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COMPLEXES OF $[(CH_3)_2N]_{3-n}PCl_n$ WITH $AlCl_3$ - THEIR REACTIONS AND EXISTENCE AS INTERMEDIATES IN LIGAND DISPROPORTIONATION PROCESSES

by
Richard Wilhelm Kopp

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ABSTRACT

COMPLEXES OF $[(CH_3)_2N]_{3-n}PCl_n$ WITH $AlCl_3$ - THEIR REACTIONS AND EXISTENCE AS INTERMEDIATES IN LIGAND DISPROPORTIONATION PROCESSES

by Richard Wilhelm Kopp

Considerable evidence exists in the recent literature to suggest that compounds containing both nitrogen and phosphorus (in the +3 oxidation state) may coordinate through either the nitrogen or the phosphorus, with the choice dependent upon the reference Lewis acid. The observed choice may be rationalized in terms of several models.

This study was initiated to observe the interaction of $AlCl_3$ on ligands of the form $[(CH_3)_2N]_{3-n}PX_n$ where X is either Cl or F and n ranges from 0 to 2. The reaction path by which the final products were formed and the bonding site in each of the adducts observed were ascertained.

Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, was known, at the outset of this study, to form $(CH_3)_2NPCl_2$ and PF_3 when mixed with $AlCl_3$.

The following reactions have been definitely established.

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \rightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + PCl_3$$

$$(CH_3)_2NPCl_2 + AlCl_3 \xrightarrow[-20^\circ C]{PCl_3} (CH_3)_2NPCl_2\cdot AlCl_3$$

$$2\ [(CH_3)_2N]_2PCl + AlCl_3 \rightarrow \{[(CH_3)_2N]_2PCl\}_2\cdot AlCl_3$$

$$[(CH_3)_2N]_2PCl\cdot AlCl_3 + [(CH_3)_2N]_3P \rightarrow [(CH_3)_2N]_3P\cdot[(CH_3)_2N]_2PCl\cdot AlCl_3$$

$$\{[(CH_3)_2N]_2PCl\}_2\cdot AlCl_3 + PCl_3 \rightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + 2\,(CH_3)_2NPCl_2$$

$$[(CH_3)_2N]_3P + AlCl_3 \rightarrow [(CH_3)_2N]_3P\cdot AlCl_3$$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_2NPCl_2 \rightarrow \{[(CH_3)_2N]_2PCl\}_2\cdot AlCl_3$$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + [(CH_3)_2N]_2PCl \rightarrow [(CH_3)_2N]_3P\cdot[(CH_3)_2N]_2PCl\cdot AlCl_3$$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + PCl_3 \rightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

In addition, in an attempt to form $(CH_3)_2NPCl_2\cdot AlCl_3$ by displacement of a base from its $AlCl_3$ adduct by $(CH_3)_2NPCl_2$, this phosphorus ligand was mixed with $(C_2H_5)_2O\cdot AlCl_3$. Only a small portion of the ether was displaced. With $[(CH_3)_2CH]_2O\cdot AlCl_3$ more $(CH_3)_2NPCl_2$ was taken up, but a large amount of isopropyl chloride, $(CH_3)_2CHCl$, was evolved. In general, for the series $[(CH_3)_2N]_{3-n}PCl_n$, where n = 2, 1 or 0, the following reaction may be written:

$$[(CH_3)_2N]_{3-n}PCl_n + [(CH_3)_2CH]_2O\cdot AlCl_3 \rightarrow (CH_3)_2CHCl + [(CH_3)_2N]_{3-n}PCl_{n-1}[OCH(CH_3)_2]\cdot AlCl_3$$

With $[(CH_3)_2N]_3P$, a simple base displacement reaction takes place.

All of the above reactions can be understood in terms of the formation of a five coordinate aluminum species. The disproportionation reaction involving $(CH_3)_2NPCl_2$ and

$AlCl_3$ can be considered to involve first the formation of the unstable double adduct $[(CH_3)_2NPCl_2]_2 \cdot AlCl_3$ followed by an exchange of groups between the phosphorus ligands and the loss of PCl_3. With $(CH_3)_2NPF_2$ the same type of unstable intermediate, $[(CH_3)_2NPF_2]_2 \cdot AlCl_3$, is proposed, but here either a disproportionation or a halogen exchange reaction may take place. Both are seen to occur. The ether reactions may be viewed as involving the initial formation of $[(CH_3)_2N]_{3-n}PCl_n \cdot [(CH_3)_2CH]_2O \cdot AlCl_3$.

Bonding in all of the adducts appears to be through the phosphorus. Chemical evidence, infrared and n.m.r. data are all generally consistent with P-Al bonding. There is no evidence to suggest N-Al bonding.

$(CH_3)_3N$ has been found to displace $[(CH_3)_2N]_3P$ from its $AlCl_3$ adduct. This is in contrast to the lack of displacement of $[(CH_3)_2N]_3P$ from BH_3 by this amine, indicating that in this case BH_3 is the stronger Lewis acid.

It has also been observed that $[(CH_3)_2N]_2PCl$ can be displaced from its BH_3 adduct by $(CH_3)_3N$. Since it is known that $[(CH_3)_2N]_2PF$ cannot be displaced in this way, the monofluoro ligand is seen to be the stronger Lewis base toward BH_3.

Relative base strengths toward $AlCl_3$ within the series $[(CH_3)_2N]_{3-n}PCl_n$ are:

$$PCl_3 < (CH_3)_2NPCl_2 < [(CH_3)_2N]_3P < [(CH_3)_2N]_2PCl$$

The decreased base strength of $[(CH_3)_2N]_3P$ compared to $[(CH_3)_2N]_2PCl$ may be explained in terms of steric factors or a decrease in P-N π bonding in trisdimethylaminophosphine.

To

My Wife, Beth,

Our Mothers,

and to

the Memory of Our Fathers

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The encouragement of Professor R. W. Parry was essential to the successful completion of this work. His insight and knowledge of inorganic chemistry provided a firm basis for the guidance which he so generously gave. I am deeply indebted to him.

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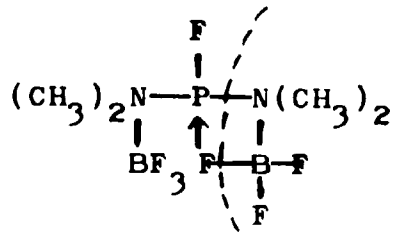
INTRODUCTION

Compounds containing both nitrogen and phosphorus (in the +3 oxidation state) are of interest in that either the nitrogen or the phosphorus can act as a potential donor toward Lewis acids. Depending upon the acid in question, either the nitrogen or the phosphorus may coordinate. As will be discussed further below, one notes that when bonding is through the nitrogen, the resulting adduct is relatively unstable with respect to simple dissociation or disproportionation.

For example, both $(CH_3)_2NPF_2$ (1) and $(CH_3)_2NPCl_2$ (2) form 1:1 adducts with BF_3. Both adducts form reversibly at low temperatures, but readily dissociate as the temperature is raised. Infrared and n.m.r. evidence suggest, although not conclusively, that in $(CH_3)_2NPF_2 \cdot BF_3$ at least, bonding is through the nitrogen. When $[(CH_3)_2N]_2PF$ is allowed to react with BF_3 (1), no simple adduct is formed, but rather one obtains $(CH_3)_2NBF_2$, which is formed in the reaction:

$$[(CH_3)_2N]_2PF + 2\ BF_3 \longrightarrow (CH_3)_2NPF_2 \cdot BF_3 + (CH_3)_2NBF_2$$

Sr. Mary Albert Fleming (1) postulated that this reaction can be pictured as involving first the formation of an unstable 1:2 adduct through the nitrogens of the aminophosphine, followed by transfer of one of the boron fluorides and a splitting off of the aminoborane:



Possibly, two BF_3 molecules attached to a single aminophosphine, as shown, provide sufficient steric strain on the adduct to cause this reaction to proceed.

Holmes and Wagner (3) have also observed reactions of this type. Reactions of BF_3, BCl_3 and $B(CH_3)_3$ on the series of compounds $[(CH_3)_2N]_{3-x}P(CH_3)_x$ (where x = 0, 1, and 2) resulted in reactions of the form:

$$[(CH_3)_2N]_{3-x}P(CH_3)_x + (3-x)\ BY_3 \longrightarrow (3-x)\ (CH_3)_2NBY_2 + (CH_3)_xPY_{3-x}$$

(where Y = $-CH_3$, F, or Cl)

In general the reactions were complex, with varied side and competing reactions. Although the authors state that there is insufficient data to predict the initial point of attack of the acid, they do suggest that it might very well be through the nitrogen.

Using a deficiency of the acid and xylene as a solvent, Nöth and Vetter (4) found that the reaction of BF_3 with $[(CH_3)_2N]_3P$ could be controlled to give the partially fluorinated phosphine:

$$[(CH_3)_2N]_3P + 2\ BF_3 \longrightarrow (CH_3)_2NPF_2 + 2\ (CH_3)_2NBF_2$$

They, too, believe that here the initial attack is through the nitrogen.

$(CH_3)_2NP(CH_3)_2$ appears to be an intermediate case in that it apparently may bond to $Al(C_2H_5)_3$ via either the phosphorus or the nitrogen. Recent n.m.r. studies (5) of the adduct $(CH_3)_2NP(CH_3)_2 \cdot Al(C_2H_5)_3$ suggest that when directly combined, the adduct formed involves bonding primarily through the phosphorus. Heating the adduct, however, appears to convert most of it to an adduct containing a nitrogen-aluminum bond.

In all other addition compounds of aminophosphines, coordination appears to occur through the phosphorus. Sr. Fleming (1) has shown, conclusively, by infrared and n.m.r. studies, that $(CH_3)_2NPF_2 \cdot BH_3$, $(CH_3)_2NPF_2 \cdot B_3H_7$, and $[(CH_3)_2N]_2PF \cdot BH_3$ are all bonded through the phosphorus atom. An x-ray study by Douglas and Nordman (6) has shown that $(CH_3)_2NPF_2 \cdot B_4H_8$ also contains a P-B bond. Nordman (7) also showed from a single crystal x-ray study that $(H_2N)_3P \cdot BH_3$ contains a P-B bond.

The BH_3 adducts of $[(CH_3)_2N]_3P$, $[(CH_3)_2N]_2PH$, $[(CH_3)_2N]_2PCl$, $[(CH_3)_2N]_2PBu$, and $(CH_3)_2NPBu_2$ have been prepared by Nöth and Vetter (4). They believe that all of the adducts involve a P-B bond since: (1.) with all of the ligands, only 1:1 adducts are obtained, and (2.) infrared absorptions generally attributable to the P-B bond are found in the spectra of all of the adducts, whereas absorptions indicating a B-N bond are absent.

Reetz and Katlafsky (8) note that the infrared spectra of $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]_3P{\cdot}BH_3$ are very nearly the same, indicating that the symmetry of the phosphine has been retained. This could only be so if the single BH_3 group were bonded to the phosphorus.

Schmutzler (9) has prepared the compounds $Ni(CO)_2L_2$, NiL_4, and $Mo(CO_3)L_3$ (where L = $(CH_3)_2NPF_2$, $(C_2H_5)_2NPF_2$, or $C_5H_{10}NPF_2$, [C_5H_{10} · piperidyl]). Infrared evidence strongly suggests that bonding to the metal in all of the compounds is through the phosphorus.

The recent x-ray study by Morris and Nordman (10) on $(CH_3)_2NPF_2$, and the physical and chemical evidence by Van Doorne (2) on this and other aminohalophosphines indicate that the nitrogen in these compounds is in an essentially planar environment, whereas the bonds around the phosphorus are essentially tetrahedral. This must mean that the lone pair of electrons on the nitrogen is at least partially shared with the phosphorus. The availability of this pair of electrons for bonding to Lewis acids will thus be reduced sharply. A low bonding capability of the nitrogen will probably be true for both the chloro- and bromo-derivatives as well (11). The resulting partial positive charge on the nitrogen and enhanced electron density on the phosphorus would certainly make the phosphorus the more attractive site for attack by a Lewis acid. While this would lessen the probability of nitrogen bonding, it certainly does not rule it out. In fact, as we have seen,

certain acids do seem to prefer this site. Therefore, it will be assumed in the discussion which follows that both the nitrogen and the phosphorus are potentially capable of coordinating with Lewis acids.

Factors which affect the choice of bonding site, and the strength of the resulting linkage have been reviewed by Parry and Keller (12) and have been specifically applied to reactions such as those mentioned above by Sr. Fleming (1) and Alton (13). Essentially one may discuss the bonding in terms of a polarized ion-dipole model. A relatively large ligand with a diffuse, easily polarized electron cloud will tend to bond more strongly to an ion of high field strength which can distort this cloud. This implies an interaction at relatively short distances since the field strength falls off rapidly with increasing distance from the nucleus. Thus the distance between acid and base is a very important factor in determining the strength of a bond involving large, easily polarized ligands.

On the other hand, a ligand containing a small donor atom or ion with a more localized electron cloud would not require an acceptor species of such high field strength, since less distortion of the cloud is necessary for stable bonding. For species of this type, distance between ligand and cation is less critical.

Comparing phosphorus to nitrogen, the relatively large, diffuse electron cloud of the phosphorus would require an

acid of high field strength to form a stable bond. The bond strength would be strongly dependent on distance between acid and base. On the other hand, acids of low field strength, or those which cannot approach sufficiently close to significantly distort the phosphorus, may still bond via the more localized, less distance dependent electron cloud of the nitrogen.

Boron, a small atom with a nuclear charge of +3, would be expected to exhibit a high field strength. But it is not the boron ion or atom alone that is reacting, but rather various compounds of boron. As we have seen, BH_3, B_3H_7, and B_4H_8 bond to the phosphorus, while BF_3, BCl_3, and $B(CH_3)_3$ seem to prefer the nitrogen. From our discussion, bonding to phosphorus implies a high field at a short distance. For the boron of a BX_3 unit to approach the phosphorus closely, it is necessary for that unit to distort from its normal planar arrangement toward a tetrahedral pattern. The closer the approach, the more the distortion required.

Using pertinent data for BH_3, BF_3, BH_4^-, and BF_4^-, namely the B-X stretching force constants, the internuclear distances, and the B-X dissociation energies, Alton (13) constructed potential energy curves for B-H and B-F interactions. He concluded that the distortion energy for BF_3 was about three times that of BH_3. Thus the relative ease of distortion allows the BH_3 unit to approach the phosphorus closely, forming a stable bond. That BH_3 exists as the dimer B_2H_6 in which the borons are in an

essentially tetrahedral environment attests to this low energy. In the B_3H_7 and B_4H_8 units, the boron which acts as the bonding site is, by the geometry of the isolated unit, significantly distorted toward the tetrahedral arrangement. Thus again a close approach is possible and bonding to phosphorus takes place.

Along with BF_3, both BCl_3 and $B(CH_3)_3$ would be expected to have high distortion energies due to both electrostatic and steric factors. The fact that all three exist as monomers, showing no tendency to dimerize, is evidence of this. Thus the energy required to sufficiently distort these molecules is not compensated for in the coordination process and no stable bonding occurs. Since nitrogen bonding is not as distance dependent, less distortion of the BX_3 molecules is necessary and a stable bond can result. Such bonds would, however, not be expected to be very strong, since the interactions would necessarily be at relatively long distances. This low stability has been noted previously.

When considering similar compounds containing only phosphorus or nitrogen - not both - one again sees the above principles illustrated. Using BH_3 as the reference acid, Graham and Stone (14) found that $(CH_3)_3P$ was a stronger base than $(CH_3)_3N$. However with BF_3, $(CH_3)_3N$ proved the stronger base, as expected. In addition, they found that trimethylamine is the stronger base with $(CH_3)_3B$ and $(CH_3)_3Al$.

Since $(CH_3)_3Al$ is an intermediate case, it is worthwhile to consider the factors involved in its coordination. In that $(CH_3)_3Al$ exists as the dimer $(CH_3)_6Al_2$, one predicts a low distortion energy. This would favor bonding to phosphorus over nitrogen. However, opposing this is the lower field strength of the aluminum, compared to boron, due to the larger size of the aluminum. The electron donating methyl groups on the aluminum would be expected to lower this field strength even more. These latter factors favor nitrogen bonding. Since preferential bonding to nitrogen is reported, the data suggest that these factors must predominate.

The trimethylamine-trimethylphosphine comparison has not been made with $AlCl_3$. This acid also is a normal dimer, Al_2Cl_6, indicating a low distortion energy. The field strength of this species, rather than being lowered by electron donating groups, would be enhanced somewhat by the electron attracting chlorines. Whether this would sufficiently enhance the field strength to permit preferential bonding to phosphorus over nitrogen will have to be experimentally demonstrated.

The compounds in the present study do not have methyl groups on the phosphorus, but rather halogens. The adducts of trihalophosphines have been studied and discussed in the literature in some detail (15). In terms of a naive model, the very electronegative fluorines attached to PF_3 would be expected to make this compound a relatively weak base,

if in fact it were basic at all. However, with respect to some species at least, it coordinates quite strongly. $Pt(PF_3)_2Cl_2$, for example, is stable up to about 200°C (16). Chatt rationalized this stability by suggesting that the d orbital electrons of the transition metal could interact with the empty, but available, d orbitals of the phosphorus in a "dative double bond," greatly supplementing the weak σ bond between the two atoms. This would suggest that for species with no available d electrons, PF_3 should not form stable adducts. Formation of $F_3P{\cdot}BH_3$ by Parry and Bissot (17), however, refutes this. Graham and Stone (14) rationalized the stability of this adduct by assuming a kind of inorganic hyperconjugation wherein the electrons of the B-H bonds can delocalize to provide the necessary electron density to form a stable bond. The fact that $F_3P{\cdot}BF_3$ has not been prepared and apparently is very unstable can be interpreted in terms of the Graham-Stone model, since one would not expect delocalization of the boron-halogen bonding electrons. However, $F_3P{\cdot}AlCl_3$ has been prepared by Alton (13). The stability of this addition compound cannot be adequately explained by $d\pi$-$d\pi$ interaction since Al has no d electrons, nor does delocalization of aluminum-chlorine bonding electrons seem probable.

Again using our ion-dipole model, the relative stabilities of the complexes mentioned above can be explained without the necessary use of either $d\pi$-$d\pi$ interactions or hyperconjugation effects. The easy distort-

ability of the BH_3 unit, coupled with the high field strength of the B^{+3} in the tetrahedral pattern, results in the formation of a short, weak bond with PF_3. One need only assume here that the lone pair electrons of the phosphorus are available to at least a small extent, a fact about which Chatt had some doubt. On the other hand, the rigidity of the BF_3 prevents its close approach to the phosphorus and no adduct is formed. Since $AlCl_3$, which one would predict to be an intermediate case, is found to coordinate with PF_3, one must say that its lower field strength - due to its larger size - is compensated by its ability to assume a tetrahedral configuration easily without a large expenditure of energy, as suggested by its existance as a dimer. An alternative to the Chatt d electron model for coordination of PF_3 to Pt^{+2} is provided by assuming the availability of the electrons of the phosphorus in the presence of the known high field strength of the Pt^{+2}.

Contrary to the simple inductive effect arguments, PCl_3 is found to be a weaker Lewis acid than PF_3. Presumably this is due to the larger size of the chlorines and thus the increased difficulty in moving a Lewis acid in close to the phosphorus for bond formation. The adduct $Cl_3P{\cdot}BF_3$, reported by Baumgarten and Bruns (18), has been shown by Holmes (19) to be $Cl_3PO{\cdot}BF_3$. $Cl_3P{\cdot}BH_3$ has never been prepared. At best, only a weak interaction has been detected between PCl_3 and $AlCl_3$ (13).

In studies of the BH_3 adducts of the series $[(CH_3)_2N]_{3-n}PH_n$ and $[(CH_3)_2N]_{3-n}PCl_n$, Nöth and Vetter (4) state that, in both cases, the stability of the adducts increase with increasing number of dimethylamino groups, as would be expected from inductive effect arguments. The electron donating tendency of the dimethylamine group would enhance the availability of the lone pair electrons on the phosphorus. $H_3P{\cdot}BH_3$ is considerably dissociated at room temperature and $Cl_3P{\cdot}BH_3$ is unknown. $[(CH_3)_2N]_3P{\cdot}BH_3$, on the other hand, is thermally stable up to at least 200°C. Intermediate behavior appears to be shown by the intermediate members of both series in that they decompose, at varying rates, at room temperature. It should be noted, however, that this decomposition is not simple dissociation, but rather a hydrogen shift reaction, evolving dimethylamine. Thus no direct evidence of the strength of the phosphorus-boron linkage is obtained. Nöth and Vetter found that $(CH_3)_2NPH_2{\cdot}BH_3$ was too unstable to isolate, and $(CH_3)_2NPCl_2{\cdot}BH_3$ was explosive, but $[(CH_3)_2N]_2PH{\cdot}BH_3$ could be distilled at 46-47°C at 0.1 mm, and $[(CH_3)_2N]_2PCl{\cdot}BH_3$ could be distilled at 52°C at 0.4 mm, both presumably without dissociation. Thus these latter two adducts do in fact exhibit a considerable stability toward dissociation.

