxing for 5 hr, the triethylammonium chloride was filtered off and washed with carbon tetrachloride. The solvents were stripped from the solution and the residue was distilled twice *in vacuo*. Pale yellow liquids were obtained (Table I).

Reaction of Phenylimino(dialkylamino)phosphorus(V) Dichlorides. A. With Liquid Ammonia.—To 150 ml of the liquid ammonia, 0.1 mol of $C_6H_5N=P(X)Cl_2$ (X = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(n-C_4H_9)_2$, $N(CH_3)CH_2C_6H_5$) was added over a period of 5 min. The entire system was kept at $-78°$. After the exothermic reaction had ceased, the excess of ammonia was distilled off. The white, nonhygroscopic solid residue was finely ground and extracted with 100 ml of dry (methanol-free) chloroform. The filtered solution was concentrated to about 50 ml. Upon cooling, a white crystalline precipitate formed, which after filtration was recrystallized from acetonitrile.

The anilino(dialkylamino)(diamino)phosphonium chlorides $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$ are not hygroscopic. They are soluble in chloroform, water, pyridine, and hot acetonitrile, extremely soluble in methanol, ethanol, and DMSO, and practically insoluble in all other organic solvents.

B. With Gaseous Ammonia.—Dry chloroform (700 ml) was saturated with dry ammonia at $-10°$ for 2 hr. Then 0.022 mol of $C_6H_5N=P(X)Cl_2$ dissolved in 50 ml chloroform was added with stirring. A white precipitate formed immediately. Ammonia was passed for another 3 hr into the reaction mixture. To remove the excess ammonia, the solution was boiled for 3 hr. After fil-

(1) V. Gutmann, Ch. Kemenater, and K. Utvary, *Monatsh. Chem.*, **96**, 836 (1965).

(2) K. Utvary, V. Gutmann, and Ch. Kemenater, *ibid.*, **96**, 1751 (1965).

(3) V. Gutmann, K. Utvary, and M. Bermann, *ibid.*, **97**, 1745 (1966).

(4) M. Bermann, unpublished data.

(5) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 3044 (1960); *Chem. Abstr.*, **55**, 17551 (1961).

(6) K. Fenkart, Thesis, Technische Hochschule, Vienna, 1966.

(7) R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

(8) G. Kortüm, "Lehrbuch der Elektrochemie," 4th ed, Verlag Chemie, Weinheim/Bergstr., 1966, p 248.

TABLE I
ANALYTICAL AND MELTING (BOILING) POINT DATA OF $C_6H_5N{=}P(X)Cl_2$ AND $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$

Compound	Mp, °C	Bp, °C	$n^{20}D$	Yield, %	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%Cl Calcd	%Cl Found	%P Calcd	%P Found
$C_6H_5N{=}P(N(CH_3)_2)Cl_2$	…	79–81 (0.001 mm)	1.5776	66.2	40.49	39.60	4.64	4.67	11.81	11.75	29.96	29.87	13.07	13.37
$C_6H_5N{=}P(N(C_2H_5)_2)Cl_2$ᵃ	…	96–98 (0.1 mm)	1.5607	54.0	…	…	…	…	…	…	…	…	…	…
$C_6H_5N{=}P(N(n\text{-}C_4H_9)_2)Cl_2$	…	150–151 (0.005 mm)	1.5387	56.4	52.33	51.56	7.08	6.82	8.72	8.76	22.12	22.18	9.66	9.68
$C_6H_5N{=}P(N(CH_3)CH_2C_6H_5)Cl_2$	…	142–143 (0.001 mm)	1.6003	45.3	53.65	52.52	4.79	5.41	8.92	8.77	22.69	22.57	9.91	10.07
$[C_6H_5NHP(N(CH_3)_2)(NH_2)_2]^+Cl^-$ (I)	139–140	…	…	60.2	40.96	39.15	6.82	6.61	23.89	24.09	15.14	14.98	13.23	13.24
$[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$ (II)	132–133	…	…	82.0	45.90	45.95	7.61	7.64	21.30	21.26	13.50	13.69	11.82	11.81
$[C_6H_5NHP(N(n\text{-}C_4H_9)_2)(NH_2)_2]^+Cl^-$ (III)	159–160	…	…	83.4	52.76	52.28	8.79	8.85	17.58	17.31	11.15	11.25	9.73	9.66
$[C_6H_5NHP(N(CH_3)CH_2C_6H_5)(NH_2)_2]^+Cl^-$ (IV)	124–125	…	…	81.5	54.19	53.74	6.44	6.29	18.02	18.50	11.42	11.20	9.98	9.83

ᵃ All data previously reported in ref 1.

