

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112**Synthesis and Characterization of Dicoordinate Phosphorus Cations. Compounds of the Type $[(R_2N)_2P]^+[Y]^-$ and Their Congeners**

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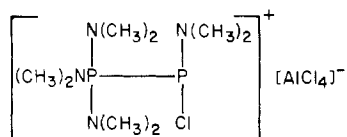
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On the basis of 1H and ^{31}P NMR spectroscopy, infrared data, measurements of electrical conductivity, and chemical information, the compound $((CH_3)_2N)_2P \cdot AlCl_3$ is assigned the ionic structure $[(CH_3)_2N)_2P]^+[AlCl_4]^-$. The related compound $(CH_3)_2NPCl_2 \cdot AlCl_3$ is assigned the structure $[(CH_3)_2NPCl]^+[AlCl_4]^-$. Salts of $((CH_3)_2N)_2P^+$ containing counterions such as PF_6^- , $B_2F_7^-$, $GaCl_4^-$, and $FeCl_4^-$ have been prepared along with the $GaCl_4^-$ salt of the $(CH_3)_2NPCl^+$ cation. The phosphorus in the cation $(CH_3)_2NPCl^+$ is the most deshielded phosphorus atom yet recorded. It has a chemical shift of -325 ppm from H_3PO_4 . Both dicoordinate phosphorus cations are strong Lewis acids combining with a base such as $(R_2N)_3P$ to give previously described cations such as $[(R_2N)_3P-P(NR_2)Y]^+$ where Y is NR_2 or Cl . The dicoordinate cations can also serve as ligands toward the metal atoms of metal carbonyls. Evidence for an $N-P$ $p\pi-p\pi$ bond is found with $(R_2N)_2P^+$.

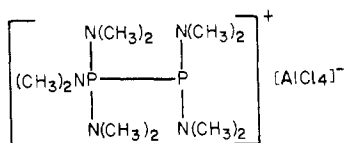
In an investigation of the acid-base interactions of chloro(dimethylamido)phosphorus(III) with aluminum(III) chloride some anomalies of both stoichiometry and structure were encountered. The following compounds could be prepared:¹ $(CH_3)_2NPCl_2 \cdot AlCl_3$, $((CH_3)_2N)_2P \cdot AlCl_3$, $2((CH_3)_2N)_2P \cdot AlCl_3$, $\{[(CH_3)_2N)_2P] \cdot [(CH_3)_2N)_3P\} \cdot AlCl_3$, and $((CH_3)_2N)_3P \cdot AlCl_3$. It was significant that the 2:1 adducts $2((CH_3)_2N)_2P \cdot AlCl_3$ and $2(CH_3)_2NPCl_2 \cdot AlCl_3$ could not be prepared even though the intermediate 2:1 adduct $2((CH_3)_2N)_2P \cdot AlCl_3$ was a stable well-defined species.

The foregoing facts raised interesting structural questions. In formulating these molecules, normal $AlCl_3$ addition to either the phosphorus or nitrogen lone pair of electrons would be anticipated. Indeed, Sollott and Peterson² invoked a nitrogen-aluminum bond in their description of $(CH_3)_2NPCl_2 \cdot AlCl_3$. Such a representation did, however, pose real structural problems in describing the 2:1 adduct $2((CH_3)_2N)_2P \cdot AlCl_3$ unless a five-coordinate aluminum atom were postulated. If this postulate were made, it was difficult to understand why the compound $2((CH_3)_2N)_3P \cdot AlCl_3$ could not be made.

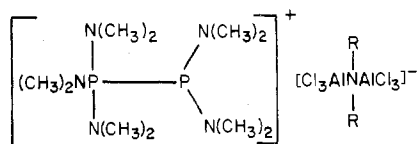
The structural puzzle of the 2:1 adducts was solved³ when it was found that $2((CH_3)_2N)_2P \cdot AlCl_3$ had the unexpected ionic structure



while the mixed diadduct $\{[(CH_3)_2N)_2P] \cdot [(CH_3)_2N)_3P\} \cdot AlCl_3$ had the related structure

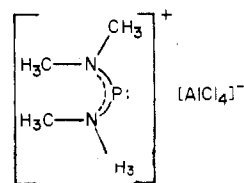


The monoadduct $((CH_3)_2N)_3P \cdot AlCl_3$ was found³ to contain a similar cation but a quite different anion which accounted for our failure to make the 2:1 adduct with this base. The structure of the monoadduct was

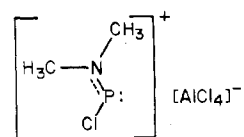


The above anion appears to be unstable and decomposes to $AlCl_4^-$ and $[Cl_2AlNR_2]^-$.

Questions now remain relative to the structure of the two remaining monoadducts: $(CH_3)_2NPCl_2 \cdot AlCl_3$ and $((CH_3)_2N)_2P \cdot AlCl_3$. Traditional acid-base theory suggests a direct $N-Al$ or $P-Al$ bond. In fact, the comparable phosphorus trichloride-aluminum chloride addition compound Cl_3PAI_3 is known⁴ to have the expected $P-Al$ donor-acceptor bond. Another possibility exists, however. By analogy to the structure assigned to $((CH_3)_2N)_3P \cdot AlCl_3$ one might write $((CH_3)_2N)_2P \cdot AlCl_3$ as $\{[(CH_3)_2N)_3P-P(N(CH_3)_2)_2]^+[Al_2Cl_7]^-$. This structure, involving chloride transfer, suggests still a different possibility. Transfer of the chloride ion from $((CH_3)_2N)_2P \cdot AlCl_3$ to $AlCl_3$ would generate a dicoordinate phosphorus cation which can be represented as

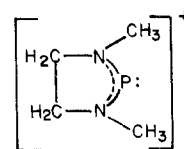


For the related complex $(CH_3)_2NPCl_2 \cdot AlCl_3$ the structure would be



[The symbol \vdots next to the phosphorus atom in the dicoordinate cation indicates a free electron pair which would be stereochemically active.]

In this paper data obtained from conductivity measurements, NMR spectroscopy, and infrared spectroscopy are used to support the representation involving the dicoordinate phosphorus cations $((CH_3)_2N)_2P^+$ and $(CH_3)_2NPCl^+$. The structure given for $((CH_3)_2N)_2P^+$ is very similar to that of the cyclic cation



first identified as the PF_6^- salt in an excellent and definitive study by Fleming⁵ and her students. While structural similarities are pronounced at low temperatures, the noncyclic compound is significantly more reactive than its cyclic counterpart. This is particularly true at ambient temperatures

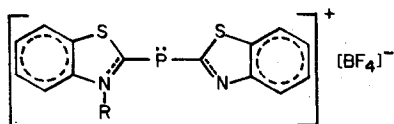
Table I. Equivalent Conductance of 10^{-2} M Solutions of Compounds in Methylene Chloride at 25°C

Compd	Equip conductance, $\Omega^{-1}\text{cm}^2$	Compd	Equip conductance, $\Omega^{-1}\text{cm}^2$
AlCl_3	0.21 ± 0.01^a	$((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$	1.1 ± 0.4^a
$((\text{CH}_3)_2\text{N})_2\text{PCl}$	$<10^{-2}$	$[(\text{R}_4\text{N})^+[\text{AlCl}_4]^-]$	5.36 ± 0.01

^a Measurements on $(\text{CH}_3)_2\text{N}_2\text{PCl}\cdot\text{AlCl}_3$ and AlCl_3 were extremely sensitive to traces of moisture. Values represent best estimates for anhydrous compounds in dry CH_2Cl_2 .

where dynamic processes are observed for the noncyclic but not for the cyclic case.