The present study involved $AlCl_3$ as the Lewis acid. This compound exists as a dimer at ordinary temperatures, as do all of the aluminum halides except the fluoride. It has been shown that this dimer contains two chlorine bridges

linking the $AlCl_3$ units (20). Thus the chlorines provide the electrons necessary to form the fourth bond to the aluminum atoms, completing their octets. For reaction to take place forming an adduct of the type $X \cdot AlCl_3$, one must first break these chlorine bridges. The heat of dissociation of Al_2Cl_6 is 29.0 $\pm$ 1 kcal/mole (21). The very fact of dimer formation attests to the strong coordinating power of the $AlCl_3$ unit and formation of strong addition compounds comes as no surprise. Its catalytic activity, specifically in Friedel-Crafts reactions, appears to be largely due to its strong polarizing effect, "since it strongly modifies the binding forces within the molecule with which it forms addition compounds" (22).

$AlCl_3$ forms two main classes of addition compounds, although the border between the classes does not appear to be a sharp one. Simple monomeric 1:1 addition is known with ammonia (23) and with various amines and ethers (24), as well as with PF_3 (13). On the other hand, with $SeCl_4$ and $TeCl_4$, the compounds formed are ionic, $SeCl_3^+AlCl_4^-$ and $TeCl_3^+AlCl_4^-$ (25). Alkali metal chlorides such as NaCl also form compounds of the type $M^+AlCl_4^-$ (26).

$AlCl_3$ is capable of coordinating more than one donor molecule. For example, compounds of the composition $[Al(NH_3)_n]Cl_3$ are reported for n = 1, 2, 3, 5, 6, 7, and 9 (27). $CH_3CN \cdot AlCl_3$ and $(CH_3CN)_2 \cdot AlCl_3$ are formed when $AlCl_3$ is dissolved in acetonitrile. They are believed to ionize in acetonitrile solution to liberate chloride ions (28).

$$(CH_3CN)_n \cdot AlCl_3 \rightleftharpoons [(CH_3CN)_n\ AlCl_m]^{(3-m)} + (3-m)\ Cl^-$$

$$m = 2,\ 1,\ \text{or}\ 0$$

Evidence to support this belief comes from the fact that addition of ICl to such a solution results in the formation of ICl_2^-. The structure $HN{=}CH{\cdot}NC{\cdot}AlCl_3$ has been suggested for the adduct $(HCN)_2 \cdot AlCl_3$ (29). Several double ether adducts, $(R_2O)_2 \cdot AlCl_3$, are known. They have been described as ionic species of the type $R_3O^+AlCl_3OR^-$, but apparently this structure is no longer accepted (30). $[(CH_3)_3N]_2 \cdot AlH_3$ is the only compound in which it has been definitely established that a five coordinate aluminum exists (31), although adducts such as $[(CH_3)_3N]_2 \cdot AlCl_3$, and possibly $(R_2O)_2 \cdot AlCl_3$, may also have such a non-ionic structure.

Very recently Clemens, Sisler, and Brey (5) have presented evidence that the adducts $(C_6H_5)_4P_2 \cdot Al(C_2H_5)_3$, $[(C_6H_5)_2P]_2NC_2H_5 \cdot Al(C_2H_5)_3$ and $[(C_6H_5)_2P]_2NCH_3 \cdot Al(C_2H_5)_3$ contain a five coordinate aluminum in which both phosphorus atoms of each ligand bond to the aluminum.

$F_3P \cdot AlCl_3$, studied by Alton (13), undergoes a rapid and complete halogen exchange above -20°C or in the presence of certain impurities.

$$F_3P \cdot AlCl_3 \longrightarrow PCl_3 + AlF_3$$

Such exchange is not uncommon with aluminum halides. Brown and Wallace (32) have observed the reactions,

$$3\ CH_3Cl + AlBr_3 \rightarrow 3\ CH_3Br + AlCl_3$$
$$3\ CH_3Cl + AlI_3 \rightarrow 3\ CH_3I + AlCl_3$$
$$3\ CH_3Br + AlI_3 \rightarrow 3\ CH_3I + AlBr_3$$

which go essentially to completion at 0^oC within 24 hours. It can be seen that the aluminum always accepts the more electronegative halogen. These reactions probably involve adduct formation prior to exchange.

In order to observe the effect of $AlCl_3$ on a compound containing both phosphorus and nitrogen, Bond (33) mixed $AlCl_3$ with $(CH_3)_2NPF_2$. The reaction observed was anything but simple. His data were such that no simple equation could be written for the interaction. Both PF_3 and $(CH_3)_2NPCl_2$ were formed, suggesting not only halogen exchange but a disproportionation reaction as well.

STATEMENT OF THE PROBLEM

The objectives of this study were:

1) To identify the products formed when $AlCl_3$ reacts with ligands of the form $[(CH_3)_2N]_{3-n}PX_n$ where X is either Cl or F, and n ranges from 0 to 2.

2) To identify the reaction path by which the original complex of $AlCl_3$ and $[(CH_3)_2N]_{3-n}PX_n$ proceeds toward the final products.

3) To identify either phosphorus or nitrogen as the bonding site in each adduct formed and to establish some rationalization for this choice.

RESULTS

Before an adequate rational can be given as to why the following reactions proceed as they do, it is necessary to look at all of the data obtained. Therefore the results will be set forth with relatively little explanation. First the direct combination of ligand with $AlCl_3$ will be presented in each system, followed by the reactions of the ligand - $AlCl_3$ adducts with other members of the $[(CH_3)_2N]_{3-n}PCl_n$ series, including PCl_3. Proceeding to the more complex, the reactions involving some ether adducts of $AlCl_3$ with the series $[(CH_3)_2N]_{3-n}PCl_n$ will then be presented.

The System $(CH_3)_2NPCl_2$-$AlCl_3$

Direct Combination.

When $(CH_3)_2NPCl_2$ and $AlCl_3$ are mixed neat in the vacuum system at 0^oC or above, the following overall reaction takes place quantitatively:

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + PCl_3$$

The $AlCl_3$ appears to dissolve in the ligand forming a clear solution. After a short time, depending upon the temperature and excess of ligand used, a white solid appears in the system. Observation of the vapor pressure above the reaction mixture monitors the evolution of PCl_3 and thus the course of the reaction; it is observed that at 0^oC the pressure reaches its equilibrium value after about one half hour. Even condensing $(CH_3)_2NPCl_2$ onto $AlCl_3$ held at -63^oC

results in the formation of small amounts of PCl_3. In this case, however, the $(CH_3)_2NPCl_2$ was not precooled, since cooling the dichloro ligand even to 0^oC prevents its volatilization at a reasonable rate. For this reason the temperature of the reactants upon contact is not known. On the other hand, a system containing $(CH_3)_2NPCl_2$ and $AlCl_3$ warmed from liquid nitrogen temperatures to -23^oC did result in the evolution of an appreciable quantity of PCl_3.

Formation of an adduct with the formula $[(CH_3)_2N]_2PCl \cdot AlCl_3$ is by no means proved by either the stoichiometry of the reaction or by the observed evolution of PCl_3. An alternate course for the reaction would be:

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \longrightarrow (CH_3)_2NPCl_2 \cdot (CH_3)_2NAlCl_2 + PCl_3$$

in which the $AlCl_3$ contributes the third chlorine to form PCl_3. This would be analogous to the reactions observed by Holmes and Wagner (3), as mentioned previously, in which various aminophosphines were combined with BF_3, BCl_3, and $B(CH_3)_3$ with formation of compounds of the type $(CH_3)_2NBX_2$. To check this possibility, a large excess of $(CH_3)_3N$ was condensed onto the adduct. One mole of $(CH_3)_3N$ was retained per mole of adduct and about 0.7 mole of $[(CH_3)_2N]_2PCl$ was pulled from the reaction tube. The low value for the amount of $[(CH_3)_2N]_2PCl$ recovered was probably due to the low vapor pressure of this adduct (about 1 mm at 25^oC) and as a consequence the difficulty in moving it through the vacuum system. The above shows that $[(CH_3)_2N]_2PCl \cdot AlCl_3$

was indeed the adduct formed. Sufficient evidence to disprove the formation of $(CH_3)_2NAlCl_2$ comes from the fact that this compound does not form a stable adduct with $(CH_3)_3N$ (34). That $(CH_3)_3N$ was retained indicates that the $AlCl_3$ was still present. In addition, the infrared spectrum of the adduct proved identical to the spectrum of $[(CH_3)_2N]_2PCl\cdot AlCl_3$ formed by direct combination of a 1:1 mole ratio of $[(CH_3)_2N]_2PCl$ and $AlCl_3$.

The infrared spectrum of $[(CH_3)_2N]_2PCl\cdot AlCl_3$ (Fig. 3) is very similar to the spectrum of the free ligand (Fig. 2). The major difference is the virtual disappearance of strong absorption at 696 cm^{-1} and the medium absorption at 668 cm^{-1} which appear in the free ligand. These peaks may be assigned to the $\begin{matrix}N\\N\end{matrix}\!>\!P\text{-}Cl$ stretches, on the basis of assignments made by Sr. Fleming for the related fluorophosphine-borane system (1). Sr. Fleming found a marked decrease in the intensity of this skeletal stretch absorption for $[(CH_3)_2N]_2PF$ upon coordination of $[(CH_3)_2N]_2PF$ to BH_3. She reasoned that since the intensity of an absorption depends upon the magnitude of the change of the dipole moment associated with the vibration, and since coordination to the phosphorus should lessen the dipole moment change for this skeletal motion, bonding in this adduct must be through the phosphorus. Significantly, the $\begin{matrix}C\\C\end{matrix}\!>\!N\text{-}P$ symmetric stretch absorptions at 980 cm^{-1} and 960 cm^{-1}, which would be affected by nitrogen-aluminum bonding, did not decrease in intensity. Using the same reasoning, we would predict

that the adduct $[(CH_3)_2N]_2PCl \cdot AlCl_3$ is bonded through the phosphorus. More will be said about bonding in a later section.

The observed disproportionation reaction is quite unexpected in view of the recent study by Van Wazer and Maier (35) in which it was found that exchange reactions between chlorophosphines and dialkylaminophosphines, forming the mixed dialkylaminochlorophosphines, are both rapid and complete. The equilibrium constants for the disproportionation of the dialkylaminochlorophosphines, for example,

$$(CH_3)_2NPCl_2 \rightleftharpoons [(CH_3)_2N]_2PCl + PCl_3$$

were established as less than 5×10^{-4}. Specifically, if PCl_3 and $[(CH_3)_2N]_2PCl$ are mixed in a 1:1 mole ratio, the mixture is essentially completely converted to $(CH_3)_2NPCl_2$ in less than 30 seconds at 25°C, as indicated by only a single ^{31}P peak in the n.m.r. spectrum of the product. The authors attribute this rapid, nonrandom equilibrium to "rehybridization of the electronic orbitals of the phosphorus upon exchange of chlorine atoms and amino groups." The precise meaning of this statement as a scientific explaination is unknown to the writer.

Such equilibria were reported earlier for various aminohalophosphines on a more qualitative basis by Nöth and Vetter (36). They observed that, while the aminochlorophosphines are quite stable to disproportionation, the amino-

bromophosphines are not as stable. For example, $(CH_3)_2NPBr_2$ cannot be distilled without decomposition. The disproportionation reaction,

$$2\ (CH_3)_2NPBr_2 \longrightarrow [(CH_3)_2N]_2PBr + PBr_3$$

occurs to a significant degree.

It is necessary to examine the possibility that the reaction observed when $(CH_3)_2NPCl_2$ and $AlCl_3$ are mixed may involve reaction not with the $(CH_3)_2NPCl_2$ itself, but rather with the very small amount of $[(CH_3)_2N]_2PCl$ which might be in equilibrium with the $(CH_3)_2NPCl_2$. Formation of the adduct would cause this equilibrium to be shifted to the right.

$$2\ (CH_3)_2NPCl_2 \rightleftharpoons [(CH_3)_2N]_2PCl + PCl_3$$

The following observation, reported in detail in later sections, seems to indicate that this is not the route by which the reaction proceeds.

If the $AlCl_3$ is first coordinated to $[(CH_3)_2CH]_2O$ and then mixed with $(CH_3)_2NPCl_2$, or if the reaction is run in diisopropyl ether solvent, in which the $AlCl_3$ exists in the form of an ether adduct, only a very small amount of PCl_3 is formed. Although other reactions cloud the exact nature of the interaction, presumably some $(CH_3)_2NPCl_2$ does coordinate to the $AlCl_3$.

One finds that the reaction of $[(CH_3)_2N]_2PCl$ with $[(CH_3)_2CH]_2O{\cdot}AlCl_3$ results in the displacement of about 60% of the ether, along with other side reactions, indicating

at least a comparable base strength for the monochloro ligand and the ether. Thus $[(CH_3)_2N]_2PCl$ is a stronger base than $(CH_3)_2NPCl_2$ toward $AlCl_3$. One would expect a pick up of the monochloro ligand in preference to the dichloro ligand in the ether solution if the above equilibrium mechanism were valid, since the equilibrium should not be affected by the ether. That $(CH_3)_2NPCl_2$ is coordinated and little or no PCl_3 ie evolved indicates that the role of $AlCl_3$ extends beyond simple removal of $[(CH_3)_2N]_2PCl$ with a consequent equilibrium shift.

The molecular weight of the adduct $[(CH_3)_2N]_2PCl \cdot AlCl_3$, calculated from the observed lowering of the vapor pressure of a methylene chloride solution at 0°C, was found to be 263 $\pm$ 35. Although this value is not very precise, it does indicate a monomeric structure for the adduct. The calculated value for $[(CH_3)_2N]_2PCl \cdot AlCl_3$ is 288.

The ^{31}P n.m.r. spectrum of $[(CH_3)_2N]_2PCl \cdot AlCl_3$, obtained both neat at 85°C and in CH_2Cl_2 solvent at ambient temperature, consisted of a single, sharp peak with a chemical shift of -268 p.p.m. This contrasts with the reported chemical shift of -160 p.p.m. for the free ligand $[(CH_3)_2N]_2PCl$ (35), implying greatly decreased shielding of the phosphorus, as would be expected upon coordination of its lone pair electrons to the Lewis acid $AlCl_3$.

The ^{1}H n.m.r. spectrum of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ (Fig. 1), obtained in CH_2Cl_2 solvent at ambient temperature, consisted of a doublet with a chemical shift of -3.25 p.p.m. The

doublet resulted from a coupling of the hydrogens with the phosphorus. The J_{PH} value was 11.0 c.p.s.

The infrared spectra of $[(CH_3)_2N]_2PCl$ (Fig. 2) and $[(CH_3)_2N]_2PCl \cdot AlCl_3$ (Fig. 3) will be compared, along with $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$, in a later section.

Solvent Reactions.

Direct combination of $(CH_3)_2NPCl_2$ and $AlCl_3$ always leads to at least local excesses of the dichloro ligand in contact with the $AlCl_3$. The model which will be proposed for the series of reactions in question suggests that it is this excess which causes the disproportionation reaction to take place. If, then, this excess is eliminated, it might be possible to prepare the adduct $(CH_3)_2NPCl_2 \cdot AlCl_3$. To check this, the reaction was run using known Lewis bases as solvents and only 1:1 mole ratios of reactants. It was hoped that the base coordinated to the $AlCl_3$ could be displaced such that local excesses of the dichloro ligand would be avoided.

Diethyl ether, though preventing the disproportionation quite effectively, proved to be too strong a base. Only a small portion of the ether was displaced by $(CH_3)_2NPCl_2$.

Diisopropyl ether was found to be a weaker base, as expected, and did largely suppress the formation of PCl_3, but the system $(CH_3)_2NPCl_2$-$[(CH_3)_2CH]_2O$-$AlCl_3$ proved to be very complex, with further reactions taking place. These are described elsewhere.

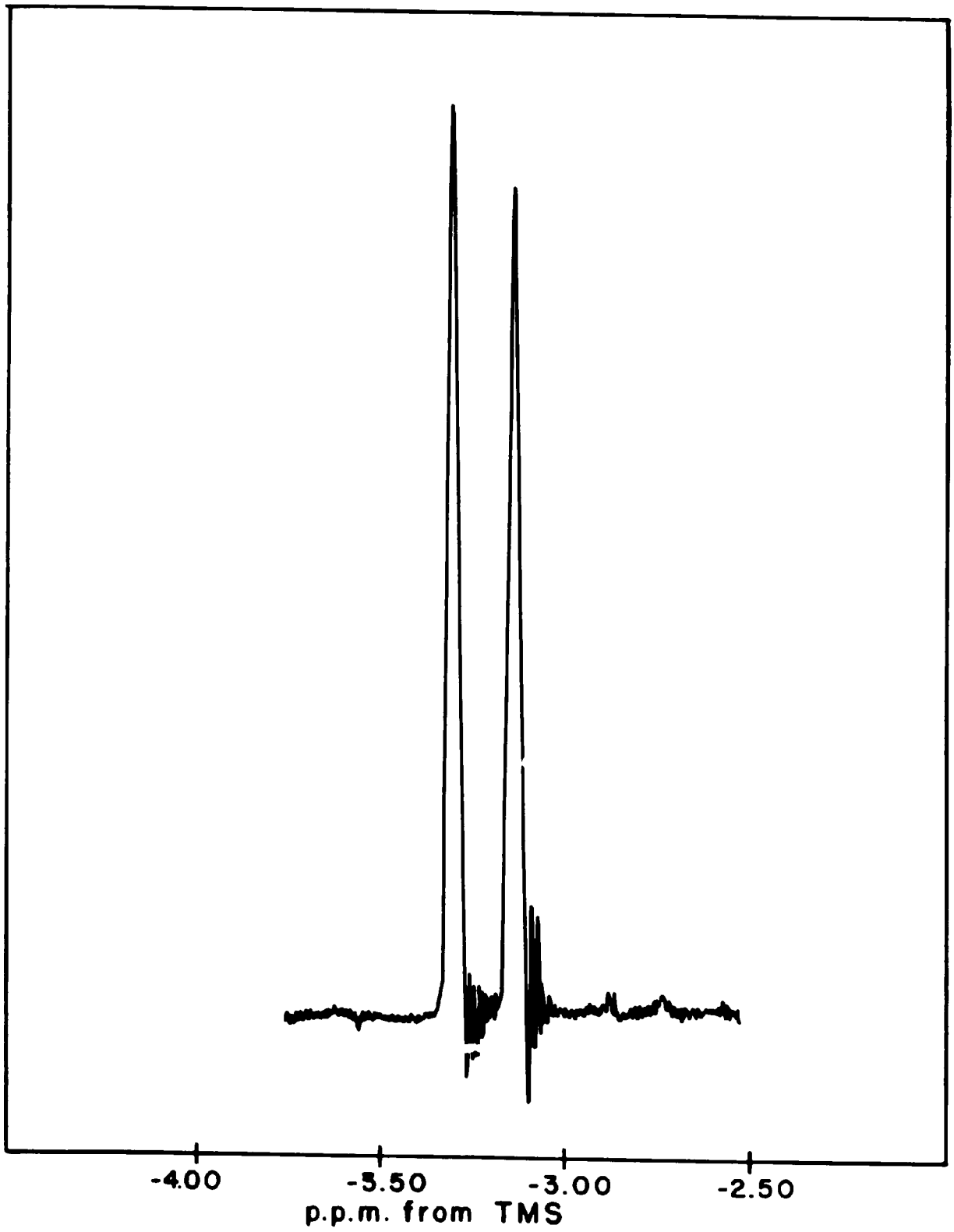


FIGURE 1 ^{1}H N.M.R. Spectrum of $[(CH_3)_2N]_2PCl \cdot AlCl_3$

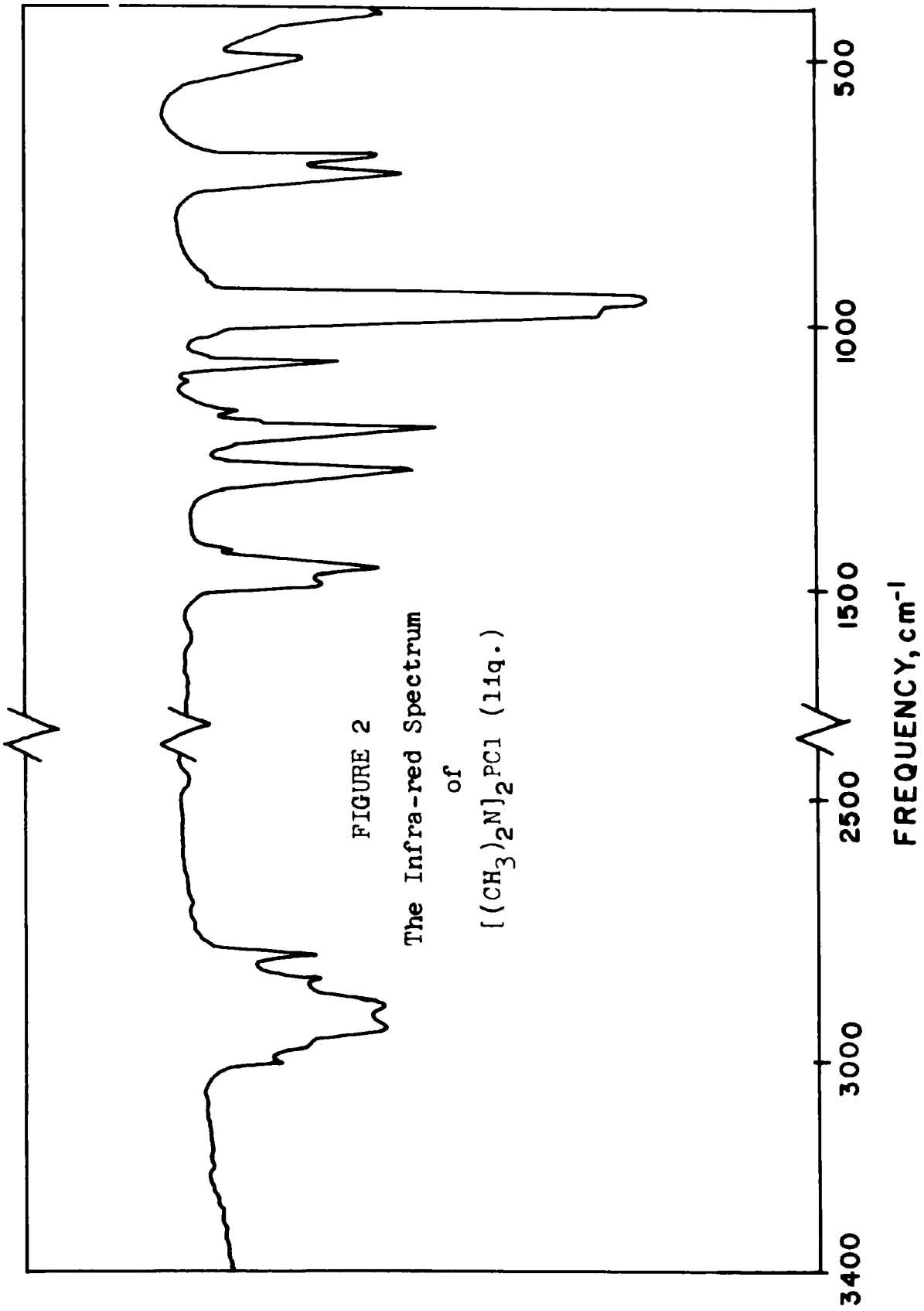


FIGURE 2

The Infra-red Spectrum

of

$[(CH_3)_2N]_2PCl$ (liq.)