TABLE II
INFRARED DATA (CM⁻¹)ᵃ

$C_6H_5N{=}P(N(CH_3)_2)Cl_2$ (Film)

3070 w, 3045 w, 3030 w, 2990–2930 m, b, 2880 w, sh, 2840 w, 2810 w, 1595 vs, 1495 vs, 1450 m, 1375 vs, 1290 m, 1225 w, 1170 s, 1070–1060 m, b, 987 vs, 890 w, 755 vs, 718 s, 690 s

$C_6H_5N{=}P(N(n\text{-}C_4H_9)_2)Cl_2$ (Film)

3070 w, 3030 w, 3020 w, 2955 s, 2930 s, 2870 m, 1597 s, 1505 vs, 1470–1460 m, b, 1380 s, 1280 w, 1235 w, 1180 w, sh, 1160 m, 1110 m, 1095 w, 1045 m, 1000 w, 932 m, 890 w, 755 s, 730 w, 690 m

$C_6H_5N{=}P(N(CH_3)CH_2C_6H_5)Cl_2$ (CCl₄–CS₂, 0.2 mm)

3080 m, 3060 s, 3030 s, 2960 w, 2930 m, sh, 2910 m, 2860 w, 2810 w, 1600 vs, 1580 s, sh, 1510 vs, sh, 1495 vs, 1460–1450 s, b, 1430 s, sh, 1380–1360 vs, b, 1272 s, 1210 vs, 1190 vs, 1170 s, 1135 vs, 1070 vs, 1030 s, sh, 1010–995 vs, b, 950 vs, 905 m, sh, 890 s, 815 w, 775 vs, 760–750 vs, b, 722 vs, 690 vs

$[C_6H_5NHP(N(CH_3)_2)(NH_2)_2]^+Cl^-$ (KBr, 0.5%)

3240–3170 vs, b, 3080 s, 2940 m, b, 1605 m, 1565 w, 1495 s, 1417 m, 1325 w, sh, 1292 s, 1245 s, 1178 m, 1085 s, sh, 1065 s, b, 997 vs, 945 s, 905 m, 805–790 w, b, 747 m, 692 m

$[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$ (KBr, 0.5%)

3260–3120 vs, b, 3080 vs, 3050 s, sh, 3020 w, 2975 s, 2930 m, 2895 m, 2830 w, sh, 1607 m, 1547 s, 1500 s, 1425 m, 1385 m, 1365 m, 1350 w, sh, 1310 m, sh, 1295 s, 1242 m, 1217 s, 1168 s, 1090 s, 1072 vs, 1042 vs, 1005 m, sh, 960 s, 905 w, 795 m, 760 s, 700 s

$[C_6H_5NHP(N(n\text{-}C_4H_9)_2)(NH_2)_2]^+Cl^-$ (KBr, 0.5%)

3270–3220 vs, b, 3180 vs, b, 3075 s, 2955 s, 2930 s, sh, 2865 m, 1600 w, 1545 m, 1495 m, 1460 m, 1375 m, 1275 w, 1225 m, 1180 m, sh, 1155 m, 1070–1000 s, b, 935 s, 910 m, sh, 740–730 m, b, 692 s

$[C_6H_5NHP(N(CH_3)CH_2C_6H_5)(NH_2)_2]^+Cl^-$ (KBr, 0.5%)

3350–3320 vs, b, 3160–3120 vs, b, 3080–3050 vs, b, 2960 s, 2890s, 2820 s, 1602 s, 1555 s, 1495 vs, 1455 m, 1418 s, 1385 m, sh, 1370 m, 1345 w, sh, 1325 m, sh, 1300 s, sh, 1290 s, 1245 m, sh, 1235 s, 1210 s, 1195 m, 1118 vs, 1080 s, sh, 1060 vs, 1020–1000 vs, b, 950 vs, 905 m, 758 vs, 740–730 s, b, 698 s

ᵃ Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very.

tration the filtrate was concentrated and the phosphonium chloride isolated as described under section A.