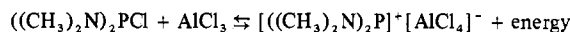
A dicoordinate phosphorus cation was first synthesized in 1964 by Dimroth and Hoffman,^{6a} who prepared the phosphamethinecyanines



The above structure was established with a high degree of certainty. X-ray studies showed a nearly planar ion.^{6b} This general class of compounds has been reviewed by Dimroth.^{6b} While some formal similarities exist between the phosphamethinecyanines and the cations being studied here, the properties and reactions of the two groups contrast rather sharply. For example the phosphamethinecyanines are weakly basic and can be protonated. In contrast the cation $(\text{R}_2\text{N})_2\text{P}^+$ is a very strong Lewis acid and has shown basic character only toward potential π -electron donors such as metal carbonyls.

Conductivity Measurements

Equivalent conductance values were obtained at room temperature for 10^{-2} M solutions of $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ in dry CH_2Cl_2 . Data are summarized in Table I. Note that the value for $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ is more than 1000 times larger than that for a comparable solution of the ligand, $((\text{CH}_3)_2\text{N})_2\text{PCl}$, in CH_2Cl_2 and about 6 times larger than that for a solution of AlCl_3 in CH_2Cl_2 .⁷ The strictly ionic solid $[(\text{CH}_3)_4\text{N}]^+[\text{AlCl}_4]^-$ has an equivalent conductance which is about 5 times larger than that of $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$. These facts suggest a reversible equilibrium which can be represented as



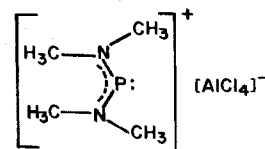
As will be seen from the NMR data the equilibrium tends to shift back somewhat toward the reactants as the temperature is raised. Such a postulate will rationalize a value for the 1:1

adduct which is somewhat less than that for the completely ionic model compound, tetramethylammonium tetrachloroaluminate. The equivalent conductance for $(\text{CH}_3)_2\text{NPCl}_2\cdot\text{AlCl}_3$ is comparable to that for $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$, but it should be noted that the former compound converts slowly to the latter on standing, so values for a completely pure sample of $(\text{CH}_3)_2\text{NPCl}_2\cdot\text{AlCl}_3$ have not yet been obtained. The conductivity measurements indicate an ionic product or an equilibrium involving an ionic product.

Proton NMR Spectra of $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ and $(\text{CH}_3)_2\text{NPCl}_2\cdot\text{AlCl}_3$

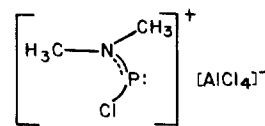
At -35°C the proton spectrum of $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ consists of two sets of doublets of equal area [δ 2.13, $J = 14.1$ Hz; δ 1.97, $J = 4.8$ Hz; CH_2Cl_2 was the internal standard]. It is instructive to compare these values with those for the cyclic cation described by Fleming, Lupton, and Jekot.⁵ Data are given in Table II.

The agreement provides striking support for a low-temperature structure analogous to that of the cyclic cation. The appearance of two kinds of protons in the noncyclic cation requires an effective barrier to rotation around the N-P bond. At $+35^\circ\text{C}$ the proton spectrum with phosphorus decoupled is a sharp singlet at δ 2.07 (CH_2Cl_2). Rotation around the N-P bond occurs at the higher temperature. The dynamics of rotation is dependent upon the presence of bases and upon the counterion in the solution. The process is reasonably complex and will be treated in a subsequent paper devoted to the dynamics of phosphorus cation systems in general. For the "salt"



in pure methylene chloride solution, ΔG^\ddagger for rotation around the P-N bond is 14.6 ± 0.5 kcal/mol.

The ^1H NMR spectrum for the related compound $(\text{C}_6\text{H}_5)_2\text{NPCl}_2\cdot\text{AlCl}_3$ is consistent with but not conclusive proof for the structure



A distinct ^1H doublet at δ 1.71 (CH_2Cl_2) and $J = 13.0$ Hz

Table II

Ref	Protons	δ	$J_{\text{P-H}}$, Hz	Area	cyclic cation			
					Protons	δ	$J_{\text{P-H}}$, Hz	Area
a	H_3C	-3.10	11.6 Hz	6				
a	H_2C	-3.83	4.8	4				
b	H_3C	2.18	11.6	6				
b	H_2C	1.45	4.8	4				
c	H_3C	2.17	11.6	6	H_3C (outer)	2.13	14.1	6
c	H_2C	1.37	4.8	4	H_3C (inner)	1.97	4.8	6

^a Reference 5. Internal standard for δ values is TMS. ^b Values of Fleming et al.⁵ were corrected by standard procedures⁸ to values using CH_2Cl_2 as a standard. ^c This work; standard is CH_2Cl_2 .

Table III. Changes in ^{31}P Chemical Shift Values of Phosphorus Ligands after Coordination^a

Ligand used	δ ^{31}P free ligand	Lewis acid coord to ligand	δ ^{31}P coord ligand	Change in δ on coord	Ref
PF ₃	-104.0 ^b	-AlCl ₃	-104.4	-0.4	4
	-105	-BH ₃	-107	-2.0	9
	-104	-Pt(PF ₃)Cl ₂	-69	+35	10
	-104	-Pd(PF ₃) ₃	-116	-12	10
P(N(CH ₃) ₂ F) ₂	-143 ^c	-BH ₃	-130	+13	11
P(N(CH ₃) ₂) ₂ F	-153 ^c	-BH ₃	-133	+20	11
P(OC ₂ H ₅) ₃	-139	-Ni(P(OC ₂ H ₅) ₃) ₂	-160	-21	10
	-139	Cu(P(OC ₂ H ₅) ₃) ₃ ⁺	-128	+11	10
P(C ₂ H ₅) ₃	+19	Ag(P(OC ₂ H ₅) ₃) ₃ ⁺	-128	+11	10
		-Ni(CO) ₂ (P(C ₂ H ₅) ₃)	-21	-40	10

^a All values are in ppm and are referred to H₃PO₄. ^b Measured in CDCl₃. ^c Neat.

appears at -35 °C. The ¹H spectrum was not temperature dependent over the range -35 to +35 °C. The result is consistent with a model having the dimethylamido group bound to phosphorus, but it provides no evidence for restricted rotation about the N-P bond. If such rotation were hindered, one would expect to see two kinds of methyl groups unless an alternative exchange process acted to make the protons equivalent.