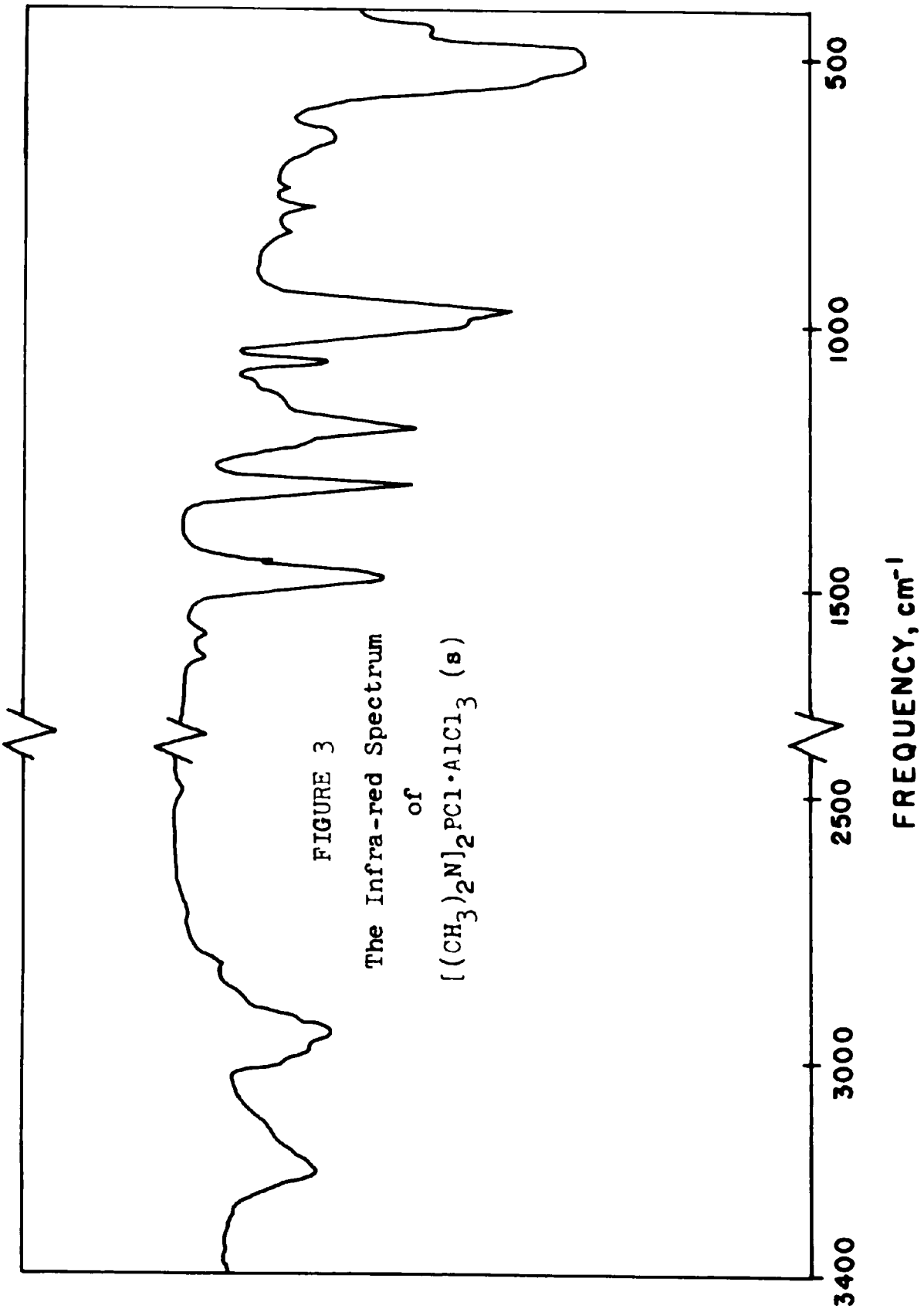


FIGURE 3

The Infra-red Spectrum of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ (s)

Although PCl_3 does not form a stable adduct with $AlCl_3$, there is some evidence to suggest that it does interact weakly with $AlCl_3$ (13). On the assumption that it does, the reaction of $(CH_3)_2NPCl_2$ with $AlCl_3$ was run in PCl_3 solvent. With a 1:1 mole ratio of reactants, at -20°C, the desired adduct, $(CH_3)_2NPCl_2 \cdot AlCl_3$ was isolated upon removal of the PCl_3. This adduct appears to be fairly stable. After standing at room temperature for several weeks, only very small quantities of PCl_3 and $(CH_3)_2NPCl_2$ could be pulled from the reaction tube. These can be accounted for by assuming that there is a small dissociation pressure of $(CH_3)_2NPCl_2$ in equilibrium with the adduct. This free ligand can then react irreversibly with the adduct, forming PCl_3.

$$(CH_3)_2NPCl_2 \cdot AlCl_3 \rightleftharpoons (CH_3)_2NPCl_2 + AlCl_3$$

$$(CH_3)_2NPCl_2 + (CH_3)_2NPCl_2 \cdot AlCl_3 \rightarrow [(CH_3)_2N]_2PCl \cdot AlCl_3 + PCl_3$$

The stability of $(CH_3)_2NPCl_2 \cdot AlCl_3$ contrasts greatly with the very rapid disproportionation which takes place when $(CH_3)_2NPCl_2$, in excess of a 1:1 mole ratio with $AlCl_3$, is present. This fits the assumption that excess of $(CH_3)_2NPCl_2$ are indeed required for the disproportionation reaction to occur.

Reaction of the adduct with $(CH_3)_3N$ results in the regeneration of $(CH_3)_2NPCl_2$.

$(CH_3)_2NPCl_2 \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + (CH_3)_2NPCl_2$

The ^{31}P n.m.r. spectrum of $(CH_3)_2NPCl_2 \cdot AlCl_3$ obtained neat at 55°C showed a single absorption with a chemical shift of -322 p.p.m. The free ligand has a chemical shift value of -166 p.p.m., indicating a very large deshielding effect upon coordination to the $AlCl_3$.

The ^{1}H n.m.r. spectrum of $(CH_3)_2NPCl_2 \cdot AlCl_3$ (Fig. 4) showed a doublet with a chemical shift of -3.57 p.p.m. along with a somewhat smaller doublet attributable to the disproportionation product $[(CH_3)_2N]_2PCl \cdot AlCl_3$. The J_{PH} for the former doublet was 13.2 c.p.s.

The infrared spectra of $(CH_3)_2NPCl_2$ (Fig. 5) and $(CH_3)_2NPCl_2 \cdot AlCl_3$ (Fig. 6) are found to be very similar, with only a few, relatively small frequency shifts distinguishing them. With reference to the work of Sr. Fleming (1), recently revised by Farran (11), the following tentative assignments may be made for $(CH_3)_2NPCl_2$, point group C_s, and $(CH_3)_2NPCl_2 \cdot AlCl_3$, point group C_s if perfectly free rotation around the P-Al bond is assumed (Table I).

The peak at 3120 cm^{-1} in the adduct is probably due to moisture in the KBr pellet in which the sample was run. The absorptions in the region from about 3000 cm^{-1} to 2800 cm^{-1} are all assigned as C-H stretching frequencies. The bands at 1480 cm^{-1} and 1460 cm^{-1} in the free ligand and at 1475 cm^{-1} and 1450 cm^{-1} in the adduct may be assigned

to deformations of the CH_3 group. The absorption at 1290 cm^{-1} in $(CH_3)_2NPCl_2$ has been attributed by Farran to stretching of the C-N bonds in the molecule, thus suggesting a like assignment for the 1295 cm^{-1} band in the adduct. Bands at 1187 cm^{-1}, 1144 cm^{-1} and 1068 cm^{-1} in the free ligand, and at 1172 cm^{-1} and 1057 cm^{-1} in the adduct are assigned to CH_3 rocking motions. The strong absorption at 981 cm^{-1} in the free ligand and at 984 cm^{-1}, with a shoulder at 1009 cm^{-1}, in the adduct, is designated as a stretching frequency for the C-N bond. The weak absorptions at 860 cm^{-1} and 805 cm^{-1} in the adduct are not readily assigned as they are not found in the free ligand. They are probably combination bands. The band at 688 cm^{-1} in $(CH_3)_2NPCl_2$, which may be correlated to the 690 cm^{-1} band, and also possibly the 712 cm^{-1} band in the adduct, is assigned to the N-P stretching frequency. It is postulated, in a latter section, that bonding in the adduct is through the phosphorus, thus one would perhaps expect that this absorption in the adduct would be greatly altered. With this in mind, plus the postulated dissociation of the adduct, it is reasonable to assign the 690 cm^{-1} band in the adduct spectrum to the dissociated free ligand and the 712 cm^{-1} absorption to the adduct. The 612 cm^{-1} band in the adduct is not found in the free ligand and is thus not readily assigned. Farran has assigned the 530 cm^{-1} and the 456 cm^{-1} bands in $(CH_3)_2NPCl_2$ as symmetric and asymmetric stretching frequencies of the P-Cl bond. The

bands at 585 cm^{-1} and 430 cm^{-1} in the adduct may thus represent these motions. Alternately, either or both of these absorptions may be hidden under the strong, broad absorption centered at about 500 cm^{-1} in the adduct, with the 585 cm^{-1} band being a combination band and the 430 cm^{-1} band due to a C-N-C deformation which occurs below 400 cm^{-1} in the free ligand. The broad absorption in the adduct may be tentatively assigned to the $AlCl_3$, either as the unreacted Al_2Cl_6 or as a possible Al-Cl stretching frequency. It is probably not all attributable to P-Cl stretching since it has been found to occur in the adduct $[(CH_3)_2N]_3P \cdot AlCl_3$ in which there are no P-Cl bonds.

The System $[(CH_3)_2N]_2PCl$-$AlCl_3$

Direct Combination.

When equimolar amounts of $[(CH_3)_2N]_2PCl$ and $AlCl_3$ are combined in the vacuum line, a waxy solid is formed which is identical to the solid formed in the disproportionation reaction with excess $(CH_3)_2NPCl_2$ and $AlCl_3$, as stated above.

$$[(CH_3)_2N]_2PCl + AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl \cdot AlCl_3$$

However, with an excess of $[(CH_3)_2N]_2PCl$, a 2:1 adduct, $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$, is formed.

$$2\ [(CH_3)_2N]_2PCl + AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$$

Due to the low volatility of the free ligand and the solubility of the adduct in an excess of the ligand, it is

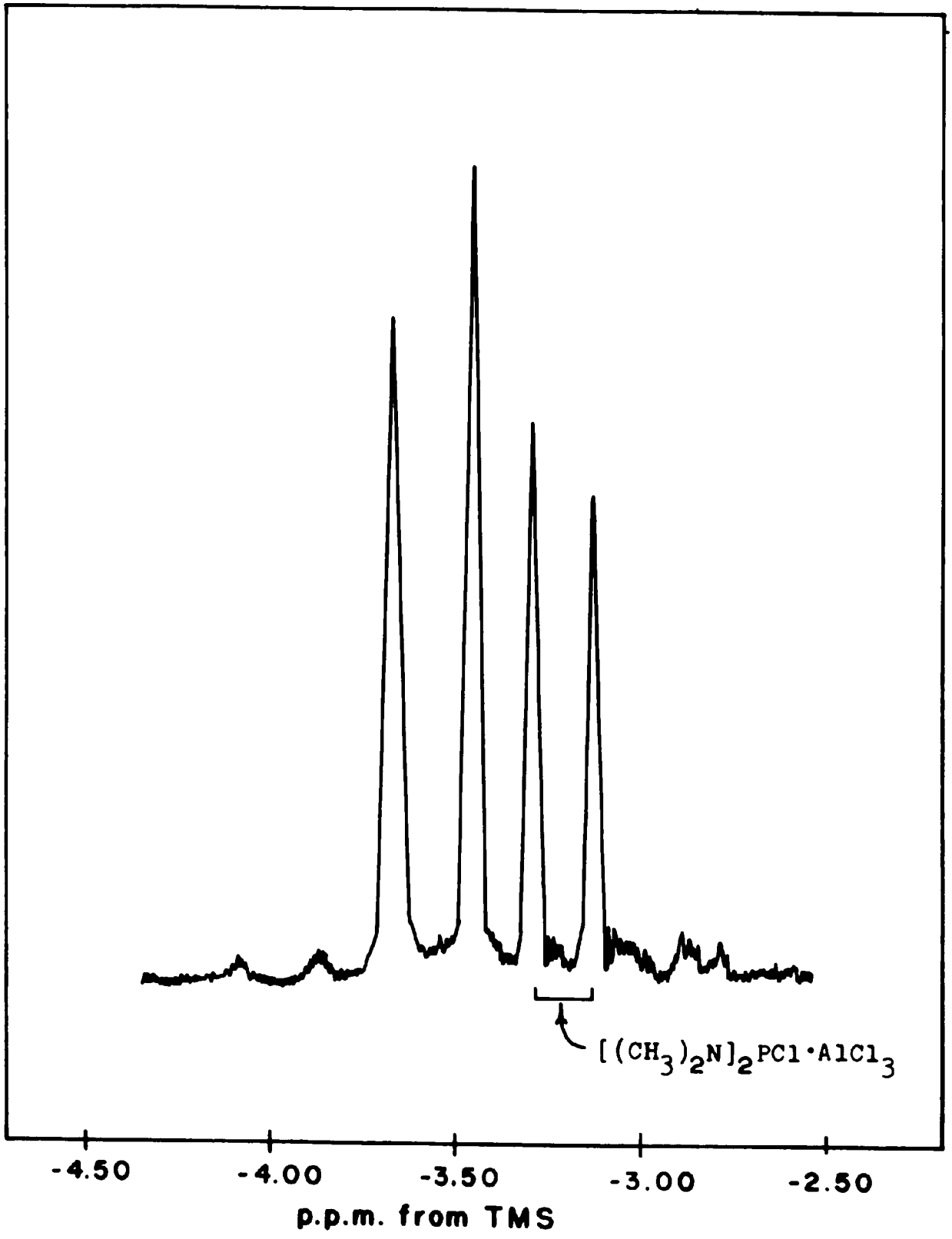


FIGURE 4 ^{1}H N.M.R. Spectrum of $(CH_3)_2NPCl_2 \cdot AlCl_3$

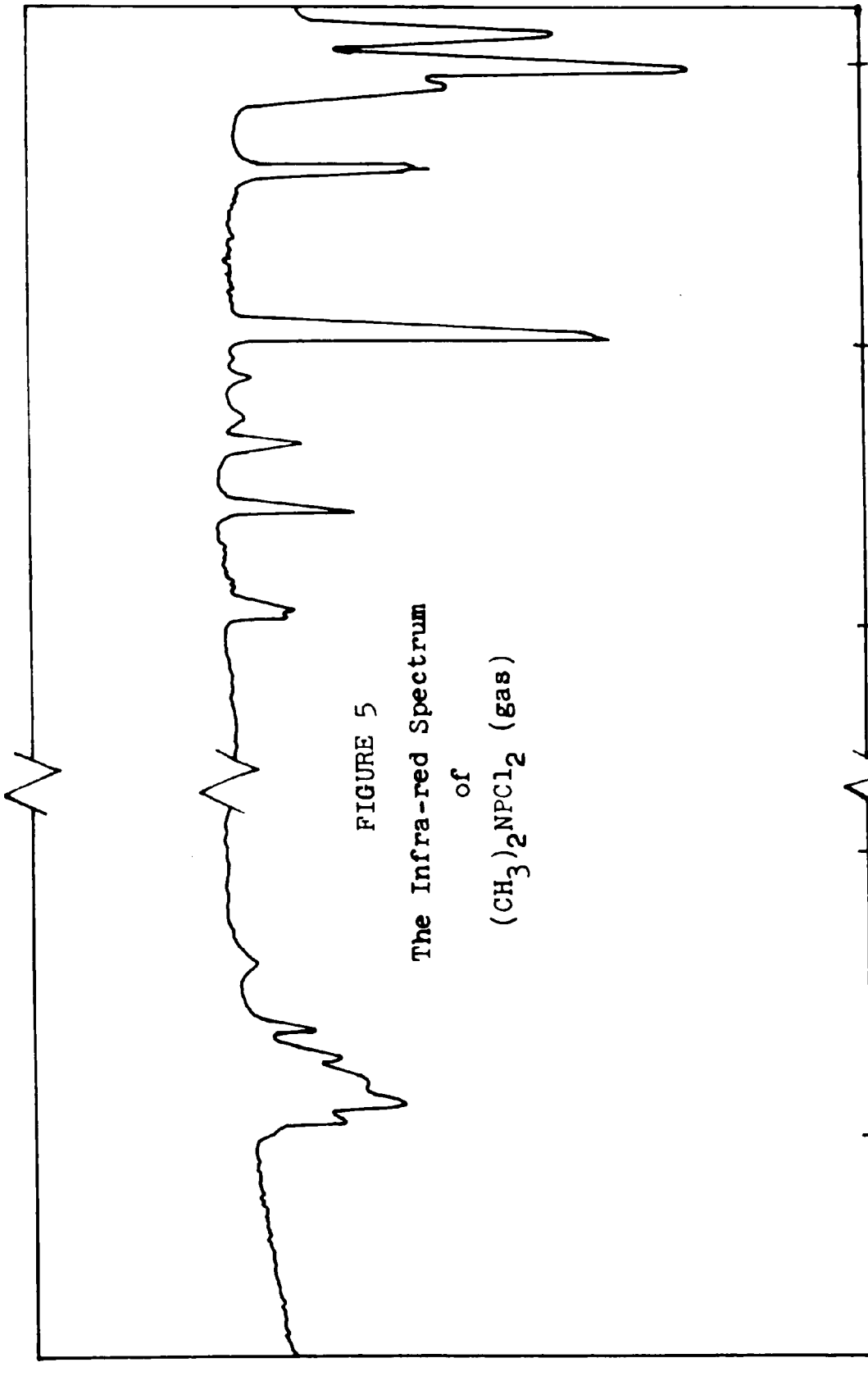


FIGURE 5

The Infra-red Spectrum

of

$(CH_3)_2NPCl_2$ (gas)