The reaction of equimolar amounts of I–IV (Table I) with $NH_4[Cr(NH_3)_2(SCN)_4]$ in methanol and precipitation with water gave the appropriate reineckates (Table V).

The hexachloroplatinate of compound II was obtained by treating II with H_2PtCl_6 in an aqueous solution. An orange precipitate formed immediately, which after drying over P_4O_{10} had a melting point of 148°; yield, 93% of theory. *Anal.* Calcd for $C_{20}H_{40}Cl_6N_8P_2Pt$: Cl, 24.72; N, 12.99. Found: Cl, 24.43; N, 13.15. The compound is soluble in acetone, methanol, ethanol, and diethyl ether.

Pyrolysis of Compound II.—A 3.60-g (13.7-mmol) amount of compound II was placed in a bulb-to-bulb distillation apparatus and heated at 140–142° (0.1 mm) for 12 days. This produced 0.78 g of diethylammonium chloride, 0.54 g of aniline (both identified by their infrared spectra), and 2.14 g of a glassy, yellowish residue which softened at 270–285° (over-all loss of material 0.14 g). Extraction of 0.95 g of this residue with 15 ml of dry acetonitrile for 2 days gave 0.47 g of white crystals, mp 280–283°. *Anal.* Found: C, 37.94; H, 6.11; N, 23.00; Cl, 14.16; P, 19.75, corresponding to a formula of $C_{4.97}H_{9.59}Cl_{0.63}N_{2.58}P$.

Results and Discussion

Ammonolysis of $C_6H_5N{=}P(X)Cl_2$ (X = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(n\text{-}C_4H_9)_2$, $N(CH_3)CH_2C_6H_5$) yields as the
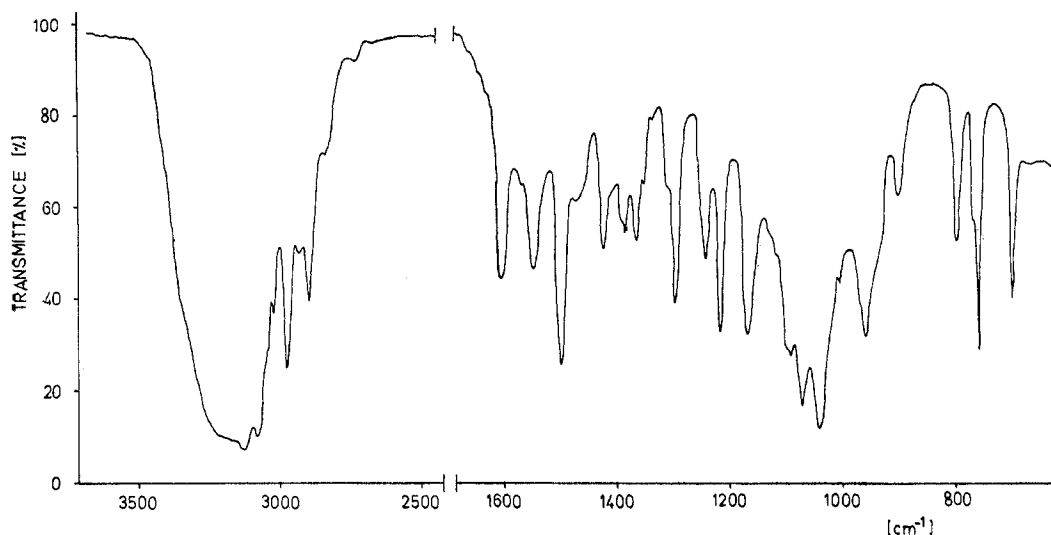
TABLE III

PROTON AND PHOSPHORUS MAGNETIC RESONANCE DATA OF $C_6H_5N{=}P(X)Cl_2$ AND $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$