³¹P NMR Spectra of ((CH₃)₂N)₂PCl·AlCl₃ and (CH₃)₂NPCl₂·AlCl₃

The ³¹P spectrum of ((CH₃)₂N)₂PCl·AlCl₃ appears as a fairly broad singlet at -264 ppm while that of (CH₃)₂NPCl₂·AlCl₃ appears similarly at -322 ppm (relative to OPA). Temperature dependence of the signals was not found. The large downfield chemical shift values are striking, particularly when they are compared to the original dicoordinate phosphorus cations of Dimroth and Hoffman^{6a} where the ³¹P signal appeared as a singlet at about -26 ppm. The value of -322 ppm indicates the most deshielded phosphorus atom yet observed. The value of -264 ppm represents the second most deshielded phosphorus atom yet recorded and is identical with the value reported by Fleming and her co-workers⁵ for the cyclic cation as the PF₆⁻ salt. The value is clearly not consistent with changes in chemical shifts generally observed when a phosphorus ligand binds to an acceptor atom. Representative data, shown in Table III, show changes in the range +11 to -40 ppm, depending on the acid used. Changes with aluminum acids appear to be small. In this study the changes observed are in the range -105 to -160 ppm using an aluminum reference acid. Normal P-Al coordination is *not* indicated.

Another aspect of the ³¹P data provides compelling evidence for the dicoordinate phosphorus cation. In Figure 1, the ³¹P chemical shift values^{8,10} for the series PCl₆⁻ (281-305 ppm),¹⁰ PCl₅ (80 ppm),⁸ PCl₄⁺ (-86 to -96 ppm),^{8,10} and PCl₃ (-220 ppm)^{8,10} are plotted against the phosphorus coordination number. The relationship is approximately linear, but a smooth gentle curve gives the best fit to the data. The chemical shift value for P(N(CH₃)₂)₂ was then put on the same graph and a curve, parallel to that observed for the halide series, was drawn. An extrapolation of the curve for the P-Cl series indicates that the dicoordinate phosphorus cation Cl₂P⁺ should have a chemical shift of -360 ± 20 ppm if it exists. A similar extrapolation of the ((CH₃)₂N)₃P curve indicates that the dicoordinate phosphorus cation ((CH₃)₂N)₂P⁺ should have a chemical shift of about -260 ± 20 ppm. The observed value of -264 ppm is in excellent agreement with this prediction. The value for the mixed cation (CH₃)₂NPCl⁺ might be expected midway between that for Cl₂P⁺ and ((CH₃)₂N)₂P⁺ or at a value of about -310 ± 20 ppm. The observed value of -326 ppm is in striking agreement with this prediction.

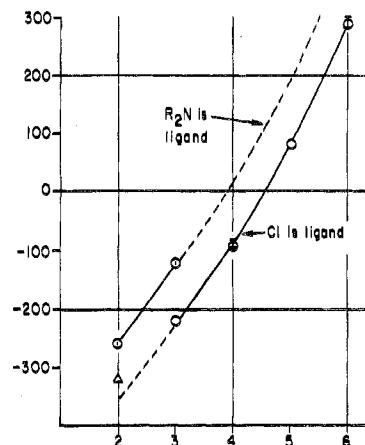
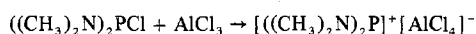


Figure 1. Values for the ^{31}P chemical shift as a function of coordination number of the phosphorus.

Infrared Spectra of ((CH₃)₂N)₂PCl·AlCl₃ and of (CH₃)₂NPCl₂·AlCl₃

Infrared spectra of the ligands (CH₃)₂NPCl₂ and ((CH₃)₂N)₂PCl and of their AlCl₃ complexes were recorded in paper 1 of this series.¹ The assignments drew heavily on the earlier work of Fleming¹² and of Farran,¹³ who studied in detail the vibrational spectra of ((CH₃)₂N)PX₂ molecules where X was F, Cl, or Br. Changes in frequency as a result of complex formation for modes involving CH₃ motions were small, thus the infrared spectrum of the free ligand and the spectrum of the complexed ligand were not significantly different at frequencies above 1300 cm⁻¹. Frequencies for free and complexed ligands below 1300 cm⁻¹ are compared in Table IV. Of particular interest are frequencies involving the P-Cl stretching motion. For PCl₃ the infrared-active P-Cl symmetric stretch is assigned¹⁴ at 507 cm⁻¹ and the asymmetric at 494 cm⁻¹. In R₂NPCl₂ one P-Cl stretching mode can be assigned at 508 cm⁻¹; the other may be the band at 530 cm⁻¹. In ((CH₃)₂N)₂PCl the $\nu(\text{P-Cl})$ is found at 510 cm⁻¹. Dimeric Al₂Cl₆ shows¹⁴ bands at 625, 484, and 420 cm⁻¹. The 484-cm⁻¹ band is strong; the other two are weak. The complex AlCl₄⁻ moiety shows only one infrared-active band in the range of our instruments. This appears at 495 cm⁻¹ and is the asymmetric Al-Cl stretching mode. Thus in principle one would expect the process



to be accompanied by the disappearance of bands at about 510 and 484 cm⁻¹ and the appearance of a sharp strong band at 495 cm⁻¹. This is in general seen, but shifts are small enough that one could not draw unequivocal conclusions from the infrared data for the AlCl₃ complexes. The infrared arguments for complexes involving other anions such as PF₆⁻ are more definitive. Certainly the sharp peak observed for the complex in the region around 495 cm⁻¹ coincides nicely with that seen in the spectrum of an authentic AlCl₄⁻ salt. Attempts to obtain Raman spectra have not yet succeeded because of a fluorescence problem in the system.

Chemical Evidence for Dicoordinate Phosphorus Cations. Other Salts of ((CH₃)₂N)₂P⁺ and ((CH₃)₂N)PCl⁺

Salts of ((CH₃)₂N)₂P⁺ containing counterions such as PF₆⁻, B₂F₇⁻, GaCl₄⁻, and FeCl₄⁻ have been prepared.

[((CH₃)₂N)₂P]⁺[PF₆]⁻. The PF₆⁻ salt can be obtained by a procedure which is analogous to that used by Fleming and her students⁵ in preparing the cyclic cation as a PF₆⁻ salt. The appropriate equation is

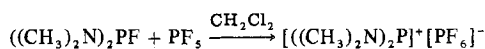
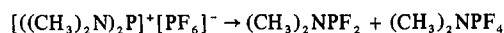


Table IV. Significant Infrared Absorptions of $((\text{CH}_3)_2\text{N})_x\text{PCl}_{3-x}$ and Their AlCl_3 Complexes in the C, N, P, and Cl Stretching Regions

Ligands				Assignments	AlCl_3 complexes (1:1)		
PCl liquid	$(\text{R}_2\text{N})\text{PCl}_2$	$(\text{R}_2\text{N})_2\text{PCl}$	$(\text{R}_2\text{N})_3\text{P}$		$(\text{R}_2\text{N})\text{PCl}_2 \cdot \text{AlCl}_3$	$(\text{R}_2\text{N})_2\text{PCl} \cdot \text{AlCl}_3$	Assignments
	1290 m	1280 s	1269 ms	$(\text{CN} \dots \text{P}) (\nu_9)$	1295 ms	1305 s	$\nu(\text{CN} \dots \text{P})$
	981 s	980 sh	974 ms		$(\text{CN} \dots \text{P}) (\nu_{12})$	984 vs	1003 s
		968 s	952 vs			985 vs	
		880 mw	938 vs				
	688 ms	790 w	671 s	$\nu(\text{PN})$		805 w	805 w
		700 ms			712 mw	733 w	?
		672 m			690 m	680 w	
					641 m	620 w	
507 vs (sym)	530 ms	510 sh		$\nu(\text{P-Cl})$	585 m, sh		$\nu(\text{AlCl}_4^-)$
494 v (asym)	508 vs	490 mw			500 vs	495 vs	
	456 s	410 w			430 m	437 sh	$\nu(\text{Al-Cl})^a$ (bridge bending)
		307 w					

^a Absent in PF_6^- salt.