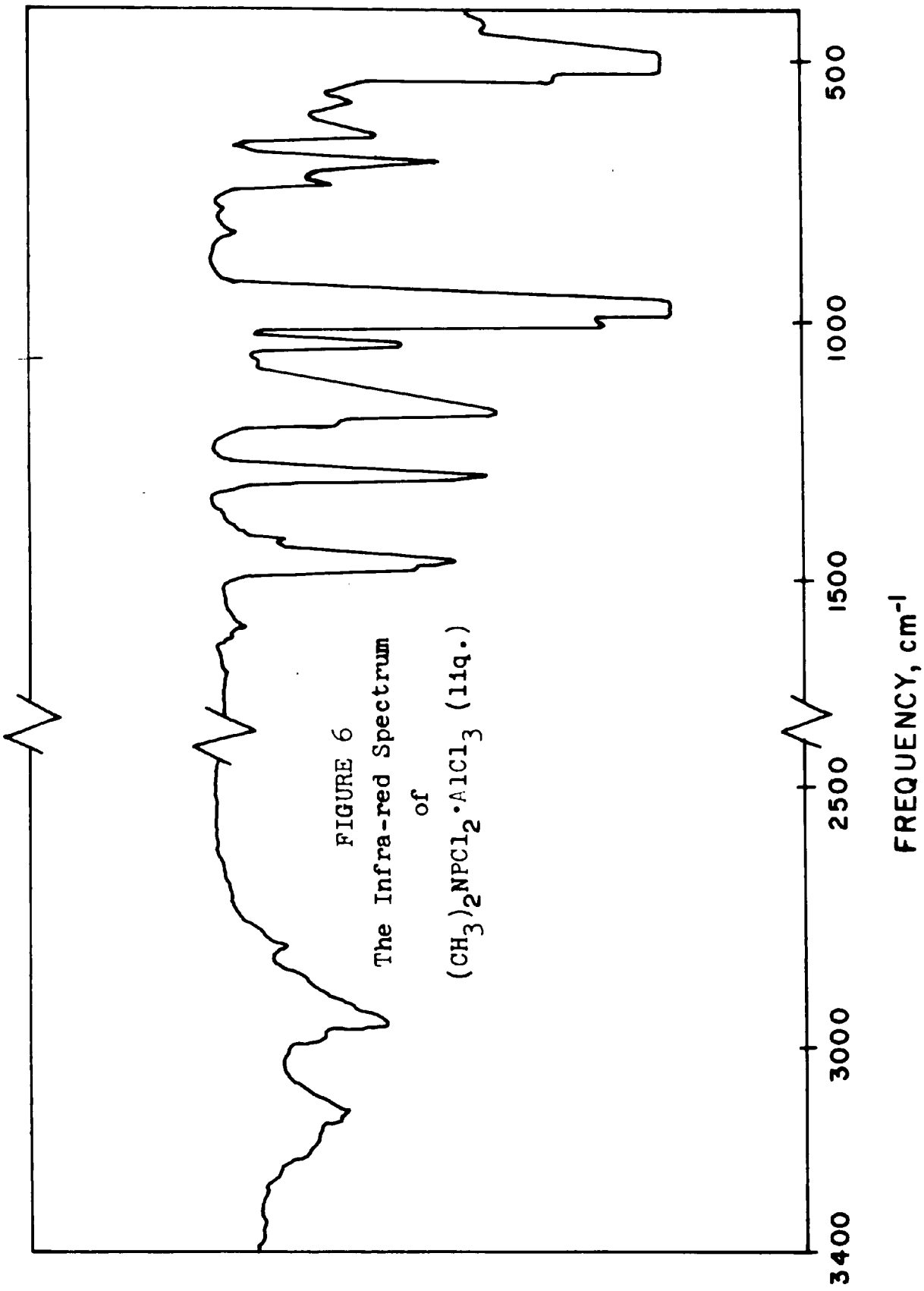


FIGURE 6
The Infra-red Spectrum
of
$(CH_3)_2NPCl_2 \cdot AlCl_3$ (liq.)

Table I

Comparison of the Infrared Spectra of $(CH_3)_2NPCl_2$ and $(CH_3)_2NPCl_2 \cdot AlCl_3$

$(CH_3)_2NPCl_2$ (gas)[a]	$(CH_3)_2NPCl_2 \cdot AlCl_3$ (solid)	Assignment[b]
	3120 M (cm^{-1})	H_2O (?)
2980 (sh) (cm^{-1})	2960 (sh)	ν(C-H)
2935 M	2940 M	
2860 (sh)		
2810 MW	2800 W	ν^s(C-H)
1480 M	1475 (sh)	δ (CH_3)
1460 M	1450 MS	
	1410 (sh)	
1290 M	1295 MS	ν (C-N)
1187 M	1172 MS (br)	ρ (CH_3)
1144 MW	1057 M	
1068 MW		
981 S	1009 (sh)	ν(C-N)
	984 VS	
	860 W	?
	805 W	
688 MS	712 MW	ν(N-P)
	690 M (?)	
	641 M	?
530 MS (sh)	585 M (sh) (?)	ν^s(P-Cl)
508 VS		PCl_3 (?)
	500 VS (br)	$AlCl_3$ (?)
456 S	430 M (sh)	ν^a(P-Cl)

(a) S = Strong
M = Medium
W = Weak
V = Very
sh = shoulder
br = broad

(b) ν = Stretching Mode
δ = Deformation Mode
ρ = Rocking Mode
s = symmetric
a = asymmetric

difficult to remove the last of the excess $[(CH_3)_2N]_2PCl$, even when the system is heated to 70°C. To facilitate its removal, n-hexane was condensed onto the wet adduct. The free ligand is soluble in this solvent, whereas the adduct is not. Hence, rapid removal of the hexane carries some of the ligand from the reaction tube. Repeated condensation and rapid pumping off of the hexane, combined with heating, lowered the ligand to $AlCl_3$ ratio to 2.06 to 1, and 2.09 to 1 in the two runs attempted. That this is in fact a 2:1 adduct and not a solid solution of ligand in 1:1 adduct is shown by a molecular weight determination which, in two separate runs, was 400 ± 60 and 462 ± 60. Theoretically one calculates a molecular weight of 442 for the monomeric adduct $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$. In addition, one finds that the infrared spectrum of this double adduct is almost identical to that of the single adduct, namely that it looks very much like the ligand itself except for the greatly diminished intensities of the peaks around 700 cm^{-1}. If the solid consisted of a mixture of adduct and free ligand, these ligand peaks would certainly be present in the spectrum.

Reaction of an excess of $[(CH_3)_2N]_2PCl$ with $[(CH_3)_2N]_2PCl \cdot AlCl_3$ also produced $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$.

$$[(CH_3)_2N]_2PCl + [(CH_3)_2N]_2PCl \cdot AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$$

The final ratio of ligand to $AlCl_3$, after repeated treatment

with hexane and heat, was 2.05 to 1. The infrared spectrum of this adduct was identical to that of the 2:1 adduct formed directly.

Treatment of the double adduct with excess $(CH_3)_3N$ resulted in the uptake of one mole of amine per mole of original $AlCl_3$. Presumably because of its low vapor pressure, only about 68% of the expected $[(CH_3)_2N]_2PCl$ was recovered.

$$\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + 2\ [(CH_3)_2N]_2PCl$$

The ^1H n.m.r. spectrum of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ was quite complex (Fig. 7). A satisfactory interpretation of the spectrum has not yet been made, although its general features appear consistant with the model to be proposed. More will be said about this in a later section.

The ^{31}P n.m.r. spectrum of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ (Fig. 8) showed two doublets with chemical shifts of -50 p.p.m. and -119 p.p.m. The coupling constants are 349 c.p.s. in both cases. This spectrum indicates two different kinds of phosphorus in the adduct, with each phosphorus coupling with the other. This will be discussed in a later section.

Again with the assistance of the work of Sr. Fleming (1), revised by Farran (11), the following tentative assignments for the infrared absorptions of $[(CH_3)_2N]_2PCl$

(Fig. 2), $[(CH_3)_2N]_2PCl \cdot AlCl_3$ (Fig. 3), and $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ (Fig. 9) may be made (Table II).

First, the broad absorption at 3?)0 cm^{-1} in the 1:1 adduct is believed due to moisture in the KBr pellet in which the solid was run. The bands in the region from about 3000 cm^{-1} to 2750 cm^{-1} are clearly assignable to C-H stretching frequencies. The weak absorptions at 2450 cm^{-1} and 1600 cm^{-1} are very possibly due to impurities in the samples as they seem to vary in intensity from sample to sample. Bands in the 1500 cm^{-1} to 1400 cm^{-1} region are CH_3 deformation frequencies. The absorption at 1280 cm^{-1} in the free ligand, which shifts to 1309 cm^{-1} in the single adduct and to 1300 cm^{-1} in the double adduct, may be assigned as C-N stretching frequencies. All peaks in the 1050 cm^{-1} to 1200 cm^{-1} region are considered to be CH_3 rocking frequencies. The bands at 980 cm^{-1} and 960 cm^{-1} in the free ligand, 1003 cm^{-1} and 996 cm^{-1} in the single adduct and 1008 cm^{-1} and 984 cm^{-1} in the double adduct are assigned as C-N stretching frequencies. The absorptions at 699 cm^{-1} and 670 cm^{-1} in $[(CH_3)_2N]_2PCl$ have been assigned to N-P stretching frequencies. For the adducts, however, it is difficult to assign the bands in this region. Clearly a great change has taken place in that the two prominent absorptions of the free ligand have decreased, but all of the bands which occur in this region in the adducts are not all necessarily assignable to the P-N stretch. They may be due either to contamination of the sample by impurities, combination bands, or possibly

bands which were forbidden in the free ligand. Thus no definite assignments will be attempted. The 490 cm^{-1} band in the free ligand is assigned to the P-Cl stretching motion. It is either covered by, or else is the cause of, the strong absorption centered at about 500 cm^{-1} in the adduct. As previously noted, this broad absorption is probably due to $AlCl_3$, as it is found in the spectra of all of the $AlCl_3$ adducts studied. The weak absorptions at 412 cm^{-1} in the free ligand and at 437 cm^{-1} in the adducts is probably assignable to a C-N-C deformation.

Reaction of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ with $[(CH_3)_2N]_3P$

An excess of $[(CH_3)_2N]_3P$, condensed onto $[(CH_3)_2N]_2PCl \cdot AlCl_3$, resulted in the formation of the double adduct $[(CH_3)_2N]_3P \cdot [(CH_3)_2N]_2PCl \cdot AlCl_3$.

$$[(CH_3)_2N]_3P + [(CH_3)_2N]_2PCl \cdot AlCl_3 \longrightarrow [(CH_3)_2N]_3P \cdot [(CH_3)_2N]_2PCl \cdot AlCl_3$$

The fact that $[(CH_3)_2N]_2PCl$ is <u>not</u> displaced from the $AlCl_3$ shows that $[(CH_3)_2N]_3P$ is <u>not</u> a stronger base than $[(CH_3)_2N]_2PCl$ in spite of the substitution of an electron donating dimethylamino group for an electron withdrawing chlorine atom. This will be discussed in a later section.

Reaction of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ with PCl_3

The reaction observed between $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ and PCl_3 follows the equation:

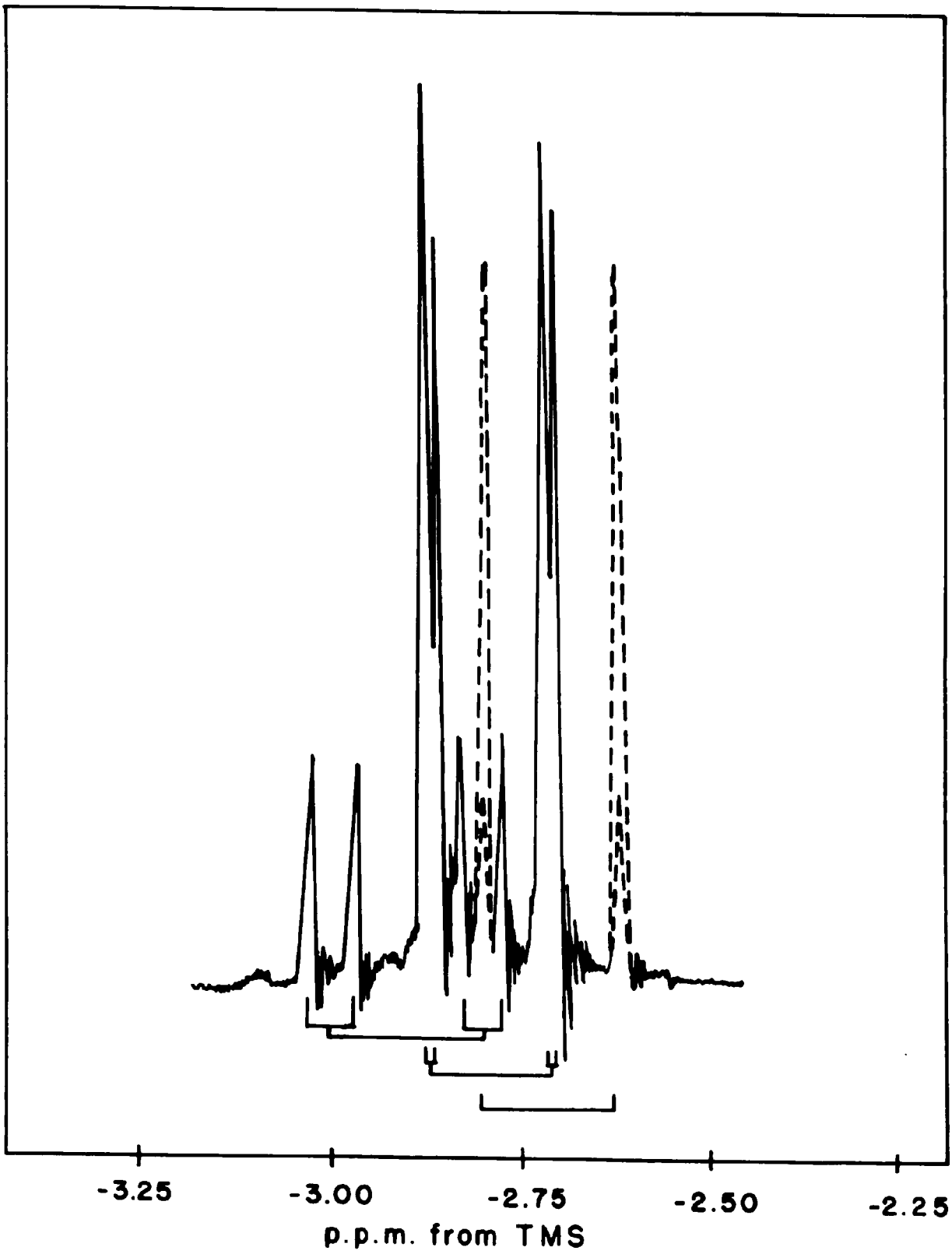


FIGURE 7 ^{1}H N.M.R. Spectrum of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$

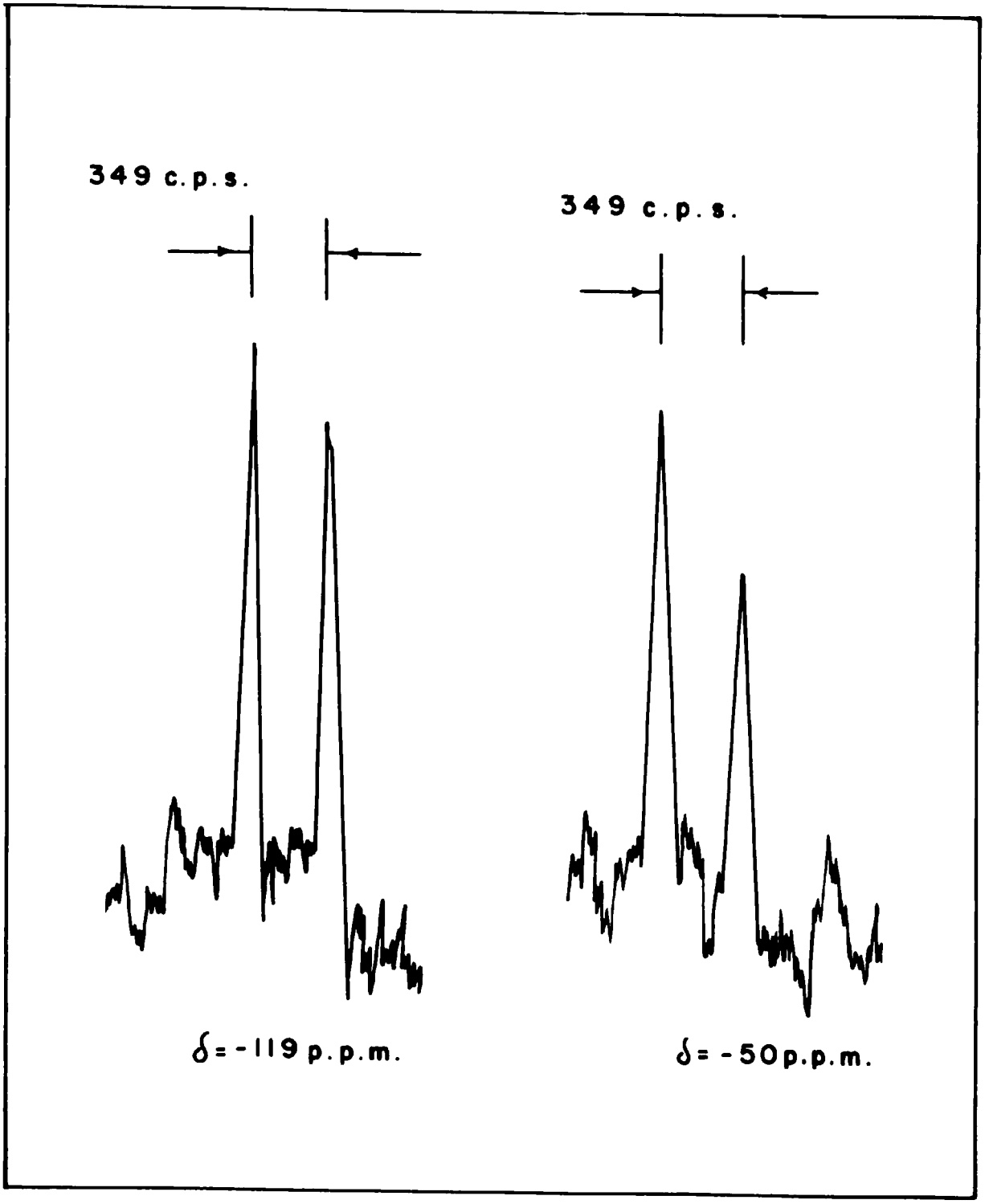


FIGURE 8 ^{31}P N.M.R. Spectrum of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$

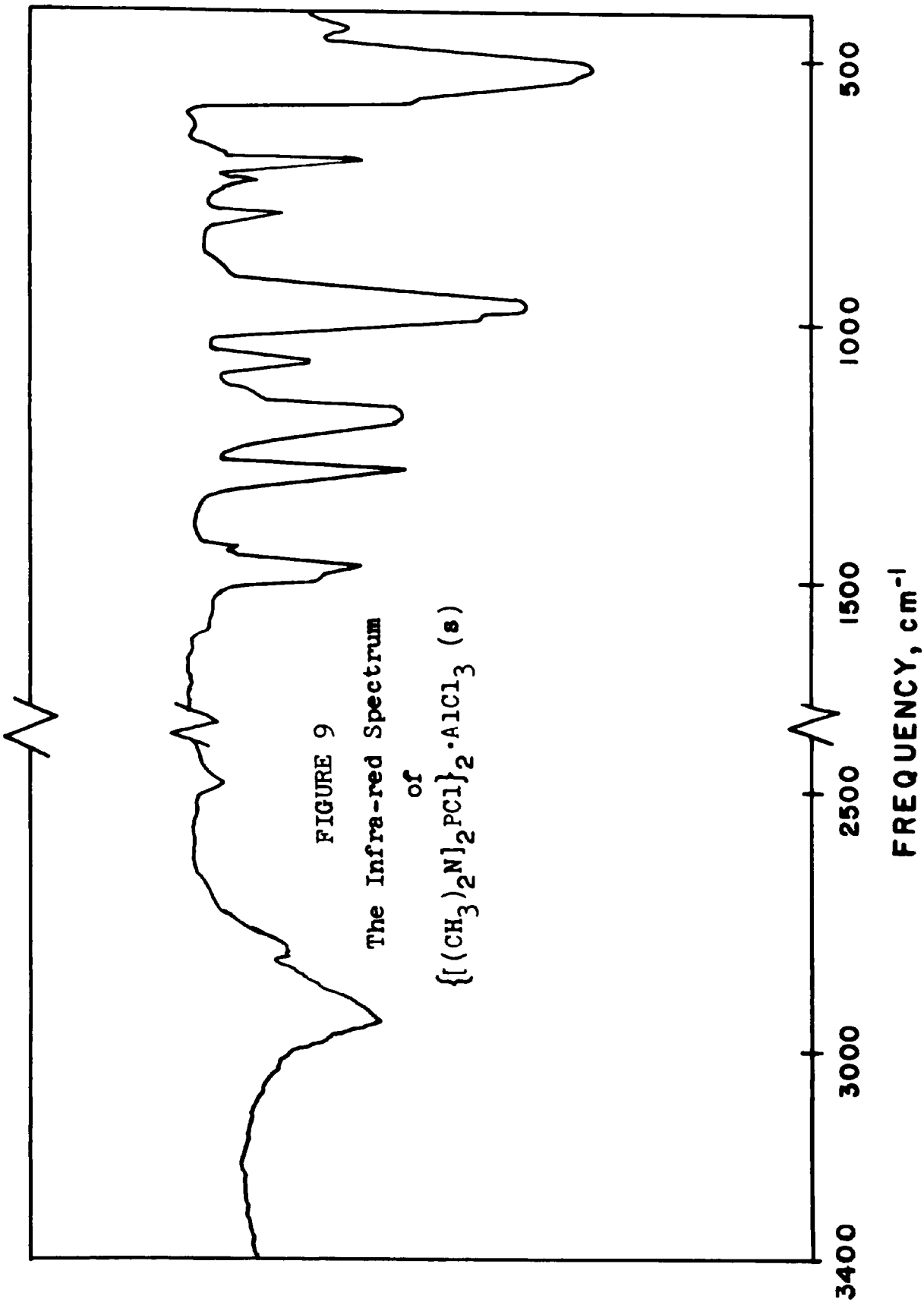


FIGURE 9

The Infra-red Spectrum

of

$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ (s)