Compound	Solvent for pmr[a]	τC_6H_5	τNCH_2[b]	τNCH_3[b]	τNH[b]	τNH_2[b]	J_{PNCH}, cps	J_{PNH}, cps	J_{PNH_2}, cps	$\delta^{31}P$, ppm	Solvent for ^{31}P nmr[c]
$C_6H_5N{=}P(N(CH_3)_2)Cl_2$	CDCl$_3$	2.99	...	7.36	...	...	15.7	...	...	+18.6	Neat
$C_6H_5N{=}P(N(C_2H_5)_2)Cl_2$[d]	CDCl$_3$	3.08	6.72	...	...	...	16.2	...	...	+21.6	Neat
$C_6H_5N{=}P(N(n{-}C_4H_9)_2)Cl_2$	CDCl$_3$	3.00	6.75	...	...	...	...	...	...	+22.1	Neat
$C_6H_5N{=}P(N(CH_3)CH_2C_6H_5)Cl_2$	CDCl$_3$	2.80	5.68	5.51	...	...	11.0 (CH$_2$) 16.2 (CH$_3$)	...	...	+19.8	Neat
$[C_6H_5NHP(N(CH_3)_2)(NH_2)_2]^+Cl^-$	DMSO-d_6	2.81	...	7.45	1.42	4.28	12.6	10.5	6.8	−28.7	DMSO
$[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$	DMSO-d_6	2.80	6.90	...	1.37	4.34	...	12.5	6.8	−26.0	DMSO
$[C_6H_5NHP(N(n{-}C_4H_9)_2)(NH_2)_2]^+Cl^-$	DMSO-d_6	2.80	6.95	...	1.35	4.41	...	11.5	6.5	−26.6	DMSO
$[C_6H_5NHP(N(CH_3)CH_2C_6H_5)(NH_2)_2]^+Cl^-$	DMSO-d_6	2.62	5.80	7.48	1.17	4.11	9.1 (CH$_2$) 12.1 (CH$_3$)	...	...	−27.8	DMSO

[a] Internal standard TMS. [b] All τ values extrapolated to $c \to 0$. [c] External standard 85% H$_3$PO$_4$. [d] All data from ref 1.

TABLE IV

ELECTRIC CONDUCTANCE DATA OF PHOSPHONIUM SALTS $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$ IN ACETONITRILE AT 25°

X = N(CH$_3$)$_2$		X = N(C$_2$H$_5$)		X = N(n-C$_4$H$_9$)$_2$		X = N(CH$_3$)CH$_2$C$_6$H$_5$	
$10^5 c$, M	Λ_c, cm² mol^{-1}	$10^5 c$, M	Λ_c, cm² ohm^{-1} mol^{-1}	$10^5 c$, M	Λ_c, cm² ohm^{-1} mol^{-1}	$10^5 c$, M	Λ_c, ohm^{-1} cm² mol^{-1}
4.339	188.5	3.678	172.6	2.439	167.6	3.253	154.0
5.007	181.3	4.700	162.3	2.815	160.6	4.156	148.7
5.625	175.8	5.640	155.0	3.162	157.4	4.987	142.8
6.199	171.0	6.508	149.3	3.485	153.5	5.755	138.0
6.734	169.3	7.312	145.0	3.785	150.6	6.465	134.6
7.232	165.9	8.058	141.5	4.066	148.3	7.125	131.6
7.699	162.3	8.752	138.8	4.328	146.0	7.739	128.7
8.136	161.0	9.401	136.1	4.805	141.9	8.312	126.3
8.547	159.1	10.007	133.9	5.023	141.0	8.849	124.3
8.934	156.7	10.576	131.4	5.228	139.1	9.351	121.9

TABLE V

ANALYTICAL AND MELTING POINT DATA OF $[C_6H_5NHP(X)(NH_2)_2][Cr(NH_3)_2(SCN)_4]$

X	Mp, °C	Yield, %	%N Calcd	%N Found
N(CH$_3$)$_2$	127–128	58.2	27.07	26.95
N(C$_2$H$_5$)$_2$	151–153	65.0	25.68	25.33
N(n-C$_4$H$_9$)$_2$	127	86.9	23.20	22.71
N(CH$_3$)CH$_2$C$_6$H$_5$	186–188	85.3	23.59	23.58

TABLE VI

^{31}P NMR CHEMICAL SHIFTS OF PHENYLAMINOPHOSPHONIUM CHLORIDES[15]