The white solid product separates from the cold methylene chloride solution. The pure salt can be warmed to room temperature either in CH_2Cl_2 or under vacuum without obvious decomposition, but it melts with decomposition at 65 °C. The equation for the process is



This irreversible reaction is also observed at 25 °C if the solid is stored in a sealed tube for several weeks.

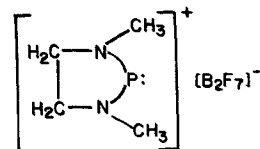
The ^1H NMR of the PF_6^- salt in CH_2Cl_2 solution at 25 °C shows one doublet at δ 2.15 (CH_2Cl_2 reference) with a J_{PNCH} of 9.8 Hz. Comparable values for the AlCl_4^- salt are δ 2.07 ppm with a J value of 9.8 Hz. The two salts clearly contain the same cation. The proton spectrum of the PF_6^- salt, like that of the AlCl_4^- salt, is temperature dependent. At low temperature a pair of doublets is seen because of hindered rotation about the P-N bond. As noted earlier, the thermodynamic activation parameters for the rotation process are dependent upon the anion present. For the PF_6^- salt the ΔG^\ddagger for rotation about the P-N bond is 12.3 ± 0.5 kcal/mol as opposed to 14.6 ± 0.5 for the AlCl_4^- salt. The process will be treated in more detail in a subsequent paper.

As expected, the ^{31}P NMR spectrum of $[(\text{CH}_3)_2\text{N}]_2\text{P}^+[\text{PF}_6]^-$ shows a broad singlet at -264 ppm which is diagnostic for the phosphorus in the cation and a septet at +144 ppm ($J_{\text{FP}} = 715$ Hz) which is diagnostic for the PF_6^- ion.¹⁰ The identity of the PF_6^- anion was further confirmed by the ^{19}F NMR spectrum; a doublet at δ 71 (CFCl_3 is reference) with a J_{PF} of 710 Hz checked literature values⁸ for the PF_6^- ion: H_2PF_6 , δ 73, $J = 715$ Hz; $\text{KPF}_6(\text{aq})$, δ 71, $J = 706$ Hz. (The literature values were converted to CCl_3F values by relationship $\delta_{\text{CFCl}_3} = \delta_{\text{F}_2\text{CCOOH}} + 78.6$.)

The infrared spectrum of $\text{FP}(\text{N}(\text{CH}_3)_2)_2$ shows a strong absorption at 747 cm^{-1} which is assigned as a P-F stretching mode by analogy to Farran's¹³ assignments of bands at 799 and 743 cm^{-1} to symmetric and asymmetric P-F stretching modes in $\text{F}_2\text{P}(\text{N}(\text{CH}_3)_2)_2$. Similarly a band at 496 cm^{-1} can be attributed to a PF bending mode. After reaction with PF_5 only a weak band is seen at 735 cm^{-1} and the 495 cm^{-1} band has disappeared. New bands appear at 830 cm^{-1} (very strong) and at 535 cm^{-1} which are diagnostic for PF_6^- . The parent PF_5 shows bands at 1026, 945, 533, and 301 cm^{-1} but not at 830 cm^{-1} . In short, a detailed correlation of infrared frequencies for $(\text{CH}_3)_2\text{N}_2\text{PF-PF}_5$ and $(\text{CH}_3)_2\text{N}_2\text{PCl-AlCl}_3$ shows excellent agreement between the two except for bands assigned to AlCl_4^- and PF_6^- .

The equivalent conductance of the PF_6^- salt in methylene chloride was $0.80\ \Omega^{-1}\text{ cm}^2$. This value is about 1000 times larger than the equivalent conductance of either PF_5 or $(\text{CH}_3)_2\text{N}_2\text{PF}$ measured under comparable conditions.

$[(\text{CH}_3)_2\text{N}]_2\text{P}^+[\text{B}_2\text{F}_7]^-$. Fleming and co-workers⁵ found that 1 mol of BF_3 adds covalently to one nitrogen of the cyclic ligand, $(\text{H}_2\text{CNCH}_3)_2\text{PF}$, but that an excess of BF_3 gives the ionic product



The noncyclic bis(dimethylamido)fluorophosphorus(III) will also pick up one BF_3 molecule through coordination on nitrogen to give a covalent product comparable to the $(\text{C}-\text{H}_3)_2\text{NPF}_2 \cdot \text{BF}_3$ which has been previously characterized.¹¹ Parameters for the BF_3 unit are essentially identical in the two cases for ^{11}B and ^{19}F NMR. The boron of $\text{F}_2\text{PNR}_2 \cdot \text{BF}_3$ is a singlet at 16.9 ppm; the fluorine of BF_3 is a singlet at 150 ppm. The boron of $\text{FP}(\text{NR}_2)_2 \cdot \text{BF}_3$ is a singlet at 17.0 ppm; the fluorine of BF_3 is a singlet at 151 ppm. Data for fluorines attached to the phosphorus atom show some differences as would be expected. The absorption for fluorine attached to phosphorus in $\text{F}_2\text{PNR}_2 \cdot \text{BF}_3$ is a doublet at δ 72, $J = 1320$ Hz; comparable data for $\text{FP}(\text{NR}_2)_2 \cdot \text{BF}_3$ show δ 122, $J = 1100$ Hz.

When an excess of BF_3 was added to $(\text{CH}_3)_2\text{N}_2\text{PF} \cdot \text{BF}_3$, the ^1H NMR spectrum at -78 °C was in good agreement with that observed previously for the protons in $(\text{CH}_3)_2\text{N}_2\text{P}^+$; further, the fluorine spectrum at -78 °C with a singlet at +67 ppm relative to F_3CCOOH agreed with that reported⁵ for B_2F_7^- . Above -45 °C the B_2F_7^- salt undergoes decomposition to give F_2BNR_2 and $\text{F}_2\text{PN}(\text{CH}_3)_2 \cdot \text{BF}_3$. These products were first reported by Fleming^{11,12} in her study of the reaction between $(\text{CH}_3)_2\text{N}_2\text{PF}$ and 2 mol of BF_3 . The mechanism by which the solid decomposes is still not certain, but a preliminary coordination of BF_3 molecules to nitrogen atoms seems most reasonable.¹¹

$[(\text{CH}_3)_2\text{N}]_2\text{P}^+[\text{GaCl}_4]^-$ and $[(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{P}^+[\text{GaCl}_4]^-]$. In the preceding paper of this group³ it was shown that GaCl_3 , like AlCl_3 , will react with an excess of $(\text{CH}_3)_2\text{N}_2\text{PCl}$ to give the ionic compound



A 1:1 adduct can also be made which shows a ^{31}P singlet at

-267 ppm. This value provides strong evidence for the formula $[(\text{CH}_3)_2\text{N})_2\text{P}]^+[\text{GaCl}_4]^-$.