Table II

Comparison of the Infrared Spectra of $[(CH_3)_2N]_2PCl$, $[(CH_3)_2N]_2PCl \cdot AlCl_3$ and $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$

$[(CH_3)_2N]_2PCl$ (liquid)	$[(CH_3)_2N]_2PCl \cdot AlCl_3$ (solid)	$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ (solid)	Assignment
	3200 (br)(cm^{-1})		H_2O (?)
3010 (sh)(cm^{-1})	2970 (sh)	2935 MS (cm^{-1})	ν (C-H)
2935 S	2920 MS		
2880 S			
2845 (sh)			
2805 MS	2810 VW	2810 MW	ν^s(C-H)
2450 W	1660 W	2430 W	(?)
1630 W	1580 W		
1480 MS	1465 MS	1470 M (sh)	δ (CH_3)
1450 S	1415 MW (sh)	1455 MS	
1410 W (sh)		1410 W (sh)	
1280 S	1309 S	1300 S	ν(C-N)
1194 S	1186 S	1177 S	ρ(CH_3)
1170 (sh)	1058 MS	1062 MS	
1141 MW			
1097 W			
1062 M			
980 S (sh)	1003 S (sh)	1008 S (sh)	ν(C-N)
960 VS	996 VS	984 VS	
	805 W	745 MW	(?)
699 MS	733 W (?)	692 W (?)	ν(N-P)
670 M	710 VW (?)	668 M (?)	
	620 W (br)		(?)
490 MW			ν(P-Cl)
	490 VS (br)	490 VS (br)	$AlCl_3$ (?)
412 W	437 W (sh)	437 W	δ(C-N-C)

See Table I for key

$$\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl \cdot AlCl_3 + 2\,(CH_3)_2NPCl_2$$

It required about fifteen minutes for the solid adduct to react, leaving two immiscible liquids, with the PCl_3 the more dense. The upper layer presumably was $[(CH_3)_2N]_2PCl \cdot AlCl_3$ with a small amount of $(CH_3)_2NPCl_2$ or PCl_3 dissolved in it, rendering it a liquid. Even though an excess of PCl_3 was used, one would not expect the resulting adduct to be $(CH_3)_2NPCl_2 \cdot AlCl_3$ since it has been shown that this adduct reacts with $(CH_3)_2NPCl_2$, formed in the above reaction, to give the monochloro ligand adduct.

In that Van Wazer and Maier (35) have observed that $[(CH_3)_2N]_2PCl$ and PCl_3 react in a matter of seconds when mixed, it appears that the $AlCl_3$ slows down this process. However, since the present reaction involves not two liquids but rather a solid and a liquid, the time observed for the disappearance of the solid may have been merely a result of the heterogeneous nature of the reaction. More sophisticated experiments would be necessary to determine the exact role of the $AlCl_3$ in this process.

The System $[(CH_3)_2N]_3P$-$AlCl_3$

Direct Combination.

Reaction of an excess of $[(CH_3)_2N]_3P$ with $AlCl_3$ results in the formation of the 1:1 adduct $[(CH_3)_2N]_3P \cdot AlCl_3$.

$$[(CH_3)_2N]_3P + AlCl_3 \longrightarrow [(CH_3)_2N]_3P\cdot AlCl_3$$

There is no evidence for the formation of a 2:1 adduct with $[(CH_3)_2N]_3P$. Any excess of ligand over a 1:1 mole ratio simply "wets" the adduct, showing no tendency to either dissolve or react with it. Treatment of the adduct with $(CH_3)_3N$ results in almost quantitative replacement of the $[(CH_3)_2N]_3P$ by the amine.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot AlCl_3 + [(CH_3)_2N]_3P$$

Two factors might account for the lack of formation of a double adduct with $[(CH_3)_2N]_3P$. First, steric factors may prevent the close approach of the phosphorus and aluminum necessary for stable coordination. Also, we have seen that $[(CH_3)_2N]_3P$ is a weaker base than $[(CH_3)_2N]_2PCl$ with respect to $AlCl_3$. This diminished base strength, assuming that it is at least partially due to factors other than simply steric ones, as discussed later, may be a second factor preventing the stable coordination of a second ligand. In any case, it appears that one has just barely passed the limiting factor preventing coordination since the double adduct $[(CH_3)_2N]_3P\cdot[(CH_3)_2N]_2PCl\cdot AlCl_3$ is stable. Replacement of only a single chlorine atom by a dimethylamino group prevents coordination under the conditions used here.

Lowering of the vapor pressure of methylene chloride solutions of $[(CH_3)_2N]_3P\cdot AlCl_3$, in two separate determinations, yielded molecular weight values of 341 $\pm$ 60 and

296 ± 50. One calculates the value 296 for the monomeric species. Although the experimental values are not very precise, they do discount the possibility of polymer formation.

The ^{31}P n.m.r. spectrum of $[(CH_3)_2N]_3P\cdot AlCl_3$, obtained in a saturated CH_2Cl_2 solution, showed two peaks of roughly equal intensity barely discernible above noise level, with chemical shifts of -56 p.p.m. and -89 p.p.m. Neither can be attributed to the free ligand which is reported to show a chemical shift of -123 p.p.m. (34). At this time it is not possible to determine which peak may be assignable to $[(CH_3)_2N]_3P\cdot AlCl_3$. The second peak apparently is caused by the same species which gives the broad ^1H n.m.r. signal mentioned below.

The ^1H n.m.r. spectrum of $[(CH_3)_2N]_3P\cdot AlCl_3$ (Fig. 10), obtained in CH_2Cl_2 solution, consisted of the expected doublet (J_{PH} = 10.5 c.p.s.) with a chemical shift of -2.62 p.p.m., plus a broad signal centered at -2.69 p.p.m. The source of this latter signal is not known, but may be the result of solvent interactions.

Once again the work of Sr. Fleming (1), revised by Farran (11), serves as the basis for the following tentative assignments for the infrared absorptions of $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]_3P\cdot AlCl_3$ (Table III).

The broad absorption above 3000 cm^{-1} in the adduct is probably the result of moisture in the KBr pellet in which the sample was run. All absorptions in the 3000 cm^{-1} to

2750 cm^{-1} region may be assigned to C-H stretching frequencies. The bands at 2445 cm^{-1} in the free ligand and at 2440 cm^{-1} in the adduct, as well as those at 1600 cm^{-1}, are probably the result of impurities in the samples in that they vary in intensity from spectrum to spectrum. The bands at 1475 cm^{-1} and 1455 cm^{-1} in the free ligand and at 1480 cm^{-1} and 1460 cm^{-1} in the adduct are assigned to CH_3 deformations. The 1272 cm^{-1} absorption in $[(CH_3)_2N]_3P$, increasing to 1310 cm^{-1} in the adduct, may be assigned to a C-N stretching frequency. Bands at 1204 cm^{-1}, 1158 cm^{-1}, and 1058 cm^{-1} in the free ligand and the broad absorptions at 1188 cm^{-1}, about 1130 cm^{-1} and 1060 cm^{-1} in the adduct are attributable to CH_3 rocking motions. Absorptions at 956 cm^{-1}, with a shoulder at 940 cm^{-1}, in the free ligand and at 995 cm^{-1} in the adduct are assigned to C-N stretches. The bands at 670 cm^{-1} and 644 cm^{-1} in the free ligand are assigned as N-P stretches. No bands at these frequencies are found in the adduct. Either they are shifted to 762 cm^{-1} and 745 cm^{-1} and have greatly diminished in intensity, or else they have disappeared. In the latter case, the 762 cm^{-1} and 745 cm^{-1} bands, as well as the other weak absorptions in this region, may be attributed to combination bands, previously forbidden bands, or impurities. The 490 cm^{-1} band in the adduct must be attributable to $AlCl_3$, either in unreacted form or as an Al-Cl stretching frequency. Alternately, it may be the result of contamination of the sample by some $[(CH_3)_2N]_2PCl$, in which case it could be

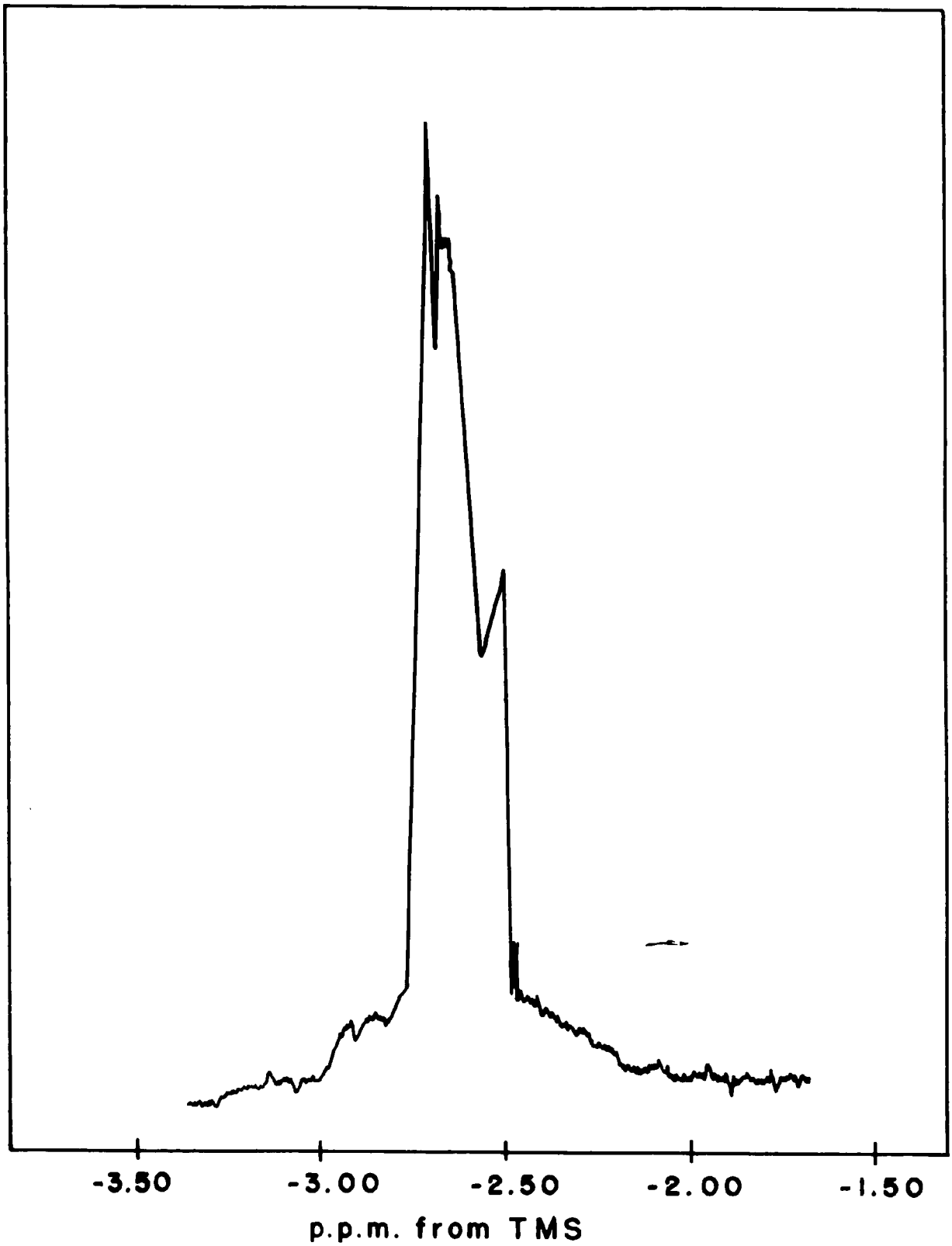


FIGURE 10 ^{1}H N.M.R. Spectrum of $[(CH_3)_2N]_3P \cdot AlCl_3$

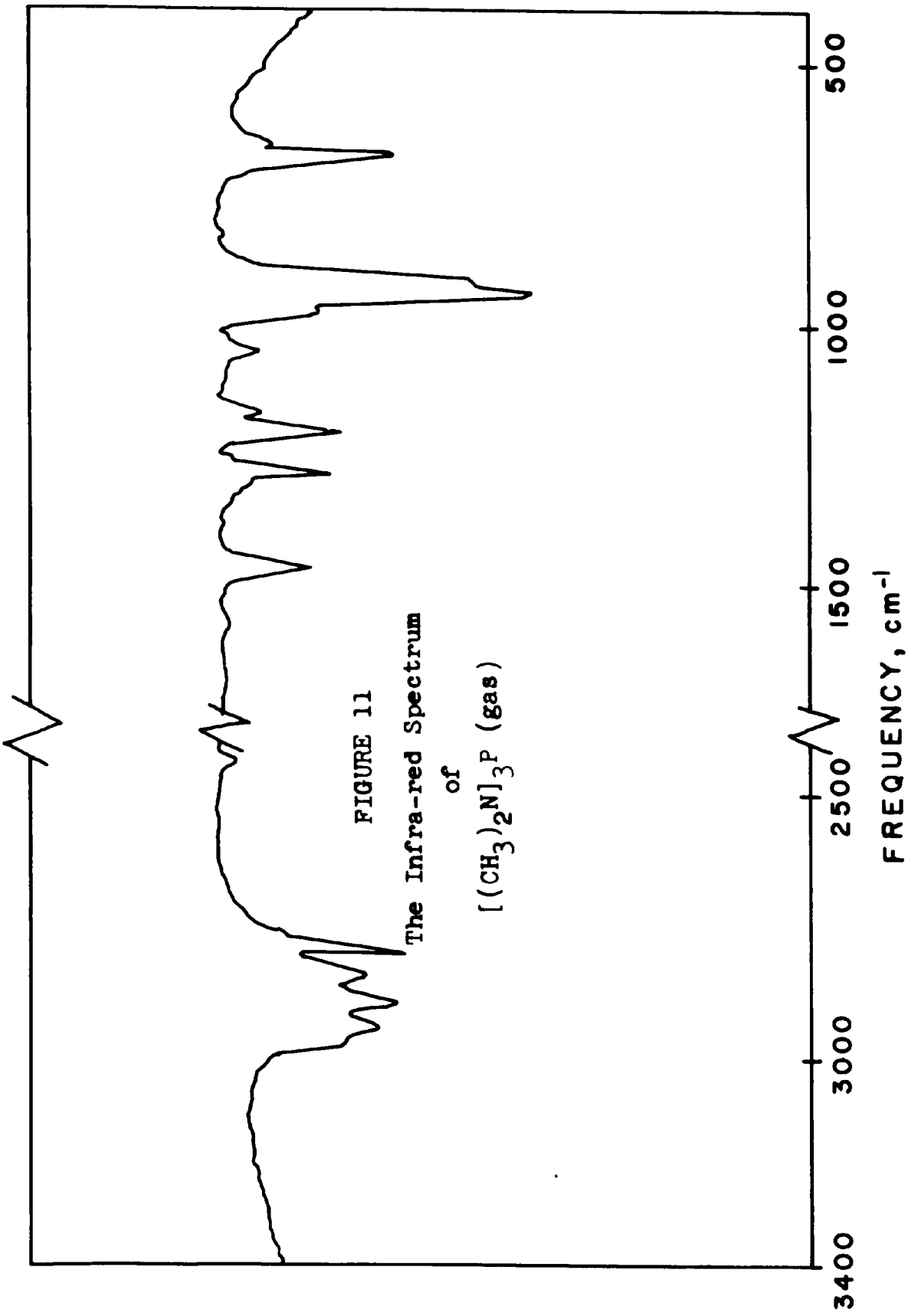


FIGURE 11
The Infra-red Spectrum
of
$[(CH_3)_2N]_3P$ (gas)

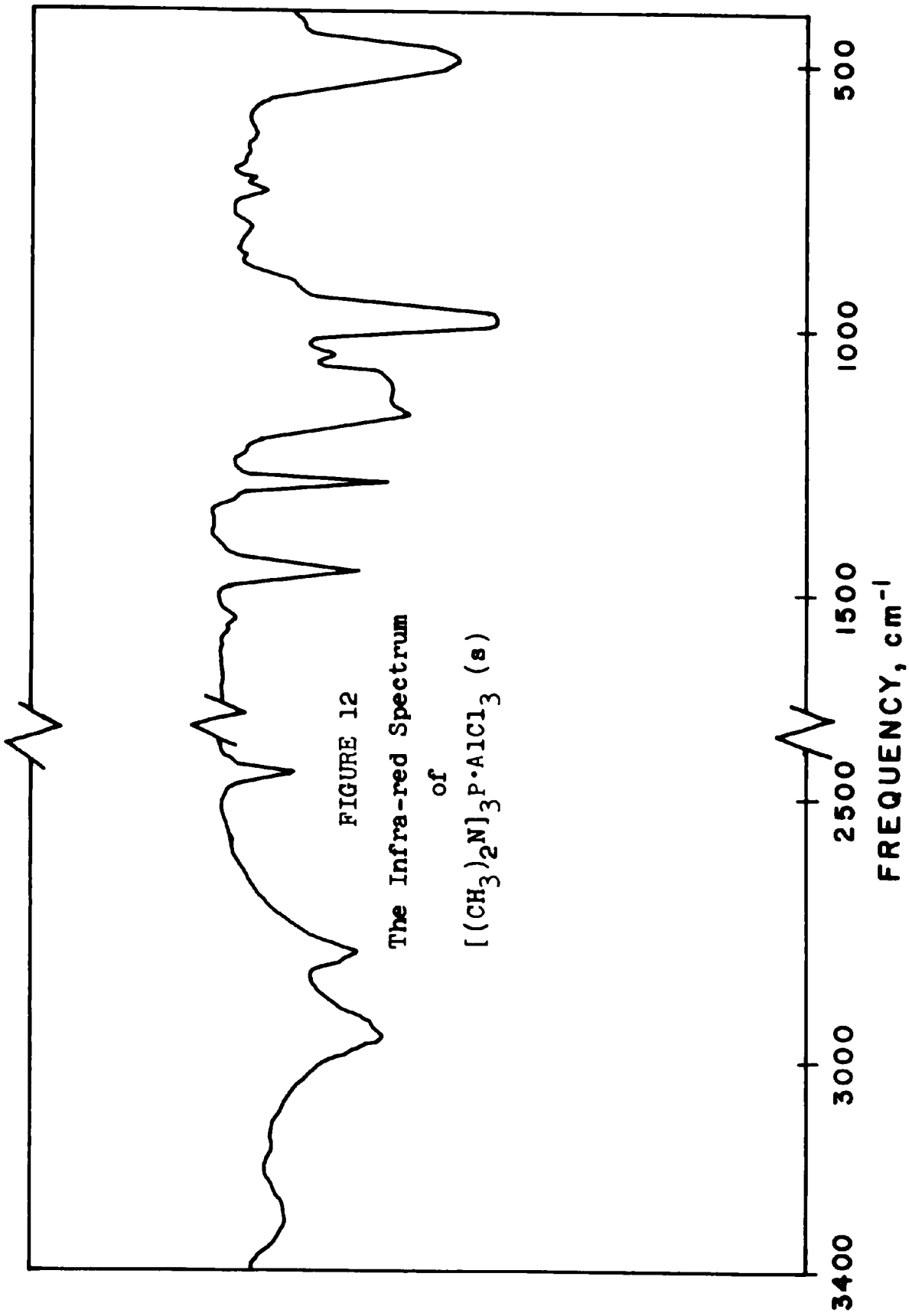


FIGURE 12

The Infra-red Spectrum

of

$[(CH_3)_2N]_3P \cdot AlCl_3$ (s)

Table III

Comparison of the Infrared Spectra of $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]_3P \cdot AlCl_3$

$[(CH_3)_2N]_3P$ (gas)	$[(CH_3)_2N]_3P \cdot AlCl_3$ (solid)	Assignment
	3390 W (br) (cm^{-1})	H_2O (?)
2960 MW (cm^{-1})	2940 M	ν (C-H)
2930 M		
2870 MS		
2820 M		ν^s(C-H)
2780 MS	2750 M	ν (C-H)
2445 W	2440 MW	(?)
1600 W	1600 W	
1475 (sh)	1480 (sh)	$\delta(CH_3)$
1455 MW	1460 M	
1272 M	1310 M	ν(C-N)
1204 M	1188 M	$\rho(CH_3)$
1158 MW	1130 M (br)	
1058 MW	1060 M	
956 S	995 S	ν(C-N)
940 MS (sh)		
	810 W (br)	(?)
670 MS	762 W (?)	ν(N-P)
644 W	745 W (?)	
	490 S (br)	$AlCl_3$ (?)