No.	Compd	$\delta^{31}P$, ppm
V	$[C_6H_5P(NH_2)_3]^+Cl^-$	−29.4
VI	$[(C_6H_5)_2P(NH_2)_2]^+Cl^-$	−31.9
VII	$[(C_6H_5)_3PNH_2]^+Cl^-$	−30.0
VIII	$[(C_6H_5)_2P(N(CH_3)_2)NH_2]^+Cl^-$	−39.9
IX	$[(CH_3)_2P(NH_2)_2]^+Cl^-$	−42.3
X	$[(CH_3)_2P(NH_2)C_6H_5]^+Cl^-$	−42.8

TABLE VII

Λ_0 AND K_c VALUES OF COMPOUNDS I–IV

Compd	Λ_0, ohm^{-1} cm² mol^{-1}	$10^4 K_c$, M
I	259.1	8.2
II	231.1	7.8
III	223.0	5.4
IV	198.0	9.3

sole reaction products the corresponding phosphonium salts, $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$, and not the expected bis(phosphoranylidene)ammonium chlorides $[(C_6H_5NHP(X)NH_2)_2]N^+Cl^-$, which are obtained with X = NH$_2$ by treating $(RN{=}PCl_3)_2$ with ammonia.[2,3] The difference in these reactions could be explained by the instability of the intermediate $[C_6H_5NHP(NH_2)_3]^+Cl^-$

$(C_6H_5N{=}PCl_3)_2 + 10NH_3 \longrightarrow$

$2[C_6H_5NHP(NH_2)_3]^+Cl^- + 4NH_4Cl$
(unstable)

$[C_6H_5NHP(NH_2)_2{\cdots}N{\cdots}P(NH_2)_2NHC_6H_5]^+Cl^- + NH_4Cl$

whereas the corresponding $[C_6H_5NHP(X)(NH_2)_2]^+Cl^-$ is stable.

Although aminophosphonium salts with one, two, three, and four[9,10] amino groups are known, these compounds represent the first examples of tetraminophosphonium chlorides which contain primary, secondary, and tertiary amino groups linked to the same phosphorus atom.

Structural evidence for the phosphonium chlorides I–IV is given by proton magnetic resonance and infrared spectra. The chemical shifts and coupling constants are presented in Table III. It is a well-known fact that the position of the NH signal of amines is dependent upon concentration,[11] temperature,[12] and solvent.[13] The ability of NH and NH$_2$ groups to act as hydrogen-bond acceptors with dimethyl sulfoxide was recently reported by Suhr.[14] The effect of change in concentration on the chemical shift of the NH and NH$_2$ protons in compounds I–IV is due to the fact that the NH and NH$_2$ groups form hydrogen bonds with the SO group of the solvent molecules. The formation of 1:1, 1:2, and cyclic associated complexes is possible.

(9) R. Appel, private communication; G. Köhnlein, Thesis, Heidelberg, 1963.

(10) (a) A. Schmidpeter and C. Weingand, *Angew. Chem.*, **80**, 234 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 210 (1968); (b) B. S. Drach, I. N. Zhmurova, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **37**, 2524 (1967); *Chem. Abstr.*, **69**, 26691 (1968); (c) H. F. Wilson and R. L. Skiles (to Rohm and Haas Co.), U. S. Patent 3271244 (1965); *Chem. Abstr.*, **66**, 2322 (1967); Belgian Patent 671026 (1966); *Chem. Abstr.*, **67**, 81799 (1967).

(11) C. Giessner-Prettre, *Compt. Rend.*, **252**, 3238 (1961); **254**, 4165 (1962).

(12) J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4495 (1956).

(13) S. Clough, *Mol. Phys.*, **2**, 349 (1959).

(14) H. Suhr, *Ber. Bunsenges. Physik. Chem.*, **71**, 1104 (1967).

Figure 1.—The ir spectrum of anilino(diethylamino)(diamino)phosphonium chloride, $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]$ $^+Cl^-$ (KBr, 0.5%).

Figure 2.—The ^1H nmr spectrum of anilino(diethylamino)-(diamino)phosphonium chloride, $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]$ $^+$-Cl^-, in DMSO-d_6 with the sodium salt of 3-(trimethylsilyl)-propanesulfonic acid as internal standard.

Figure 3.—Mass spectrum of anilino(diethylamino)(diamino)-phosphonium chloride, $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]$ $^+Cl^-$.