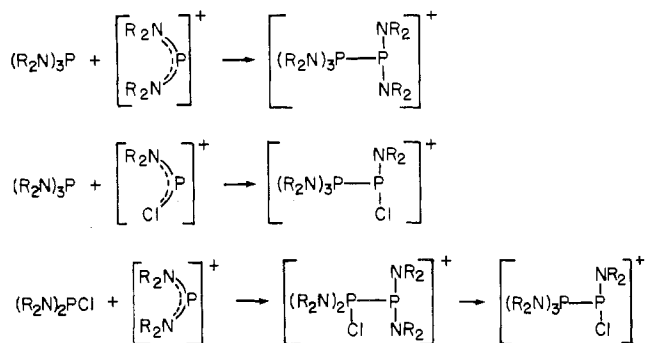
Addition of $\text{Cl}_2\text{PN}(\text{CH}_3)_2$ to GaCl_3 in a 1:1 ratio using PCl_3 as a solvent in a manner completely analogous to the procedure used by Kopp et al.¹ to prepare $[(\text{CH}_3)_2\text{NPCI}]^+[\text{AlCl}_4]^-$ gave a product with a ^{31}P singlet at -329 ppm from H_3PO_4 . This value provides good evidence for the presence of the cation $(\text{CH}_3)_2\text{NPCI}^+$ in the products.

$[(\text{CH}_3)_2\text{N})_2\text{P}]^+[\text{FeCl}_4]^-$. When $(\text{CH}_3)_2\text{N}_2\text{P}$ is condensed onto an equimolar quantity of FeCl_3 at -78°C and the mixture is allowed to stand at room temperature, a clear crystalline solid is obtained. In our hands the ^1H NMR signal at room temperature was a broad, poorly resolved singlet at δ 2.1 (CH_2Cl_2 reference). The low resolution can be attributed to the paramagnetism of the FeCl_4^- ion. No phosphorus signal could be obtained. While characterization of the product by NMR could not be classed as successful, infrared data were helpful. The spectra for $[(\text{CH}_3)_2\text{N})_2\text{P}]^+[\text{AlCl}_4]^-$, $[(\text{CH}_3)_2\text{N})_2\text{P}]^+[\text{PF}_6]^-$, and $(\text{CH}_3)_2\text{N}_2\text{P}\cdot\text{FeCl}_3$ were essentially identical except for frequencies assigned to the anion. A medium band at 385 cm^{-1} seen in the IR spectrum of the iron(III) chloride complex checks well with the absorption found for the FeCl_4^- ion by Woodward and Taylor.¹⁵ While the equivalent conductance in methylene chloride solution was somewhat less than that for the AlCl_4^- and PF_6^- salts ($\Lambda = 0.45\ \Omega^{-1}\text{ cm}^2$), the value is indicative of an ionic product.

Chemical Evidence for Dicoordinate Phosphorus Cations

The cation $(\text{R}_2\text{N})_2\text{P}^+$ has two ligands and a free electron pair in the valence level of the phosphorus atom; hence it should be a fairly strong Lewis acid. Because of the electron pair it should also be a Lewis base, particularly in those cases where π back-bonding into the partially open p orbital on the phosphorus is possible.

Reactions as a Lewis Acid. The reaction described in the original report¹ on the synthesis of this family of compounds can now be recognized as an acid-base reaction with the cation as the acid. Three equations are pertinent, i.e.



In the last process an exchange reaction which transfers the chloride to the three-coordinate phosphorus atom was observed. The diphosphorus cations were identified by ^1H and ^{31}P NMR and by their infrared spectra.³ According to present data the base-addition process is quite independent of the anion in the system. Salts with AlCl_4^- and PF_6^- show the same behavior. Similar kinds of base-addition reactions have been carried out with a variety of bases including $(\text{CH}_3\text{O})_3\text{P}$, $(\text{C}_2\text{H}_5)_3\text{N}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_5\text{H}_5\text{N}$ (or pyridine), $(\text{C}_6\text{H}_5)_3\text{P}$, $(\text{C}_2\text{H}_5)_2\text{O}$, and $\text{C}_2\text{H}_5\text{OH}$. The reactions with $(\text{CH}_3\text{O})_3\text{P}$, $(\text{C}_2\text{H}_5)_3\text{N}$, pyridine, $(\text{C}_6\text{H}_5)_3\text{P}$, and $\text{C}_2\text{H}_5\text{OH}$ are not reversible; in contrast the reaction with diethyl ether is reversible, since the ether can be removed quantitatively from the acid cation by use of the vacuum pump. In many cases base addition may be followed by secondary reactions.

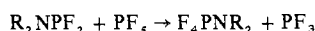
On the basis of the chemical shift values for phosphorus, one would predict that $(\text{CH}_3)_2\text{NPCI}^+$ with a ^{31}P δ value of -325 ppm is more acidic than $[(\text{CH}_3)_2\text{N})_2\text{P}]^+$ with a ^{31}P δ

of -264 ppm. The lower stability of $(\text{CH}_3)_2\text{NPCI}^+$ would appear to be consistent with this view.

Reactions as a Lewis Base. The dicoordinate phosphorus cation will serve as a Lewis base in forming coordination complexes with metal carbonyls. This chemistry will be described in a subsequent publication.

Attempts To Synthesize Cations Containing Fluorine

In an earlier study in this laboratory³ we were not successful in our attempts to synthesize $(\text{R}_2\text{N})_3\text{PP}(\text{NR}_2)\text{F}^+$ from excess $(\text{R}_2\text{N})_2\text{PF}$ and PF_5 . Similarly all recent attempts to prepare $(\text{CH}_3)_2\text{NPF}^+$ from an equimolar mixture of $(\text{CH}_3)_2\text{NPF}_2$ and PF_5 were unsuccessful. The existence of $(\text{CH}_3)_2\text{NPCI}^+$ suggested that the fluoro complex might exist. This was never found. When R_2NPF_2 and PF_5 were condensed together in equimolar amounts at -196°C and then warmed to 25°C , a ligand-exchange process was observed. The equation is



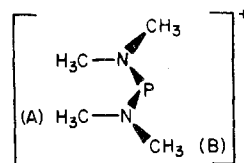
While an unstable ionic structure containing fluoride in the cation might have been formed as an intermediate in the process, no direct evidence comparable to that given for R_2NPCI^+ could ever be obtained for a cation containing fluorine.¹⁶

By using procedures which rationalized the ^{31}P chemical shift values for $(\text{CH}_3)_2\text{N}_2\text{P}^+$ and $(\text{CH}_3)_2\text{NPCI}^+$, it is possible to estimate that F_2P^+ should have a chemical shift of about -150 ppm and R_2NPF^+ should have a chemical shift near -200 ppm. No evidence for absorption in these regions was ever found. Adding PF_3 to the reaction system at pressures of 15 atm did *not* promote formation of the fluoro cation.

Discussion

It is well-known that AlCl_3 can act as a Lewis acid to receive a chloride ion from a species such as XCl . Thus it is not unprecedented that AlCl_3 would react with chloro(di-methylamido)phosphorus(III) ligands to give compounds containing the AlCl_4^- anion. The really unexpected feature was that chloride transfer took place in preference to coordination of AlCl_3 to either the phosphorus or nitrogen site in the ligand. It was also significant that no evidence for PCl_2^+ or PF_2^+ was ever obtained and that the mixed compound R_2NPCI^+ was identified but the corresponding mixed fluoro cation, R_2NPF^+ , was *not* obtained. These facts raise questions of bonding and structure which are of some importance in the broader area of phosphorus-nitrogen chemistry.