See Table I for key

a P-Cl stretching frequency. This latter possibility is probably not very likely.

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with $[(CH_3)_2N]_2PCl$

Reaction of a 1:1 molar ratio of $[(CH_3)_2N]_3P\cdot AlCl_3$ and $[(CH_3)_2N]_2PCl$ results in the formation of the double adduct, $[(CH_3)_2N]_2PCl\cdot[(CH_3)_2N]_3P\cdot AlCl_3$.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + [(CH_3)_2N]_2PCl \longrightarrow [(CH_3)_2N]_2PCl\cdot [(CH_3)_2N]_3P\cdot AlCl_3$$

This adduct was also formed by adding the ligands to $AlCl_3$ in the reverse order, as stated above. Since $[(CH_3)_2N]_2PCl$ is a stronger base than $[(CH_3)_2N]_3P$ however, it is necessary that an excess of $[(CH_3)_2N]_2PCl$ not be used, since it would displace the $[(CH_3)_2N]_3P$ already coordinated.

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with $(CH_3)_2NPCl_2$

Reaction of an excess of $(CH_3)_2NPCl_2$ with $[(CH_3)_2N]_3P\cdot AlCl_3$ forms another double adduct.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_2NPCl_2 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3$$

The infrared, ^1H n.m.r. and ^{31}P n.m.r. spectra of this adduct show it to be the same as the double adduct formed by addition of an excess of $[(CH_3)_2N]_2PCl$ onto $AlCl_3$.

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with PCl_3

An excess of PCl_3 reacts with $[(CH_3)_2N]_3P\cdot AlCl_3$ as shown by the following equation:

$$[(CH_3)_2N]_3P\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

The reaction seems to be complete in about 30 minutes. Again an exchange reaction is taking place between the phosphorus compounds, and again the $AlCl_3$ seems to be slowing down this exchange compared to mixing the free ligands. In spite of the excess PCl_3, $(CH_3)_2NPCl_2\cdot AlCl_3$ is not the adduct formed since we have seen that $AlCl_3$ reacts with an excess of $(CH_3)_2NPCl_2$ to form $[(CH_3)_2N]_2PCl\cdot AlCl_3$. In addition, we have already seen that no stable double adduct is formed with $(CH_3)_2NPCl_2$ and $[(CH_3)_2N]_2PCl\cdot AlCl_3$.

Reactions with Ether Adducts.

The System $(CH_3)_2NPCl_2$-$(C_2H_5)_2O$-$AlCl_3$

As stated previously, in trying to prepare $(CH_3)_2NPCl_2\cdot AlCl_3$ it was decided that disproportionation might be avoided by first forming a Lewis base-$AlCl_3$ adduct and then displacing this Lewis base with $(CH_3)_2NPCl_2$. Diethyl ether was the first base attempted.

Reaction of an excess of $(CH)_2NPCl_2$ with a diethyl ether solution of $AlCl_3$, in which the $AlCl_3$ is in the form $(C_2H_5)_2O\cdot AlCl_3$, followed by removal of the volatile material, resulted in the uptake of some dichloro ligand and consequently the displacement of some of the ether coordinated to the $AlCl_3$ in the ether solution. A very small amount of PCl_3 was evolved, presumably due to an excess of $(CH_3)_2NPCl_2$ in the ether solution, coupled with some displacement

of the ether from the $AlCl_3$ in the solution.

Reaction of a 1:1 mole ratio of $(CH_3)_2NPCl_2$ with solid $(C_2H_5)_2O \cdot AlCl_3$ produced only traces of PCl_3 but also decreased the amount of ether displaced from the $AlCl_3$.

Clearly diethyl ether was too strong a Lewis base, thus largely preventing its substitution from $AlCl_3$ by $(CH_3)_2NPCl_2$.

The System $(CH_3)_2NPCl_2$-$[(CH_3)_2CH]_2O$-$AlCl_3$

When an excess of $(CH_3)_2NPCl_2$ was allowed to react with a diisopropyl ether solution of $AlCl_3$, in which the $AlCl_3$ is in the form $[(CH_3)_2CH]_2O \cdot AlCl_3$, a much larger proportion of $(CH_3)_2NPCl_2$ was taken up than with the diethyl ether solution, a possible reflection of the decreased base strength of the diisopropyl ether. A small amount of PCl_3 was evolved along with a significant amount of isopropyl chloride. Addition of $(CH_3)_2NPCl_2$ to the nonvolatile residue from the above reaction resulted in the evolution of more PCl_3 and more isopropyl chloride and an uptake of a total of almost two moles of $(CH_3)_2NPCl_2$ per mole of original $AlCl_3$.

Contact of equimolar amounts of $(CH_3)_2NPCl_2$ and $[(CH_3)_2CH]_2O \cdot AlCl_3$ for one hour at 0^oC resulted in the conversion of approximately 25% of the isopropyl groups of the ether to isopropyl chloride. Some of the $(CH_3)_2NPCl_2$ could still be recovered. After six hours at 0^oC, about 50% of the isopropyl groups were released as isopropyl chloride. Also evolved were small amounts of diisopropyl

ether and PCl_3. No $(CH_3)_2NPCl_2$ could be recovered. Small amounts of isopropyl chloride evolved slowly but continuously over a period of several weeks. A distinct yellow color developed when the reaction was initiated. This color slowly darkened to red-brown as isopropyl chloride was evolved.

Treatment of the nonvolatile material in the reaction tube with an excess of $(CH_3)_3N$ resulted in the uptake of roughly one mole of amine per mole of original $AlCl_3$, but at the most only about one quarter of the original dichloro ligand was recoverable. If an excess of $(CH_3)_2NPCl_2$ was used originally, small amounts of $[(CH_3)_2N]_2PCl$ were also recovered, but no other phosphorus containing compounds could be pulled from the reaction tube.

Dimethylaminodichlorophosphine and diisopropyl ether do not react in the absence of $AlCl_3$. Equimolar amounts of the two compounds could be separated by fractionation after standing together overnight. No isopropyl chloride was formed.

The adduct $[(CH_3)_2CH]_2O \cdot AlCl_3$ has been found to be a white solid. If very pure, it is stable for at least three days in the vacuum system. If traces of impurities, probably mostly water, are present, however, it changes in a matter of a few hours to a moist yellow solid. Within a few days this has changed to a large amount of reddish liquid covering a red-brown solid. The liquid is mostly isopropyl chloride, along with some HCl.

The presence of isopropyl chloride seems to catalyze the further decomposition of the adduct. Once a yellowing of the adduct and formation of some liquid is noted, further darkening is quite repid. If a mixture of diisopropyl ether and isopropyl chloride are condensed onto an excess of $AlCl_3$ at -196°C, before the system has reached room temperature the contents of the tube are red-brown and the pressure in the system is well over one atmosphere, due primarily to the presence of HCl.

Formation of addition complexes between ethers and Lewis acids is known for a large number of ethers (37). With some combinations, two molecules of ether are coordinated, but this second molecule is generally lost upon exposing the solid to the pump of the vacuum system.

The stability of the adducts with respect to an ether cleavage reaction of the type (37):

$$R_2O \cdot MX_n \longrightarrow ROMX_{n-1} + RX$$

and the further decomposition:

$$ROMX_{n-1} \longrightarrow OMX_{n-2} + RX$$

is dependent upon both the Lewis acid and the nature of the R groups on the ether. The purity of the reagents used is also important. For example, ether adducts of BCl_3 and BBr_3 in general decompose readily at room temperature (38), whereas BF_3 adducts are much more stable; $(C_2H_5)_2O \cdot BF_3$ can be distilled at normal pressures without decomposition.

The greater the electron releasing power of the R group on the ether, the greater the chances for ether cleavage (37). As noted, the adduct $(C_2H_5)_2O{\cdot}BF_3$ can be distilled at atmospheric pressure (b.p. = 125°C), whereas the isopropyl ether complex with BF_3 decomposes slowly at 50°C to a polymeric substance. The isopropyl group is more electron releasing than the ethyl group.

The diethyl ether-aluminum chloride complex is stable up to about 150°C (39). Beyond this temperature it gives ethyl chloride, 1-butene, HCl, and traces of ethylene as volatile products. The residue consisted of olefinic polymers and a substance reported to be $C_2H_5AlCl(OH)$.

Triphenylmethyl ethyl ether in carbon disulfide is readily cleaved by $AlCl_3$ to give $(C_6H_5)_3CCl$ and $(C_2H_5O)_2AlCl$ (40), consistant with the more electron releasing R group being split out to form the chloride.

The adduct formed between di-n-propyl ether and aluminum chloride was reported in 1915 to be a red liquid (41). However, the observation that the diisopropyl ether-aluminum chloride adduct is a white solid which turns red, with the formation of a red liquid, probably indicates that this red liquid was not the pure adduct but rather largely a solution of the adduct in its cleavage products.

Wertyporoch and Firla found, in preparing solutions of $AlCl_3$ in n-propyl chloride and isopropyl chloride, that HCl was evolved and the solution became yellow, changing with continued evolution to a red-brown color (42). They report

the formation of unsaturated hydrocarbons which are incorporated into a complex with the $AlCl_3$. A greatly increased conductivity is also noted, but this may simply be due to the HCl being formed in the solution. The conductivity, change in color, and HCl evolution were found to increase with increased $AlCl_3$ concentration.

Brown and Wallace (32) noted the same type of reaction with the bromides. A solution of $AlBr_3$ in n-propyl bromide or isopropyl bromide readily evolved HBr and a "typical Friedel Crafts red oil" was produced. They also noted that $AlBr_3$ in ethyl bromide slowly evolved HBr with a yellowing of the solution. Removal of the ethyl bromide left a colored, non-volatile material which, when hydrolyzed, liberated an unsaturated oil. This decomposition was confirmed by Fairbrother and Scott (43), who also observed that it is catalyzed by the presence of water.

Burbage and Garrett (44) report the evolution of HBr when liquid n-butyl bromide was added to solid $AlBr_3$. A "scarlet, liquid addition complex," 1-butene-aluminum bromide, was isolated and analyzed quantitatively.

The above information suggests that the source of the isopropyl chloride might be from the reaction of diisopropyl ether with the $AlCl_3$,

$$[(CH_3)_2CH]_2O \cdot AlCl_3 \longrightarrow (CH_3)_2CHCl + (CH_3)_2CHAlCl_2$$

with the chlorine coming from the $AlCl_3$. Alternately, the source of the chloride could be from the $(CH_3)_2NPCl_2$, with

the $AlCl_3$ serving only as a catalyst.

$$(CH_3)_2NPCl_2 + [(CH_3)_2CH]_2O\cdot AlCl_3 \longrightarrow (CH_3)_2CHCl$$

$$+ \quad (CH_3)_2N-\underset{(CH_3)_2CHO}{\overset{Cl}{P}}\rightarrow AlCl_3$$

These two possibilities will now be examined, starting with the former.

1. Chlorine from $AlCl_3$

Although reactions between ethers and $AlCl_3$ are known, as we have seen, the reaction of diisopropyl ether and $AlCl_3$ has been found to be slow (a matter of hours or days) compared to the rate of the reaction when $(CH_3)_2NPCl_2$ is added to ether-$AlCl_3$ adduct (a matter of minutes). Thus, at the very least, the dichloro ligand is acting as a catalyst. The fact that no other phosphorus containing compound could be pulled from the reaction tube after reaction with $(CH_3)_3N$ supports this role, but in that only 25% or less of the $(CH_3)_2NPCl_2$ could be recovered suggests that it may well be undergoing a reaction.

2. Chlorine from $(CH_3)_2NPCl_2$

The major argument, at this point, against the second reaction is the fact that only $(CH_3)_2NPCl_2$, and small amounts of PCl_3 and $[(CH_3)_2N]_2PCl$, could be pulled from the reaction tube. It is known that an alkoxyphosphine, ROPXY, will isomerize in the presence of RCl to the form $RP^{=O}$ XY (45).

$$ROPXY \xrightarrow{RCl} RP^{=O}XY$$

Thus in the present case, $(CH_3)_2NPCl[OCH(CH_3)_2]$ would isomerize in this way due to the presence of $(CH_3)_2CHCl$ in the system.

$$(CH_3)_2NPCl[OCH(CH_3)_2] \xrightarrow{(CH_3)_2CHCl} (CH_3)_2NP^{=O}Cl[CH(CH_3)_2]$$

At what stage this reaction would take place one cannot say, but there is no doubt that the form of the phosphorus compound after reaction with $(CH_3)_3N$ would be as a phosphonyl cloride. From the table below it is clear that this new species would not be sufficiently volatile to permit its recovery from the reaction tube by pumping.

Table IV

Boiling Points of Selected Phosphorus Compounds

compound	b.p.
PCl_3	76°C (46)
$P^{=O}Cl_3$	105.8°C (46)
$(CH_3)_2CHP^{=O}Cl_2$	70°C/23mm (47) 35.5°C/1.5mm (45)
$(CH_3)_2NPCl_2$	150°C (48)
$(CH_3)_2NP^{=O}Cl_2$	194-195°C (49)
$(CH_3)_2NP^{=O}Cl[CH(CH_3)_2]$	?

This would explain why so little of the dichloro ligand was recovered under the conditions described above.

Presumably this new species would have to be isolated by extraction from the material in the reaction tube. Further discussion of this reaction will follow the examination of the following system.

The System PCl_3-$[(CH_3)_2CH]_2O$-$AlCl_3$

In the hope of more clearly viewing the interaction involving the system just described, it was decided to study the reaction of PCl_3 with the diisopropyl ether-aluminum chloride adduct. Since PCl_3 does not form a stable adduct with $AlCl_3$, and does not undergo a reaction of any kind with $AlCl_3$, it should prove a more straightforward system to observe. If it does not react with the ether adduct, PCl_3 should be easily recoverable from the system. If, on the other hand, it does react, it would not be recoverable, but would ultimately result in the liberation of $(CH_3)_2CHP^{=O}Cl_2$ after treatment with $(CH_3)_3N$.

$$PCl_3 + [(CH_3)_2CH]_2O \cdot AlCl_3 \longrightarrow (CH_3)_2CHCl + (CH_3)_2CHOPCl_2AlCl_3$$

$$(CH_3)_2CHOPCl_2 \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_2CHOPCl_2 + (CH_3)_3N \cdot AlCl_3$$

$$(CH_3)_2CHOPCl_2 \xrightarrow{(CH_3)_2CHCl} (CH_3)_2CHP^{=O}Cl_2$$

Again, at what stage the isomerization reaction forming isopropyl phosphonyl dichloride takes place is not known. Reaction with PCl_3 did indeed take place, forming $(CH_3)_2CHP^{=O}Cl_2$.

Kinnear and Perren (45) found that addition of 0.25 mole of diethyl ether to 0.5 mole each of PCl_3 and $AlCl_3$, when heated to 100°C for 7 hours, then dissolved in methylene chloride and hydrolyzed with 6 moles of water, filtered and distilled, yielded 0.19 mole of $C_2H_5P^{=O}Cl_2$. Hydrolysis of the compound to the corresponding acid apparently does occur, but such reactions are fairly slow, probably because of the insolubility of phosphonyl halides in water (50). The above system seems quite analogous, although the ether and PCl_3 were added in the reverse order, heating was not necessary, and the adduct formed was not hydrolyzed but rather was treated with $(CH_3)_3N$ to recover the $RP^{=O}Cl_2$.

Returning to our discussion of the reaction with $(CH_3)_2NPCl_2$ then, it is clear that reaction between the dichloro ligand and the ether-aluminum chloride adduct is quite probable. The bulk of the evidence, particularly the results of the reaction with PCl_3, supports the supposition that the chlorine in the isopropyl chloride evolved comes from the phosphorus compound. The data below provide more evidence to help ascertain the course of this interaction.

The System $[(CH_3)_2N]_2PCl$-$[(CH_3)_2CH]_2O$-$AlCl_3$

Reaction of equimolar amounts of $[(CH_3)_2N]_2PCl$ and $[(CH_3)_2CH]_2O \cdot AlCl_3$ for about 18 hours at room temperature resulted in the complete uptake of the monochloro ligand and the evolution of a large amount of diisopropyl ether

along with a significantly decreased amount of isopropyl chloride compared to the reaction with $(CH_3)_2NPCl_2$. This is consistant with the decreased number of chlorides on the ligand and the increased base strength of $[(CH_3)_2N]_2$-PCl over $(CH_3)_2NPCl_2$. If the chlorine in the isopropyl chloride comes from the $[(CH_3)_2N]_2PCl$, one would expect that less isopropyl chloride would be formed with $[(CH_3)_2N]_2PCl$ than with $(CH_3)_2NPCl_2$, as observed.

The System $[(CH_3)_2N]_3P$-$[(CH_3)_2CH]_2O$-$AlCl_3$

Reaction of equimolar amounts of $[(CH_3)_2N]_3P$ and $[(CH_3)_2CH]_2O\cdot AlCl_3$ resulted in the complete displacement of ether with no formation of isopropyl chloride.

$$[(CH_3)_2N]_3P + [(CH_3)_2CH]_2O\cdot AlCl_3 \longrightarrow [(CH_3)_2N]_3P\cdot AlCl_3 + [(CH_3)_2CH]_2O$$

This straightforward base displacement reaction is consistant with the assumption that, in fact, it is the phosphorus ligand which supplies the chlorine in the isopropyl chloride evolved in the above reactions. Since $[(CH_3)_2N]_3P$ has no chlorine, no isopropyl chloride is formed.

In summary, the interaction of the series $[(CH_3)_2N]_nPCl_{3-n}$, where n = 0, 1, and 2, with $[(CH_3)_2CH]_2O\cdot AlCl_3$ is consistant with the general reaction:

$$[(CH_3)_2N]_nPCl_{3-n} + [(CH_3)_2CH]_2O\cdot AlCl_3 \longrightarrow$$

$$[(CH_3)_2N]_nPCl_{2-n}[OCH(CH_3)_2]\cdot AlCl_3 + (CH_3)_2CHCl$$

In addition, some simple base displacement occurs as a competing reaction, increasing with increasing n.

DISCUSSION

The Model

The following reactions have been observed:

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + PCl_3$$

$$(CH_3)_2NPCl_2 + AlCl_3 \xrightarrow[-20^{\circ}C]{PCl_3} (CH_3)_2NPCl_2\cdot AlCl_3$$

$$2\ [(CH_3)_2N]_2PCl + AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3$$

$$[(CH_3)_2N]_2PCl\cdot AlCl_3 + [(CH_3)_2N]_3P \longrightarrow [(CH_3)_2N]_3P\cdot [(CH_3)_2N]_2PCl\cdot AlCl_3$$

$$\left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + 2\ (CH_3)_2NPCl_2$$

$$[(CH_3)_2N]_3P + AlCl_3 \longrightarrow [(CH_3)_2N]_3P\cdot AlCl_3$$

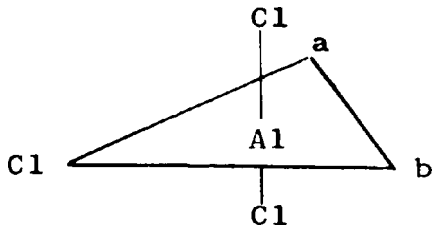
$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_2NPCl_2 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3$$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + [(CH_3)_2N]_2PCl \longrightarrow [(CH_3)_2N]_3P\cdot [(CH_3)_2N]_2PCl\cdot AlCl_3$$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

Each reaction will be discussed in the same order in which it is listed above, followed finally by a discussion of the reactions of the $[(CH_3)_2N]_{3-n}PCl_n$ series with ether-$AlCl_3$ adducts.