The chemical shifts of ^{31}P nuclei in the aminophosphonium compounds, listed in Table III, are nearly constant with respect to the nature of the dialkylamino group. The replacement of the NH_2 group by a phenyl group apparently causes no changes in chemical shift[15] (V–VII, IX, and X) as can be seen from Table VI. Therefore if $[(C_6H_5)_2P(N(CH_3)_2)NH_2]^+Cl^-$ has a chemical shift of -39.9 ppm, $[C_6H_5P(N(CH_3)_2)(NH_2)_2]^+Cl^-$

should have about the same chemical shift ($\simeq -40.0$ ppm). Replacement of the phenyl group by an anilino group causes an upfield shift to -28.7 ppm. This may be explained to some extent from the more electronegative nature of the anilino group than of the phenyl group. Since Letcher and Van Wazer[16] established the fact that in a quaternary phosphorus compound there is a substantial contribution to the chemical shift from the electronegativity as well as from the amount of π bonding, it seems that in the case of $[C_6H_5NHP-(N(CH_3)_2)(NH_2)_2]^+Cl^-$ the amount of π bonding from the anilino group is negligible. This is also consistent with the coupling constants J_{P-NH} and J_{P-NH_2} (J_{P-NH} = 10.5–12.5 cps; J_{P-NH_2} = 6.5–6.8 cps) indicating increased s character of the P–NH bond.

Infrared spectra of the new phosphonium chlorides are summarized in Table II. The NH_2 group absorbs at 3120–3350 cm^{-1} (NH_2 stretch), 1545–1565 cm^{-1} (NH_2 deformation), 795–800 cm^{-1} (NH_2 wagging), and 1060–1075 cm^{-1} (P–N stretch). The anilino group has spectral bands at 1275–1295 cm^{-1} (C_{arom}–N) and 930–960 cm^{-1} (P–N). Absorptions at 995–1045 and 725 cm^{-1} can be assigned to P–N–C_{aliph} asymmetric and symmetric stretch vibrations. Additional bands occur for P–N(CH$_3$)$_2$ at 1245 and 1075 cm^{-1}, at 1217 and 1168 cm^{-1} for P–N(C$_2$H$_5$)$_2$, at 1285, 1180, and 1165 cm^{-1} for P–N(n-C$_4$H$_9$)$_2$, and for P–N(CH$_3$)(CH$_2$C$_6$H$_5$) at 1235, 1210, and 1195 cm^{-1}.

(15) S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *Inorg. Chem.*, **6**, 515 (1967).

(16) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
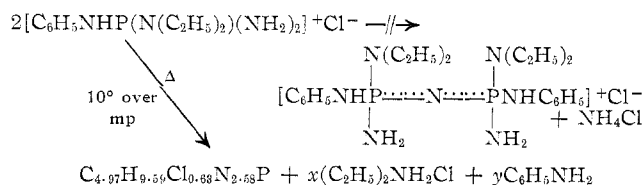
The mass spectra show in each case the presence of the dialkylamine ion, i.e. (m/e): $N(CH_3)_2^+$, 44; $N(C_2H_5)_2^+$, 72; $N(n\text{-}C_4H_9)^+$, 128; $N(CH_3)CH_2C_6H_5^+$, 120. Moreover, the mass peak of aniline (m/e 93) can be found in all cases; this is in agreement with the results of the pyrolysis of $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$, where splitting off of the corresponding secondary amine (as diethylammonium chloride) and of aniline could be shown. The mass peak of the mother ion could be found in the mass spectra of compounds II and III.

The aminophosphonium chlorides behave in acetonitrile as 1:1 electrolytes. The Λ_0 and the K_c values at 25° are summarized in Table VII.

Polarographic measurements of $[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^-$ in dimethyl sulfoxide gave the result that the cation is reduced in one step with $E_{1/2} = -2.43$ V (vs. the aqueous saturated calomel electrode). The limiting current is diffusion controlled in the investigated concentration range of 5×10^{-4} to 1.2×10^{-3} M. The reduction was found to be irreversible (82 mV) and the diffusion coefficient is $D = 1.5 \times 10^{-6}$ cm² sec⁻¹ (25°, tetraethylammonium perchlorate), with a diffusion current constant $I = 0.74$. The temperature coefficient of the diffusion current is 0.43%/deg in the investigated temperature range (20–40°).