Structural information on all cations is provided by NMR data. The low-temperature, -35°C , ^1H NMR spectrum for $(\text{CH}_3)_2\text{N}_2\text{P}^+$ indicates two kinds of methyl groups—a fact which is consistent with an almost planar structure¹⁷ analogous to the known structure of the dicoordinate cation of Dimroth⁶ and co-workers. If we use this analogy, the low-temperature structure for the ion of this study is best represented as



All carbon, nitrogen, and phosphorus atoms are assumed to be planar. The protons of the methyl groups pointing "inside" [labeled A] give an ^1H NMR signal at δ 1.97 (vs. CH_2Cl_2) and $J = 4.8$ Hz while those pointing "outside" [labeled B] give a signal at δ 2.13 (CH_2Cl_2) and $J = 14.1$ Hz.

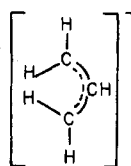
If the electron pair on the phosphorus atom is stereochemically active, the phosphorus will be hybridized as sp^2 with an unused p orbital perpendicular to the plane of the NPN unit. Such an orbital has the proper symmetry to combine

Table V. Net Atomic Charges Calculated^a for Atoms in ((CH₃)₂N)₂P⁺ by Extended Hückel MO Procedures²³

Atom	Net charge	Atom	Net charge
P	0.182+	H atoms of	0.000 to 0.095+
N ₁	0.025-	inner CH ₃	
N ₂	0.025-	(groups A)	
C _{1A}	0.133+	H atoms of	0.020+ to 0.022+
C _{2B}	0.098+	outer CH ₃	
C _{1B}	0.148+	(groups B)	
C _{2B}	0.145+		

^a Geometric parameters used in calculation: NPN = 120°, PNC = 120°, NCH = 109° 28', PN = 1.63 Å, CN = 1.47 Å, CH = 107 Å.

with the available p orbitals on the nitrogen atoms (also sp² hybridized) to give 3π orbitals comparable to those of the allyl anion



The positive charge on the phosphorus atom should contract the p level of phosphorus and make it more effective in the formation of a π system. Three π-energy levels are expected.¹⁸

The cation also has some resemblance to the carbenes of form XYZ except that P⁺ replaces the central carbon. As is well-known, carbenes¹⁹ are stabilized best when X and Y are atoms or groups which can serve as π-electron donors to the carbon. Thus NR₂ and OR groups are frequently found in carbenes. This fact suggests that the phosphorus cation, like the carbene, is stabilized by π bonding back to the empty p orbital on the central atom.²⁰ It is noteworthy that the phosphorus cation, unlike the carbene, can exist as a discrete unit. Like carbenes, the ligand (R₂N)₂P⁺ can form organometallic complexes.

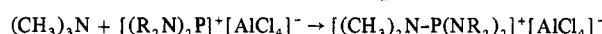
A somewhat more sophisticated theoretical analysis of the cationic system was carried out using an extended Hückel program.²¹ Planar geometry for the C-N-P-N-C system was assumed and the 42 valence electrons in the cation were considered. The lowest unoccupied molecular orbital in this calculation was an N-P-N antibonding one at -9.688 eV. The highest occupied orbital was nonbonding and arose largely from the two nitrogen p_x orbitals. It had an energy of -11.759 eV. An orbital at -12.185 eV had electron density essentially on the carbons. One at -13.277 eV contained the nonbonded electron pair on phosphorus, and a level at -13.969 eV was the bonding N-P-N π orbital. Thus orbitals at -9.688 eV (antibonding), at -11.759 eV (nonbonding), and at -13.969 eV (bonding) would represent the π system alluded to earlier in the simple calculation. Atomic charges estimated from the calculation are shown in Table V.

Chemical shift values for ³¹P and ¹H NMR are of interest in considering experimental implications of electron distri-

bution. The ³¹P and ¹H chemical shift values for various phosphorus(III) ligands, cations, and complexes are shown in Table VI. Several trends are of interest. First as NR₂ groups attached to the phosphorus atom are replaced by more electronegative chlorine atoms in which possible back-bonding is negligible, the phosphorus nucleus becomes less shielded. That is, the shielding of the phosphorus goes down when an NR₂ group is replaced by a Cl while the coordination number remains the same. It is also not unexpected that the shielding of the cation phosphorus goes up when a Lewis base such as (R₂N)₃P coordinates to the (R₂N)₂P⁺ cation and increases the coordination number of the phosphorus. It is interesting to note that both phosphorus atoms in (R₂N)₃PP(NR₂)₂⁺ are more shielded (-53 and -94 ppm) than are the phosphorus atoms in the component parts, (R₂N)₃P (-123 ppm) and (R₂N)₂P⁺ (-264 ppm). This may be correlated with an increase in the coordination number of both central phosphorus atoms (see Figure 1) when the P-P bond is formed.

Comparable trends in shielding are noted for the protons of the methyl groups. When an NR₂ radical attached to a phosphorus atom in (R₂N)₂P⁺ is replaced by a chlorine atom, the protons of the remaining methyl groups become less shielded. Similarly, when ((CH₃)₂N)₃P adds to the cationic ((CH₃)₂N)₂P⁺, the protons of (R₂N)₃P become less shielded (about 0.3 ppm). In a self-consistent manner, the protons of ((CH₃)₂N)₂P⁺ become more shielded (about 0.6 ppm) when (R₂N)₃P coordinates to give the diphosphorus cation. In this case the coordination number of the proton is not changed; hence the deshielding must reflect shifts in electron distribution. The phenomenon appears to be general. When any base is added to ((CH₃)₂N)₂P⁺, the CH₃ groups of the cation become more shielded and the magnitude of the change seems to be related to the degree of the interaction as would be expected. Representative data are shown in Table VII. Those bases giving the most stable, nonreversible complexes also show the largest proton shifts. On the other hand, bases such as diethyl ether, dimethyl sulfide, diethyl sulfide, diethyl ketone, and the polyether CH₃OCH₂CH₂OCH₃, which interact weakly and reversibly under vacuum with ((CH₃)₂N)₂P⁺, had little effect on either the ³¹P or ¹H chemical shift values of the phosphorus cation.²² All did, however, have an effect on the barrier to rotation of the R₂N groups about the N-P bond. This question will be treated later.