All of the reactions above can be understood by assuming the formation of a five-coordinate aluminum species, as shown,



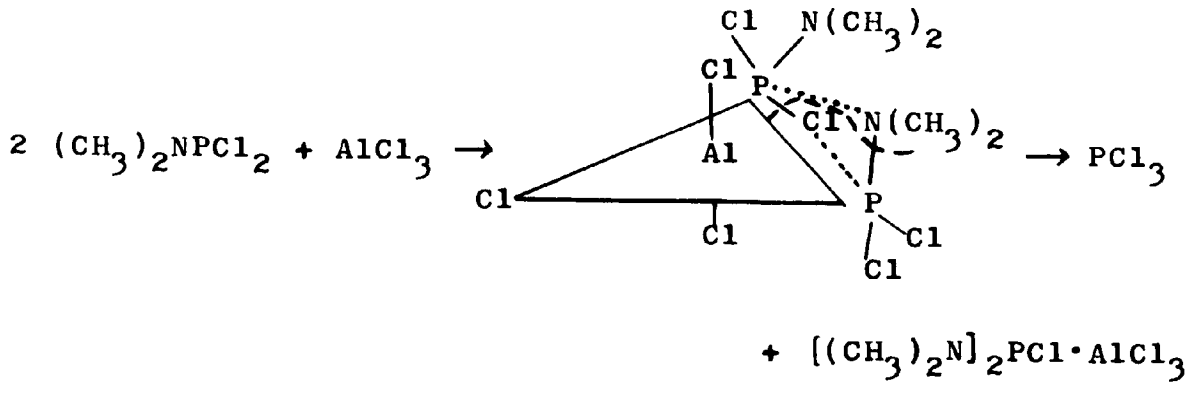
with the phosphorus species bonded at a and b. Bonding at the equatorial positions is consistant with the observation, in pentavalent phosphorus compounds, that the more electropositive groups occupy the equatorial positions (51).

The System $(CH_3)_2NPCl_2$-$AlCl_3$

The observed reaction,

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + PCl_3$$

may be rationalized by assuming first the formation of an unstable 2:1 adduct with $AlCl_3$, with a bridging chlorine and dimethylamino group as shown. Exchange of groups between the two phosphorus ligands is then easily achieved by rearrangements in the bridges (see - - - line).



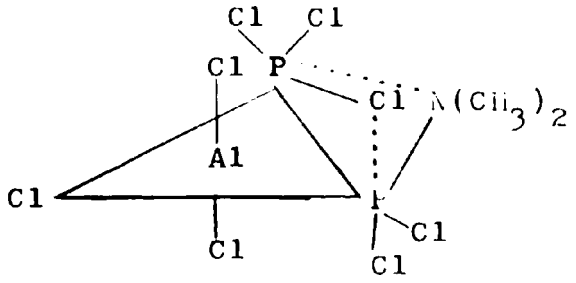
PCl_3 does not form a stable bond to the $AlCl_3$ and thus is lost, leaving the observed adduct, $[(CH_3)_2N]_2PCl \cdot AlCl_3$. This is consistant with the observation that whenever an excess of $(CH_3)_2NPCl_2$ is present in a situation such that more than one $(CH_3)_2NPCl_2$ may coordinate to the $AlCl_3$, PCl_3 is evolved. When PCl_3 is formed as a result of exchange, it coordinates only weakly to $AlCl_3$ and is lost. This, then, is the driving force for the reaction as written.

In using the above model it is necessary to assume that a five-coordinate aluminum species, with two phosphorus ligands coordinated, is possible. The formation of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$, which has been shown to be a monomer, is proof that such a species can exist. In addition, the recent work of Clemens, Sisler, and Brey (5) has shown that a five-coordinate aluminum, with two phosphorus atoms bonded, is possible, as has been previously discussed.

The above suggests why it is possible to prepare $(CH_3)_2NPCl_2 \cdot AlCl_3$ in PCl_3 solvent.

$$(CH_3)_2NPCl_2 + AlCl_3 \xrightarrow[-20^{\circ}C]{PCl_3} (CH_3)_2NPCl_2 \cdot AlCl_3$$

If one assumes that there is a weak interaction between PCl_3 and $AlCl_3$, then, with the required 1:1 amount of $(CH_3)_2NPCl_2$ and $AlCl_3$ in a large excess of PCl_3 at fairly low temperatures, the following species is likely to form:



The only meaningful exchange reaction possible here is exchange of the dimethylamino group between the two phosphorus ligands. But such an exchange does not change the nature of the adduct. It still consists of $AlCl_3$ with one PCl_3 and one $(CH_3)_2NPCl_2$ attached. Pumping on the system then releases the weakly bonded PCl_3, leaving the $(CH_3)_2NPCl_2$ as the only ligand attached to the $AlCl_3$. Disproportionation can only occur if the 1:1 adduct dissociates to provide local excesses of $(CH_3)_2NPCl_2$ which can form the unstable 2:1 adduct with $AlCl_3$.

$$(CH_3)_2NPCl_2 \cdot AlCl_3 \rightleftharpoons (CH_3)_2NPCl_2 + AlCl_3$$

$$(CH_3)_2NPCl_2 + (CH_3)_2NPCl_2 \cdot AlCl_3 \rightarrow [(CH_3)_2N]_2PCl \cdot AlCl_3 + PCl_3$$

It appears that this dissociation is quite slow, with only about 20% of the adduct decomposed after 8 days.

The System $[(CH_3)_2N]_2PCl\text{-}AlCl_3$

The original evidence to suggest a five-coordinate aluminum model for the above reactions came from the

formation of a double adduct between $[(CH_3)_2N]_2PCl$ and $AlCl_3$.

$$2\ [(CH_3)_2N]_2PCl + AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$$

The fact that this compound has been shown to be a monomer is rather clear evidence that it must contain a five-coordinate aluminum.

If an exchange of groups were to occur in this system, the resulting product would be $(CH_3)_2NPCl_2 \cdot [(CH_3)_2N]_3P \cdot AlCl_3$. We have seen that this double adduct is stable to loss of one of the ligands. Thus no reaction takes place.

The ^1H n.m.r. spectrum of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ (Fig. 7), obtained in CH_2Cl_2 solution, has not yet been completely interpreted. It consisted of a doublet of doublets, centered at -2.90 p.p.m., with splittings of 12.0 c.p.s. and 3.5 c.p.s., a doublet centered at -2.78 p.p.m. (J_{PH} = 9.5 c.p.s., with a slight further splitting of about 1 c.p.s.), and another doublet centered at -2.70 p.p.m. (J_{PH} = 11.5 c.p.s.). In addition, small peaks at -2.88 p.p.m. and -2.67 p.p.m. appear in most of the spectra taken. These latter two peaks may be attributed to impurities.

The doublet of doublets and the doublet centered at -2.78 p.p.m. are in a ratio of 1 to 3. The other doublet, at -2.70 p.p.m., varied greatly in intensity from sample to sample. In general it also increased with time for an individual sample. Since it did vary from sample to sample, it is probably attributable to a decomposition product of

the double adduct. The nature of this product is still unknown, but it is under study.

On the assumption that only the doublet of doublets and the doublet centered at -2.78 p.p.m. are directly assignable to $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$, the following tentative interpretation of the spectrum may be given.

The complex may be pictured as a bridge complex as shown in Figure 13. Each phosphorus atom is at the center of an approximate trigonal bipyramid. The two trigonal bipyramids share a side.

The proton signal of the bridged dimethylamino group would be expected to be split first by the phosphorus to which the group is attached, and then further split by the other phosphorus, resulting in a doublet of doublets. The environments of the other protons in the complex are clearly not exactly the same, but one might expect that they would be similar. If it is assumed that they are similar, the only other signal in the spectrum should be a doublet, due to a single absorption split by the phosphorus. Further splitting by the second phosphorus should be small. Indeed, the fact that each member of the doublet is split into very closely spaced doublets is consistent with this assignment. The ratio of bridge dimethylamino protons to end dimethylamino protons is 1 to 3. This interpretation fits the spectrum.

The ^{31}P n.m.r. spectrum of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ (Fig. 8), obtained in CH_2Cl_2 solution, shows two kinds of

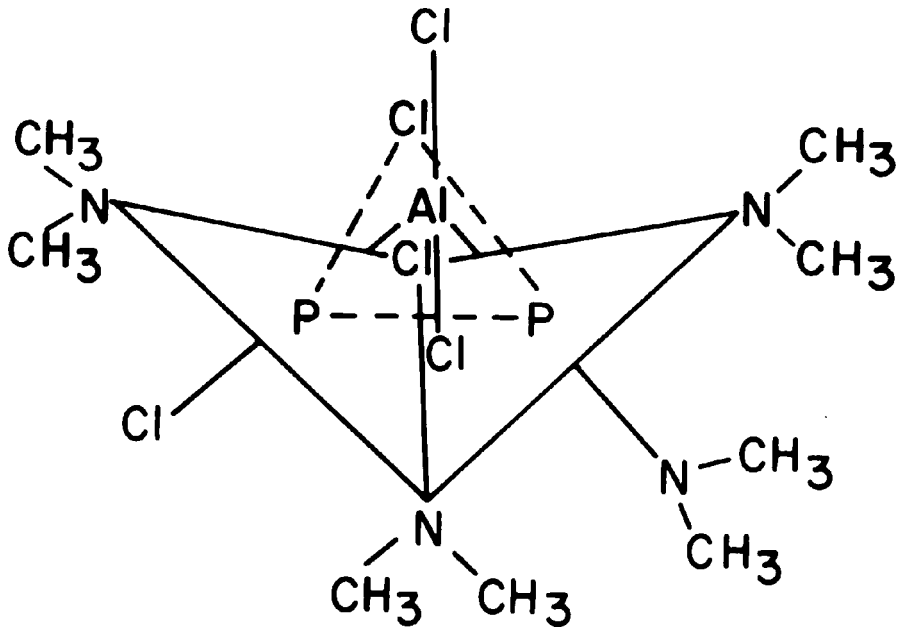


FIGURE 13 Proposed Model for $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$

phosphorus, with chemical shifts of -50 p.p.m. and -119 p.p.m. The relatively high noise level of the spectrum prohibited observation of any possible splittings of the signals. The assigned model would predict different phosphorus environments since one phosphorus has a bridged chlorine and the other phosphorus has an end chlorine. The downfield peak can probably be assigned to the phosphorus with the end chlorine, and the upfield peak to the phosphorus with the bridge chlorine on the assumption that the end chlorine would withdraw electrons more effectively from the phosphorus to which it is attached than would the bridge chlorine. Thus the former phosphorus would be less shielded, leading to a greater downfield chemical shift.

The stability of the double adduct $[(CH_3)_2N]_3P\cdot[(CH_3)_2N]_2PCl\cdot AlCl_3$, formed by the reaction

$$[(CH_3)_2N]_2PCl\cdot AlCl_3 + [(CH_3)_2N]_3P \longrightarrow [(CH_3)_2N]_3P\cdot[(CH_3)_2N]_2PCl\cdot AlCl_3$$

may be rationalized in the same manner as the adducts just discussed. The only possible meaningful exchange reaction here would involve the lone chlorine atom. But such an exchange would not alter the adduct in any way, as one would still have a $[(CH_3)_2N]_2PCl$ and a $[(CH_3)_2N]_3P$ on the aluminum chloride.

The reaction

$$\left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + 2\,(CH_3)_2NPCl_2$$

is somewhat more difficult to rationalize. Since a five-coordinate aluminum is already present in the double adduct, a reaction such as that above might require an expansion of the coordination number of aluminum to six. While this is possible, it is probably less likely than the alternative given below.

With two $[(CH_3)_2N]_2PCl$ molecules bound to a single aluminum, each bond is presumably fairly weak due to steric factors. Thus with a large excess of PCl_3 it would be possible for the following displacement reaction to take place:

$$\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3 + PCl_3 \rightleftarrows PCl_3 \cdot [(CH_3)_2N]_2PCl \cdot AlCl_3 + [(CH_3)_2N]_2PCl$$

The liberated monochloro ligand would be rapidly converted to $(CH_3)_2NPCl_2$ by the reaction with PCl_3,

$$[(CH_3)_2N]_2PCl + PCl_3 \longrightarrow 2\ (CH_3)_2NPCl_2$$

as noted by Van Wazer and Maier (35).

Exchange within the double adduct formed is also possible, again resulting in the formation of $(CH_3)_2NPCl_2$. Any PCl_3 coordinated to $AlCl_3$ would be lost upon removal of excess PCl_3 from the system.

The System $[(CH_3)_2N]_3P$-$AlCl_3$

Trisdimethylaminophosphine does not form a stable 2:1 adduct.

$$[(CH_3)_2N]_3P + AlCl_3 \longrightarrow [(CH_3)_2N]_3P\cdot AlCl_3$$

Thus a five-coordinate aluminum is not formed in this case. Presumably steric factors prevent the close approach of a second $[(CH_3)_2N]_3P$ to form a stable double adduct such as has been found with the other systems. In view of this, it is curious that a double adduct does form when the ligands are one $[(CH_3)_2N]_3P$ and one $[(CH_3)_2N]_2PCl$.

$$[(CH_3)_2N]_2PCl + [(CH_3)_2N]_3P\cdot AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot [(CH_3)_2N]_3P\cdot AlCl_3$$

The stability of this double adduct in terms of exchange of groups between phosphorus species has just been discussed.

The reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with $(CH_3)_2NPCl_2$ results in the formation of a double adduct which has been shown to be identical to the adduct formed by adding an excess of $[(CH_3)_2N]_2PCl$ to $AlCl_3$.

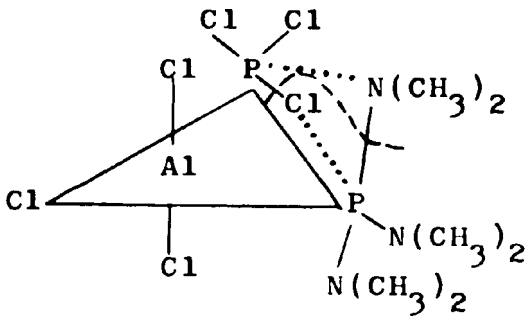
$$(CH_3)_2NPCl_2 + [(CH_3)_2N]_3P\cdot AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2\cdot AlCl_3$$

This reaction shows that an exchange of groups between two phosphorus ligands attached to $AlCl_3$, as described in the preceding paragraphs, is indeed possible.

An exchange reaction also takes place when $[(CH_3)_2N]_3P\cdot AlCl_3$ reacts with PCl_3.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

Here again one may view the interaction as involving first the formation of a five-coordinate aluminum species with bridging groups between the ligands, followed by an exchange of the bridging groups between the two phosphorus ligands.

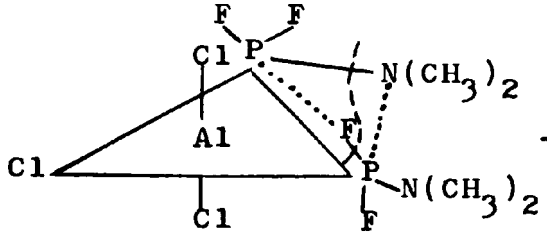


$$\rightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

The low stability of a bond between $[(CH_3)_2N]_2PCl\cdot AlCl_3$ and $(CH_3)_2NPCl_2$ results in the evolution of the latter compound.

The System $(CH_3)_2NPF_2$-$AlCl_3$

The reaction observed by Bond (33) involving $(CH_3)_2NPF_2$ and $AlCl_3$ can now be understood as a combination of two reactions; disproportionation analogous to the $(CH_3)_2NPCl_2$-$AlCl_3$ system, and halogen exchange of the type observed by Alton (12). One postulates here the formation of the unstable double adduct, $[(CH_3)_2NPF_2]_2\cdot AlCl_3$. Two essentially independent reactions may then take place; either an exchange between the two phosphorus species as occurs in the dichloro system,

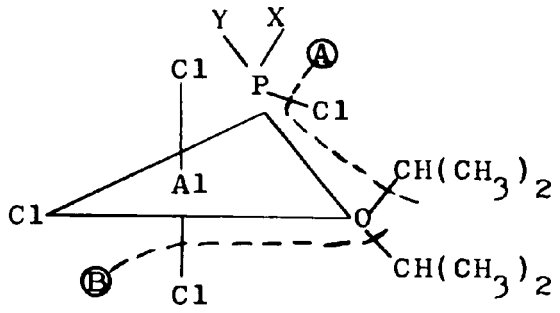


$$\rightarrow [(CH_3)_2N]_2PF\cdot AlCl_3 + PF_3$$

or else a multistep reaction involving halogen exchange between the $AlCl_3$ and the $(CH_3)_2NPF_2$, forming $(CH_3)_2NPCl_2$. Both reactions are seen to occur. As with the system studied by Alton, exchange seems to be complete, with no stable mixed halide species formed. Further exchange between the $[(CH_3)_2N]_2PF$ formed and the remaining $AlCl_3$ may also take place.

Reactions with Ether Adducts.

The ether reactions, too, can be understood in terms of the formation of a five-coordinated aluminum species. They are, in fact, analogous to the reactions involving only the phosphorus ligands. In general, we may write the adduct as



where X and Y may be Cl-, $(CH_3)_2N$-, or one of each. Isopropyl chloride may split off along line A as shown. The remaining isopropoxy group then takes the place of the chlorine on the phosphorus. If the aluminum also contributes chlorines for the formation of isopropyl chloride, it would split off via line B. It must be stated that with the reaction involving $[(CH_3)_2N]_3P$, no isopropyl chloride

was formed, indicating no splitting along line B.

Bonding in the $AlCl_3$ Adducts.

In the model just discussed, it has been assumed that bonding in each case was through the phosphorus. The reasons for this assumption will now be summarized and discussed.

$[(CH_3)_2N]_3P \cdot AlCl_3$

Since $[(CH_3)_2N]_3P$ forms only a 1:1 adduct with $AlCl_3$, it is more reasonable to assume that the aluminum is bound to the single phosphorus than to one of the three nitrogen atoms in the ligand. In addition, it would be expected that the three electron donating dimethylamino groups would enhance the electron density on the phosphorus to such a degree that the phosphorus would be quite an attractive bonding site for a Lewis acid.

The infrared spectrum of $[(CH_3)_2N]_3P \cdot AlCl_3$ is very much like that of the free ligand, $[(CH_3)_2N]_3P$, as noted previously. This close similarity implies that no great changes in symmetry have taken place in the ligand upon coordination. This could only be true if bonding were to the lone pair of the already tetrahedrally oriented phosphorus, since bonding to the planar nitrogen end of the molecule would require a rearrangement away from this planarity. The only great difference between the spectra involves the disappearance of the absorption assigned to the N-P stretch. As stated previously, such a change denotes

bonding to the phosphorus.

Another criterion used to determine bonding in adducts of this nature has been proposed by Sheppard (52) and co-workers, and has been used by Sr. Fleming and others. This involves the presence or absence of an infrared absorption in the region of 2800 cm^{-1}. It is in this region that a symmetric C-H stretching frequency characteristic of a methyl group attached to a nitrogen is found. The presence of such a band implies the presence of a lone pair of electrons on the nitrogen. Its absence implies coordination of the lone pair. In $[(CH_3)_2N]_3P$ (Fig. 10) this absorption is found at about 2820 cm^{-1}. The $[(CH_3)_2N]_3P \cdot AlCl_3$ spectrum (Fig. 11) shows essentially two broad bands at 2940 cm^{-1} and 2755 cm^{-1}, with a possible additional absorption at about 2850 cm^{-1}. It is not of sufficient quality to permit the identification of this characteristic band if it is present. Since one would expect no more than one, or possible two, nitrogens to be coordinated to the aluminum, such a band should be present. The presence of this band in the spectra of the other adducts will be refered to shortly.

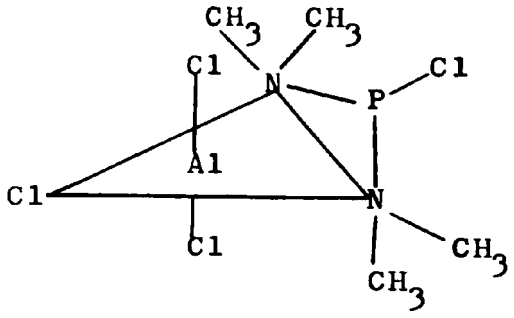
Only one clear doublet is found in the proton n.m.r. of $[(CH_3)_2N]_3P \cdot AlCl_3$. This implies that all of the protons of the molecule are equivalent, since the absorption would be expected to be split due to coupling with the phosphorus. However the broad, unresolved absorption also found in the spectrum, which may be due to solvent interactions, prevents

one at this point from relying solely on this piece of evidence.

$[(CH_3)_2N]_2PCl \cdot AlCl_3$

Essentially the same reasoning in favor of phosphorus-aluminum bonding can be given for $[(CH_3)_2N]_2PCl \cdot AlCl_3$ as for $[(CH_3)_2N]_3P \cdot AlCl_3$. First, although the ligand has two nitrogens, only one $AlCl_3$ is coordinated. There are three possibilities: either bonding is to the single phosphorus, bonding is to one of the two nitrogen, or $[(CH_3)_2N]_2PCl$ is acting as a bidentate ligand and both nitrogens are coordinated.

Taking the last possibility first, bonding of both nitrogens would require a bridging structure of the form



Two factors make this structure quite unlikely.

First, the infrared spectrum of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ (Fig. 3) is much like that of the free ligand, $[(CH_3)_2N]_2PCl$ (Fig. 2), except in the region of the N-P stretching frequency. As previously noted, this in itself implies bonding through the phosphorus. In addition, the similarity in the spectra indicates that very little change in the

symmetry of the ligand has taken place upon coordination. The symmetry of the ligand upon coordination in a manner such as to form a chelate bridge would be greatly altered. Also, the absorption at 2805 cm^{-1} in the free ligand, assigned to the C-H stretching frequency of a methyl group attached to an uncoordinated nitrogen, is found, although lessened in intensity, in the adduct spectrum. This would indicate that a least one of the nitrogens is uncoordinated.