The thermal condensation reaction and the mass spectra of I–IV indicate that the phosphonium chlorides do not lose NH_4Cl on heating but do lose dialkylammonium chloride and aniline in primarily an intramolecular condensation, where the most basic species are split off

$$2[C_6H_5NHP(N(C_2H_5)_2)(NH_2)_2]^+Cl^- \;-\!/\!\!\rightarrow$$

$$[C_6H_5NHP\cdots N\cdots PNHC_6H_5]^+Cl^- + NH_4Cl$$

$$C_{4.97}H_{9.59}Cl_{0.63}N_{2.58}P + x(C_2H_5)_2NH_2Cl + yC_6H_5NH_2$$

It was not possible to assign a definite structural formula to the above pyrolysis product.

Complexes of Trivalent Phosphorus Derivatives. IX. Reactions of Cyclopentadienylmetal Carbonyl Halides with Chelating Oligotertiary Phosphines[1]

By R. B. KING,[2] L. W. HOUK,[3] AND K. H. PANNELL[3]

Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with chelating ditertiary phosphines gives the red to orange monocarbonyls $C_5H_5Mo(CO)(diphos)Cl$ which can also be prepared by ultraviolet irradiation of the salts $[C_5H_5Mo(CO)_2(diphos)]Cl$. Ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with the chelating tritertiary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ gives red C_5H_5Mo-$(CO)(triphos)Cl$ with one of the three phosphorus atoms not bonded to the metal atom. Ultraviolet irradiation of the halides $C_5H_5Fe(CO)_2X$ (X = Cl or Br) with the chelating ditertiary phosphines in benzene solution gives the black derivatives $C_5H_5Fe(diphos)X$. However, reaction of $C_5H_5Fe(CO)_2I$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$ gives the green binuclear derivative $[C_5H_5Fe(CO)I](CH_3)_2PCH_2CH_2P(CH_3)_2[Fe(CO)IC_5H_5]$ with a bridging ditertiary phosphine ligand. Ultraviolet irradiation of the halides $C_5H_5Fe(CO)_2X$ (X = Cl or Br) with the chelating tritertiary phosphine listed above followed by chromatography on alumina gives yellow salts of the $C_5H_5Fe(triphos)^+$ cation. Reaction of $C_5H_5Co(CO)I_2$ with the chelating ditertiary phosphines at room temperature gives the brown ionic iodides $[C_5H_5Co(diphos)I]I$ which can be converted to the corresponding brown hexafluorophosphates $[C_5H_5Co(diphos)I][PF_6]$. A similar treatment of $C_5H_5Co(CO)I_2$ with the tritertiary phosphines gives the orange ionic diiodide $[C_5H_5Co(triphos)]I_2$ which can be converted to the corresponding yellow bis(hexafluorophosphate) $[C_5H_5Co(triphos)][PF_6]_2$.

The development of the chemistry of cyclopentadienylmetal derivatives containing the strongly π-accepting carbonyl ligands into a major area of transition metal organometallic chemistry makes of interest the development of the chemistry of cyclopentadienyl-metal derivatives containing the relatively weakly π-accepting tertiary phosphine ligands. However, compounds containing only π-cyclopentadienyl and tertiary phosphine ligands analogous to the cyclopentadienyl-metal carbonyls are unknown. A useful series of intermediates for exploration of this area of chemistry are cyclopentadienylmetal halides containing tertiary phosphine ligands but no carbonyl groups. Known examples of such compounds are $C_5H_5MX_2PR_3$ (M = Co[4]

(1) (a) For part VIII of this series see R. B. King and T. F. Korenowski, *J. Organometal. Chem.*, in press. (b) The generic term "oligotertiary phosphine" is used to describe phosphines containing more than one tertiary phosphine group. The more conventional term "polytertiary phosphine" seems inappropriate here since the tertiary phosphines presently under study all contain less than four phosphorus atoms.

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) Postdoctoral fellows supported by the Air Force Office of Scientific Research during the period of this work.

(4) (a) R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964); *Inorg. Chem.*, **5**, 82 (1966); (b) R. F. Heck, *ibid.*, **4**, 855 (1965); (c) H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, **38**, 2212 (1965).