In the original report¹ on the synthesis of the AlCl₃ addition products of the (dimethylamido)halophosphorus(III) ligands, it was noted that (CH₃)₃N will displace ((CH₃)₂N)₂PCl from ((CH₃)₂N)₂PCl·AlCl₃. At one point it was assumed that this reaction indicated the coordination of the phosphorus(III) ligand as a unit without decomposition. It is now clear that the process is more complex. The first step is the coordination of the amine base to the cation acid



The second step is a base displacement process. If (CH₃)₃N is a stronger base toward AlCl₃ than is the Cl⁻ ion, Cl⁻ is displaced from the AlCl₄⁻ and returns to the cation while

Table VI. Chemical Shift Values for Some Phosphorus(III) Ligands and Phosphorus(III) Cations

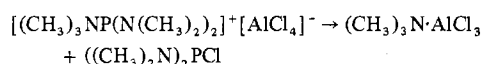
Compd or ion	Chem shifts, ppm					
	³¹ P (rel to H ₃ PO ₄)			¹ H (rel to TMS)		
	2-coord P	3-coord P	4-coord P	2-coord P	3-coord P	4-coord P
((CH ₃) ₂ N) ₃ P		-123			2.9	
((CH ₃) ₂ N) ₂ PCl		-160			2.65	
((CH ₃) ₂ N)PCl ₂		-166			2.45	
PCl ₃		-219				
((CH ₃) ₂ N) ₂ P ⁺	-264			2.01		
((CH ₃) ₂ N)PCl ⁺	-325			1.7		
((CH ₃) ₂ N) ₃ PP(N(CH ₃) ₂) ₂ ⁺		-94	-53		2.59	2.65
((CH ₃) ₂ N) ₃ PPN(CH ₃) ₂ Cl ⁺		-118	-50		2.33	2.46

Table VII. Proton Chemical Shift Values (ppm)^a for Nonreversible Base Adducts of ((CH₃)₂)₂P⁺

Free base	$\delta(^1\text{H})$ of complexed base	$\delta(^1\text{H})$ for CH ₃ protons of cation after complexing	Change in $\delta(^1\text{H})$ for protons of cation on complexing
(CH ₃ O) ₃ P	1.74	2.6 ($J = 11.5$ Hz)	+0.5 ($\Delta J = 1.7$ Hz)
((CH ₃) ₂ N) ₃ P ^b	2.65	2.65	+0.6
(CH ₃ CH ₂) ₃ N	2.22 (CH ₂) 2.6 (CH ₃)	2.67 ($J = 11.5$ Hz)	+0.6 ($\Delta J = 1.7$ Hz)
Pyridine	-2.47 -2.1	2.67 ($J = 12$ Hz)	+0.6 ($\Delta J = 2.2$ Hz)
(C ₂ H ₅) ₃ P	-2.23	2.38 ($J = 11.4$ Hz)	+0.3 ($\Delta J = 1.6$ Hz)
CH ₃ CH ₂ OH	4.18 (CH ₃) 2.63 (H)	2.67 ($J = 11.0$ Hz)	+0.6 ($\Delta J = 1.2$ Hz)

^a Values given are for the H₃C- protons in the room-temperature spectrum of the [base→((CH₃)₂N)₂P]⁺ cation. The ¹H δ of the free cation, ((CH₃)₂N)₂P⁺, is 2.07; $J_{\text{PNCH}} = 9.8$ Hz. ^b For ((CH₃)₂N)₃P the ¹H δ of the free base is 2.9; the change on complexing is 2.65 - 2.9 or -0.25 ppm.

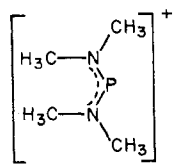
(CH₃)₃N·AlCl₃ forms. The equation is



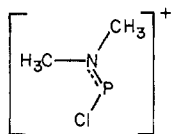
If (CH₃)₃N is not a particularly strong base toward the acid of the anion, the diadduct remains stable. The argument is illustrated by the fact that if PF₆⁻ is the anion, the adduct [(CH₃)₃NP(N(CH₃)₂)₂]⁺[PF₆]⁻ is stable. This observation can be associated with the relatively low stability of (C-H₃)₃N·PF₅ as opposed to PF₆⁻. Steric details also appear to be important. Triethylamine, (H₃CCH₂)₃N, in contrast to trimethylamine, adds to the AlCl₄⁻ salt to give a stable cation which does not break down to give ((CH₃)₂N)₂PCl even after heating to 100 °C. The (CH₃)₃N·AlCl₃ adduct would be more stable for steric (and electronic) reasons than (CH₃CH₂)₃N·AlCl₃.

A final point of interest is our failure to prepare a cation with fluorine rather than chlorine atoms coordinated to the central phosphorus atom. No cations such as (CH₃)₂NPF⁺ or ((CH₃)₂N)₃PP(N(CH₃)₂)F⁺ were ever isolated. This observation was quite unexpected since fluorine is more effective in back-donation of electrons to phosphorus than is chlorine (the ³¹P δ for PCl₃ is -219; for PF₃, -97) and such back-donation appears to be a major factor in stabilizing the dicoordinate phosphorus cation. Two factors may be important in rationalization of this anomaly. First, the dicoordinate species containing chloride in the cation was obtained only when liquid PCl₃ was used as a solvent. Because PF₃ was not a liquid under the temperature and pressure used in synthesis, the activity of PF₃ could never be made comparable to that of PCl₃. Second it is possible that the existence of R₂NPCl⁺ and not R₂NPF⁺ reflects relative rates of decomposition of the two ions since it is known that [R₂NPCl]⁺[AlCl₄]⁻ does go spontaneously and slowly to PCl₃ and a salt of (R₂N)₂P⁺. Under this situation thermodynamic factors and bond strength may be a secondary question. Kinetics would dominate.

Another anomaly which may be tied up with exchange rates is the observation that the methyl groups in



may be differentiated by NMR into two types, inner and outer. Yet comparable differentiation in the related cation



was not achieved even though a double bond between N and P in the latter compound would be expected.²³ This fact may be related to rapid exchange of Cl⁻ groups in the solution through bridging with AlCl₄⁻ or other Cl⁻ donors rather than to anomalies in the P-N bond. The strongly deshielded phosphorus atom ($\delta(^{31}\text{P}) - 325$) should interact strongly with chloride ions in the system to give facile exchange.

Experimental Section

General Techniques. Standard high-vacuum techniques were used in the preparation and handling of compounds investigated. Valves and joints were greased with Apiezon N or M. Solids and nonvolatile liquids were handled in a glovebox under dry N₂. Infrared spectra were taken with a Beckman IR-12 or IR-20. A gas cell (10-cm path) was used with KBr windows. Liquids were studied as liquid films or as CH₂Cl₂ solutions. Solids were examined in Nujol mulls or KBr pellets. The NMR spectrometers used included a Varian Associates 56/60A, an XL-100-12, and an XL-100-15. Chemical shifts for ³¹P were measured by tube interchange using H₃PO₄ as a standard. Internal standards were used for ¹⁹F (CFCl₃ reference). Internal standards CH₂Cl₂ and Si(CH₃)₄ were also used for protons. Procedures for conductivity measurements were described elsewhere.¹

Materials. Compounds used were prepared using procedures which have been described elsewhere.^{1,4,9,11} In all cases resublimed AlCl₃ was used and the dicoordinate cation was prepared taking care to exclude moisture or air.

Procedures. In carrying out reactions of Lewis bases with the dicoordinate phosphorus cation, NMR tubes were used as reaction vessels. In each case, approximately 2 mmol of the Lewis base was transferred in a glovebag to an NMR tube containing an equimolar amount of a CH₂Cl₂ solution of the (R₂N)₂P⁺ salt. The tubes were capped and allowed to stand at room temperature for 8 h. The ¹H NMR spectra were then recorded. The tubes were then connected to the vacuum line via a connecting apparatus of Tygon tubing fastened to a 10/30 ground-glass joint. Volatiles were removed by distillation. Ether could be removed quantitatively but other bases could not be removed in this way. Each of the 1:1 adducts were white solids at room temperature.

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Registry No. ((CH₃)₂N)₂P·AlCl₃, 60607-14-9; (CH₃)₂NP·Cl₂·AlCl₃, 60594-92-5; [(CH₃)₂N]₂P⁺[PF₆]⁻, 52653-69-7; [(CH₃)₂N]₂P⁺[B₂F₇]⁻, 61788-02-1; [(CH₃)₂N]₂P⁺[GaCl₄]⁻, 61788-03-2; [(CH₃)₂NPCl]⁺[GaCl₄]⁻, 61788-05-4; [(CH₃)₂N]₂P⁺[FeCl₄]⁻, 61788-06-5; AlCl₃, 7446-70-0; ((CH₃)₂N)₂P·Cl, 3348-44-5; [Me₄N][AlCl₄], 21481-78-7; ((CH₃)₂N)₃P, 1608-26-0; ((CH₃)₂N)P·Cl₂, 683-85-2; ((CH₃)₂N)P·Cl₃, 19049-19-5; ((CH₃)₂N)₃PP(N(CH₃)₂)₂⁺, 60594-82-3; ((CH₃)₂N)₃PP(N(CH₃)₂)₂Cl⁺, 60594-84-5; [(CH₃O)₃P]((CH₃)₂N)₂P⁺, 61770-32-9; [(CH₃CH₂)₃N]((CH₃)₂N)₂P⁺, 61770-33-0; [py((CH₃)₂N)₂P]⁺, 61770-34-1; [(C₂H₅)₃P]((CH₃)₂N)₂P⁺, 61770-35-2; [(CH₃CH₂OH)((CH₃)₂N)₂P]⁺, 61770-36-3.

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- (7) AlCl_3 itself might be expected to give a weak interaction with the solvent through a process such as $\text{CH}_2\text{Cl}_2 + \text{AlCl}_3 \rightleftharpoons \text{CH}_2\text{Cl}^+ + \text{AlCl}_4^-$. Also AlCl_3 is very hygroscopic and the measurements are very sensitive to traces of water.
- (8) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon Press, London, 1966, pp 263, 951. (b) Measurements indicated that best conversions under our conditions were obtained by using δ (for CH_2Cl_2) -5.28 relative to TMS.
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- (17) Because of the nonbonding electron pair on the nitrogen atom, one of the NR_2 groups would be expected to deviate from planar geometry at any one instant. A dynamic structure is visualized in which both NR_2 groups are equivalent.
- (18) Simple applications of Hückel MO theory to the cation give a bonding orbital, $\alpha + [(\lambda^2 + 8)^{1/2}/2]\beta$, the nonbonding orbital on the nitrogen atom, and the antibonding orbital, $\alpha - [(\lambda^2 + 8)^{1/2}/2]\beta$. In these expressions α is the Coulomb integral on the nitrogen atom and β is the resonance integral involving the 2p orbitals of nitrogen and the 3p orbitals of P^+ . ($\alpha - \lambda\beta$) is the Coulomb integral of the phosphorus ion.
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- (22) Reactions between Lewis bases and the $((\text{CH}_3)_2\text{N})_2\text{P}^+$ cation appear to be fundamental to many chemical processes such as the reaction of $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ with diisopropyl ether which was described earlier.¹ A more detailed analysis of this and related processes is in preparation.
- (23) The P-N bond in R_2NPCI^+ should have a high degree of double-bond character because of electron withdrawal by the chlorine and the lack of competition between NR_2 and Cl for the p orbital on the phosphorus atom.

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Characterization of Mixed Oxidation State Poly(chlorotitanium) Anions

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Treatment of tris(triphenylphosphine)platinum(0), $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}$, with titanium tetrachloride, TiCl_4 , affords species with the composition $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}[\text{TiCl}_4]_{3,5}$. The latter have been examined by ^{31}P NMR, photoelectron, and ESR spectroscopy, and their magnetic susceptibilities have been measured. For both species the cation $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{PtCl}^+$ has been identified. The anions are suggested to consist of poly(titanium chloride) species containing titanium in the III and IV oxidation states, $\text{Ti}_3\text{Cl}_{11}^-$ and $\text{Ti}_3\text{Cl}_{19}^-$.

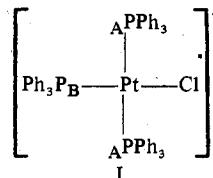
Introduction

We have recently reported the preparations, conductivities, infrared spectra, and several chemical reactions for $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Pt}(\text{TiCl}_4)_n$, where $n = 3$ and 5, I and II, respectively.² The suggested geometries for I and II involved insertion of TiCl_4 into the Pt-P bond affording formally Pt(0) complexes. Development of the chemistry of I included treatment with acetonitrile, CH_3CN , and unexpectedly afforded $\text{TiCl}_3(\text{CH}_3\text{CN})_3$.^{3,4} The isolation of a Ti(III) derivative from I, under reaction conditions where TiCl_4 is not reduced by CH_3CN , prompted further studies of I and II with regard to specifying the oxidation state for Ti and Pt. These studies have included ^{31}P NMR, ESCA (Pt, Cl, Ti), and hydrolysis of various mixtures of $\alpha\text{-TiCl}_3$ with Pt(II) and Pt(0) complexes and $(\text{C}_6\text{H}_5)_3\text{P}$. The latter were carried out because base hydrolysis of I and II did not afford H_2 which was interpreted to indicate the absence of Ti(III) associated with either I or II. It has now been established that both I and II contain Ti(III) and Pt(II) and that, during basic hydrolysis, oxidation of Ti(III) takes place but without quantitative H_2 evolution.^{3,4}

Results and Discussion

^{31}P Studies. The ^{31}P NMR spectrum of I in CH_2Cl_2 is shown in Figure 1 and the data are summarized in Table I utilizing both CH_2Cl_2 and *o*-dichlorobenzene (ODCB) as solvents. The spectrum of I consists of two main signals, a

triplet and doublet, and each signal has its satellite doublet due to $^{195}\text{Pt}\text{-}^{31}\text{P}$ coupling (^{195}Pt in 33.7% natural abundance, $I = 1/2$).



For this geometry there are two sets of phosphorus atoms, one consisting of two chemically and magnetically equivalent phosphorus atoms designated as A while the other set is a single phosphorus designated as B. The resonance signal of P_B is split by two P_A 's into a triplet of 1:2:1 intensities with $^2J_{\text{P}_A\text{-P}_B} = 19$ Hz. This triplet is flanked by a pair of small triplets due to coupling with ^{195}Pt , $^1J_{^{195}\text{Pt}\text{-P}_B} = 3628 \pm 4$ Hz. The resonance signal of P_A is split by a single P_B into a doublet with $^2J_{\text{P}_A\text{-P}_B} = 19$ Hz and also flanked by a pair of small doublets due to coupling with ^{195}Pt , $^1J_{^{195}\text{Pt}\text{-P}_A} = 2486 \pm 4$ Hz. The relative area of resonance signals of P_A to that of P_B is in good agreement with the calculated value, 2:1. The assignment of the oxidation state of platinum, in I, as Pt(II) is supported by the data in Table II where $^1J_{\text{Pt-P}}$ values are shown to be strongly dependent on the oxidation state of Pt. The