Secondly, it has been found that $[(CH_3)_2N]_2PCl \cdot AlCl_3$ readily picks up a second ligand to form the double adduct $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$. This adduct would have to involve bonding to only one nitrogen of each ligand, with one nitrogen and one phosphorus of each ligand uncoordinated. But the infrared spectrum of the double adduct also appears much like that of the free ligand, implying essentially no symmetry change upon coordination. This could not be the case if bonding in the ligands were through the nitrogen.

That the single adduct $[(CH_3)_2N]_2PCl \cdot AlCl_3$ does not involve bonding of a single nitrogen to the aluminum is clear from the proton n.m.r. of the adduct which shows only a doublet, indicating that all protons in the molecule are equivalent. Splitting of the signal is due to the phosphorus.

All of the accumulated evidence is consistant with phosphorus-aluminum bonding in $[(CH_3)_2N]_2PCl \cdot AlCl_3$. Very little change in the symmetry of the molecule would be required for coordination, which is consistant with the

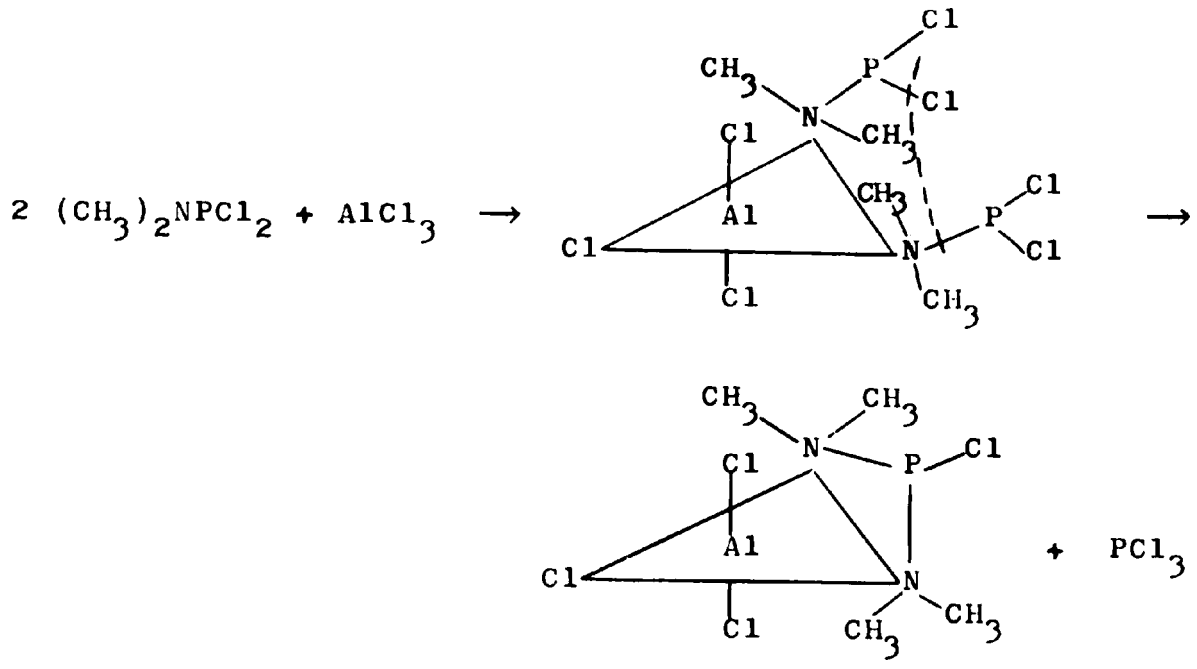
infrared spectrum; all protons are equivalent, which is consistant with the proton n.m.r.; and formation of a monomeric double adduct is readily understood in terms of the formation of a five-coordinate aluminum species.

$\underline{(CH_3)_2NPCl_2 \cdot AlCl_3}$

Bonding in the adduct $(CH_3)_2NPCl_2 \cdot AlCl_3$, by itself, would be more difficult to predict. Since it does dissociate at room temperature one might suspect a weak nitrogen-aluminum bond, as has been suggested in $(CH_3)_2NPCl_2 \cdot BF_3$ and $(CH_3)_2NPF_2 \cdot BF_3$, as previously discussed. The proton n.m.r. consists of a doublet, indicating equivalent protons split by the phosphorus. This is consistant with either phosphorus or nitrogen bonding. The infrared spectrum of the adduct is very much like that of the free ligand with no peaks radically altered, indicating no significant symmetry change in the molecule and thus implying phosphorus bonding. The absorption at 689 cm^{-1} assigned to the $N-P\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ stretch is still present in the spectrum. It would be expected that this peak would be greatly diminished in the adduct, by analogy with the other adducts just discussed, if a phosphorus-aluminum bond were formed. It is quite possible that this peak is due to dissociated free ligand rather than to the adduct itself, but this has not yet been verified. The absorption at 2810 cm^{-1} in the free ligand spectrum (Fig. 5), attributed to the C-H stretching frequency of a methyl group attached to an uncoordinated

nitrogen is found at 2800 cm^{-1} in the adduct spectrum (Fig. 6), but again this could possibly be due to dissociated $(CH_3)_2NPCl_2$ in the sample.

One piece of evidence strongly suggests that bonding in this adduct is not through the nitrogen, namely the disproportionation reaction which this adduct undergoes with an excess of dichloro ligand. If the ligands were bonded through the nitrogen, the following sequence would have to be proposed:



This would result in the formation of the bridged nitrogen, five-coordinate aluminum structure just rejected as a possible structure for the single monochloro ligand adduct. Thus, phosphorus-aluminum bonding appears most likely for $(CH_3)_2NPCl_2 \cdot AlCl_3$.

Double Adducts.

Phosphorus-aluminum bonding in the single adducts necessarily implies phosphorus-aluminum bonding in the double adducts. The infrared spectrum of $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ supports this in that it is much like that of the free ligand, suggesting very little change in symmetry upon coordination of the ligands. This could only be true with phosphorus-aluminum bonding.

Relative Strengths of Acids and Bases.

In the course of this study it was inevitable that certain observations were made concerning both the relative base strengths of the aminophosphines and the relative acid strengths of $AlCl_3$ and BH_3.

Acid Strengths

It was learned that all of the aminophosphines studied can be displaced from their $AlCl_3$ adducts by $(CH_3)_3N$. This is not entirely expected since, for example, no reaction is observed between $[(CH_3)_2N]_3P \cdot BH_3$ and $(CH_3)_3N$ (8).

$$[(CH_3)_2N]_3P \cdot BH_3 + (CH_3)_3N \longrightarrow \text{N. R.}$$

This study showed that the reaction,

$$[(CH_3)_2N]_3P \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + [(CH_3)_2N]_3P$$

proceeds to the extent of at least 80%. This is in accord with our earlier discussion comparing $AlCl_3$ and BH_3. The lower field strength of the aluminum, due to its larger size,

results in a weaker bond. In addition, the larger overall size of the $AlCl_3$ unit, compared to BH_3, would result in a longer, and thus weaker, bond to the phosphorus. The above observation, then, is completely consistant with our earlier model concerning the necessity of a close approach to phosphorus for stable bond formation.

The observed reaction,

$$[(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot AlCl_3 + [(CH_3)_2N]_2PCl$$

contrasts with the reported lack of displacement involving $[(CH_3)_2N]_2PF\cdot BH_3$ and $(CH_3)_3N$ (53).

$$[(CH_3)_2N]_2PF\cdot BH_3 + (CH_3)_3N \longrightarrow \text{N.R.}$$

Since both acid and base differ here, one cannot make any definite conclusions concerning acid strength in this case.

Base Strengths

In order to determine the relative base strengths of $[(CH_3)_2N]_2P\underline{Cl}$ compared to $[(CH_3)_2N]_2P\underline{F}$, with BH_3 as the reference acid, $[(CH_3)_2N]_2PCl\cdot BH_3$ was prepared and reacted with $(CH_3)_3N$. The following reaction did take place:

$$[(CH_3)_2N]_2PCl\cdot BH_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot BH_3 + [(CH_3)_2N]_2PCl$$

Since we have just seen that $[(CH_3)_2N]_2PF$ is not replaced

from its BH_3 adduct by $(CH_3)_3N$, it is clear that the base strength of the aminophosphine has been reduced upon replacing the fluorine by chlorine. Although this is contrary to what one might expect from simple inductive arguments, it is consistant with the observation, discussed earlier, that PCl_3 is a weaker base than PF_3 with respect to BH_3.

Relative base strengths within the series $[(CH_3)_2N]_{3-n}PCl_n$, with $AlCl_3$ as the reference acid, have also been observed. The order is:

$$PCl_3 < (CH_3)_2NPCl_2 < [(CH_3)_2N]_3P < [(CH_3)_2N]_2PCl$$

The base strength does not vary smoothly across the series, but rather reaches a peak at $[(CH_3)_2N]_2PCl$. This maximum requires an explanation involving two or more parameters. First, the base strength should rise steadily due to the electron donating ability of the dimethylamino groups. Opposing this trend may be a steric effect which prevents the close approach of the $AlCl_3$ to the phosphorus in $[(CH_3)_2N]_3P$. This would be analogous to the series $(CH_3)_{3-n}NH_n$ in which a steady rise in base strength is found with decreasing n up to $(CH_3)_2NH$, then a decrease for $(CH_3)_3N$. This has been explained in steric terms.

Another possible factor opposing a steady increase in base strength across the series is suggested by the recent work of Nordman and coworkers (10) and of Van Doorne (2). The lone pair electrons on the nitrogen are

drawn to the phosphorus in at least a partial multiple bond. This is presumably due to, or at least enhanced by, the electron attracting ability of the halogens attached to the phosphorus. This could paradoxically somewhat enhance the electron density on the phosphorus. In $(CH_3)_2NPCl_2$ the electron density on the phosphorus is fairly low because of the two chlorines, which presumably withdraw more electron density than they attract from the nitrogen. $[(CH_3)_2N]_2PCl$, however, appears to be the case in which the balance is in the other direction, with the single chlorine attracting more electron density from the nitrogen than it is withdrawing from the phosphorus. For $[(CH_3)_2N]_3P$, no enhancement of the electron donating ability of the dimethylamino groups can take place because of the absence of chlorine, and thus the base strength drops off. Another way of saying this is that a sudden drop in N-P π bonding occurs in $[(CH_3)_2N]_3P$, with a resulting decrease in its base strength.

SUMMARY

The reactions of the series $[(CH_3)_2N]_{3-n}PCl_n$ with $AlCl_3$ and several $AlCl_3$ adducts have been studied and the products identified. The ratio of the ligands to $AlCl_3$ in the adducts formed, and the stability of these adducts can be explained by assuming the formation of a five-coordinate aluminum species in the 2:1 adducts.

The ability of the ligands to coordinate is dependent upon the substituents attached to the phosphorus. The relative base strengths with respect to $AlCl_3$ as the reference acid are:

$$PCl_3 < (CH_3)_2NPCl_2 < [(CH_3)_2N]_3P < [(CH_3)_2N]_2PCl$$

The deviation from the expected steady increase in base strength with increasing dimethylamino groups may be explained in terms of a steric restriction in the case of the $[(CH_3)_2N]_3P$, or due to a sudden decrease in N-P π bonding in $[(CH_3)_2N]_3P$.

Bonding of the aminophosphines with $AlCl_3$ in all of the adducts observed appears quite certainly to be through the phosphorus. There is no evidence to suggest nitrogen-aluminum bonding.

EXPERIMENTAL

General Procedures

Standard vacuum line techniques were used throughout. To eliminate possible contamination of the adducts by stopcock grease, rubber O-ring joints and Teflon Fischer-Porter valves (4 mm needle valve, Fischer and Porter Co., Warminster, Pa.) were used to connect the reaction tube to the vacuum system. The remainder of the system was fitted with standard taper and ball joints and stopcocks greased with Apiezon-N.

Molecular weight determinations were made by dissolving a known amount of adduct, typically about 300 mg, in a known amount of methylene chloride, typically about 8 g. The vapor pressure of this solution was compared directly at $0^{o}C$ to pure methylene chloride. Each cell was connected to one arm of a manometer. Pressure differences were on the order of 1.0 mm and were read with the aid of a cathetometer.

Infra-red spectra were taken on a Perkin Elmer 337 Grating Spectrometer which has a range of 4000-400 cm^{-1}. Gas spectra were obtained in a cell with a 7 cm path length fitted with KBr windows. Liquids were run as films on KBr plates. Solids were dispersed in KBr pellets.

Nuclear magnetic resonance spectra were run on Varian Associates NMR Spectrometers. Proton n.m.r. spectra were run on an A-60 operating at 60 Mc. and ^{31}P spectra on an

HR-100 operating at 40.4 Mc. The reference for the phosphorus spectra was 85% H_3PO_4 and chemical shifts were obtained by tube interchange. All proton spectra were run in CH_2Cl_2 solvent. The solvent peak was set at its known chemical shift value of -5.30 p.p.m., compared to TMS, and the chemical shifts of the protons in question were read directly. The spectra were run by Mr. Frank Parker.

Starting Materials

Aluminum chloride (Baker and Adamson reagent grade) was purified by multiple sublimation in a stream of dry nitrogen. The sublimed aluminum chloride was transfered to the reaction tube in a glove bag flushed with dry nitrogen.

Phosphorus trichloride (Mallinckrodt reagent grade) was first condensed onto $AlCl_3$ to remove any contaminating $POCl_3$, then fractionated through traps held at -45°C, -83°C, and -196°C, the -83°C contents being used.

Dimethylamine (Matheson anhydrous) was fractionated through traps held at -83°C and -196°C. The material in the -83°C trap was used.

Trimethylamine was generated from trimethylamine hydrochloride (Eastman reagent grade) by adding 50% NaOH dropwise to the solid in the vacuum line. The material collected was fractionated through traps at -83°C and -196°C to remove water. The material in the -196°C trap was used.

Diethyl ether (Mallinckrodt anhydrous) was used without further purification.

Diisopropyl ether (Eastman reagent grade) was dried by storage over CaH_2 in the vacuum system.

Methylene chloride (Merck reagent grade) was stored in the vacuum system over Drierite prior to its use.

Diborane was obtained from the Callery Chemical Co. and was purified by distillation through traps at -78°C and -126°C to remove higher hydrides.

Dimethylaminodichlorophosphine was prepared by adapting the procedure of Burg and Slota (48) to vacuum line techniques and quantities. Typically 0.08 mole of $(CH_3)_2NH$ in 5.5 ml of anhydrous diethyl ether was added slowly to 0.046 mole of PCl_3 in 20 ml of diethyl ether at 0°C over a period of about 30 minutes. After stirring the reaction mixture for another 30 minutes the volatile material was passed through traps held at -45°C and -196°C. The -45°C trap contained the $(CH_3)_2NPCl_2$ along with some PCl_3. Refractionation of this material through traps at -45°C and -196°C resulted in pure $(CH_3)_2NPCl_2$ in the -45°C trap.

Trisdimethylaminophosphine was prepared by adapting the procedure of Holmes and Wagner (3) to vacuum line techniques and quantities. Typically 0.046 mole of PCl_3 in 10 ml of diethyl ether was added slowly to 0.30 mole of $(CH_3)_2NH$ in 20 ml of diethyl ether at 0°C over a period of about 30 minutes. Fractionation through traps at -10°C,

$-78^{\circ}C$ and $-196^{\circ}C$ effects a good separation, with the product remaining in the $-10^{\circ}C$ trap.

Bisdimethylaminochlorophosphine was prepared by direct combination of the correct stoichiometric amounts of PCl_3 and $[(CH_3)_2N]_3P$ in the vacuum system. Typically PCl_3 was condensed onto $[(CH_3)_2N]_3P$ held at $-196^{\circ}C$. The system was allowed to warm to room temperature and stirred briefly. The pure product was obtained quantitatively.

Reaction of $(CH_3)_2NPCl_2$ with $AlCl_3$

Direct Reaction

$$2\ (CH_3)_2NPCl_2 + AlCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + PCl_3$$

In a typical reaction 5.15 mmole of $(CH_3)_2NPCl_2$ was condensed onto 1.09 mmole of $AlCl_3$ at $-196^{\circ}C$ in the vacuum line. The system was warmed to $0^{\circ}C$ and was held at this temperature with occasional stirring for about 20 hours. The volatile material was pulled from the reaction tube at $0^{\circ}C$ and passed through traps held at $-45^{\circ}C$ and $-196^{\circ}C$. The $-45^{\circ}C$ trap contained 2.91 mmole of unreacted $(CH_3)_2NPCl_2$ and the $-196^{\circ}C$ trap 1.06 mmole of PCl_3. This gives a ratio of $AlCl_3$ and $(CH_3)_2NPCl_2$ reacted to PCl_3 evolved of 1 to 2.06 to 0.97. A white, non-volatile, waxy solid remained in the reaction tube. The solid melted, in a sealed capillary, at $60-65^{\circ}C$. It was very sensitive to moisture, fuming and liquifying very rapidly even in an incompletely dried, nitrogen flushed glove bag. The infra-

red spectrum of this solid was identical to that of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ prepared directly from $[(CH_3)_2N]_2PCl$ and $AlCl_3$.

A large excess of $(CH_3)_3N$ (9.27 mmole) was condensed onto a 0.91 mmole sample of the above adduct at -196°C and stirred at 0°C for 3 hours. The volatile material was pulled from the reaction tube and passed through traps held at -45°C and -196°C. The -45°C trap contained 0.63 mmole of $[(CH_3)_2N]_2PCl$, identified by its infrared spectrum, and the -196°C trap contained 8.35 mmole of $(CH_3)_3N$. This corresponds to an adduct to $(CH_3)_3N$ ratio of 1 to 1.01 and a $[(CH_3)_2N]_2PCl$ yield of 69% according to the equation:

$$[(CH_3)_2N]_2PCl \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + [(CH_3)_2N]_2PCl$$

Presumably the low volatility of the monochloro ligand (about 1 mm at room temperature) prevented its complete recovery.

In variations of the above procedure, the reactants were combined at room temperature in ratios up to about a fourfold excess of ligand and for periods of time from six hours to 49 days. In every case the disproportionation reaction took place essentially quantitatively. Several runs were made by passing the dichloro ligand over or onto $AlCl_3$ held at -23°C and -63°C. Although the reactions were incomplete, some PCl_3 was formed in each case.

To get some idea as to the speed and course of the above reaction, 2.66 mmole of $(CH_3)_2NPCl_2$ was condensed onto 2.66 mmole of $AlCl_3$ at -196°C and quickly warmed to 0°C. Time vs. Pressure readings were taken as shown below.

Time, min.	Pressure, mm
0	0
2	6
5	9
10	14
25	20
35	21
55	22
90	23

The 0°C vapor pressure of $(CH_3)_2NPCl_2$ is about 3 mm while the 0°C vapor pressure of PCl_3 is 38 mm. The low pressure, even after 90 minutes, indicates an appreciable solubility of the adduct in the PCl_3. Equilibrium conditions appear to be reached in about 25 minutes. This should be considered an upper limit since the contents of the tube consisted of a thick "slush", preventing the use of a magnetic stirrer. Thus good contact between the reactants could not be achieved.

Additional $(CH_3)_2NPCl_2$ (2.71 mmole) was condensed into the reaction tube at -196°C, the tube was quickly warmed to 0°C, and again time vs. pressure readings were taken.

Time, min.	Pressure, mm
0	0
5	16
10	22
25	27
45	30
65	30
90	30

This further reaction also appears to reach equilibrium in about 30 minutes.

The molecular weight of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ was determined by vapor pressure lowering in CH_2Cl_2 (Table V).

Table V

Molecular Weight of $[(CH_3)_2N]_2PCl \cdot AlCl_3$

p, mm	ΔP, mm	$\Delta P/P$	$n_{solvent}$, mole	Mol. Wt. $\frac{\text{wt. solute} \times (1-\Delta P/P)}{\Delta P/P \times n_{solvent}}$
147	1.7	0.0116	0.124	264 ± 35

Solute: 0.384 g.

Solvent: CH_2Cl_2

Temperature: $0^{\circ}C$.

Low Temperature, PCl_3 Solvent Reaction

$$(CH_3)_2NPCl_2 + AlCl_3 \xrightarrow[-20^oC]{PCl_3} (CH_3)_2NPCl_2 \cdot AlCl_3$$

A 2.67 mmole sample of $AlCl_3$ was suspended in 6.526 g (47.51 mmole) of PCl_3. Condensed above this frozen suspension at -196°C was 2.53 mmole of $(CH_3)_2NPCl_2$. The system was warmed to -20°C and held at this temperature, with occasional stirring, for 9 hours. Fractionation of the total volatile material pulled from the reaction tube at -20°C through traps at -45°C and -196°C produced 6.537 g (47.59 mmole) of PCl_3 in the -196°C trap and 0.28 mmole of $(CH_3)_2NPCl_2$ in the -45°C trap. Thus less than 0.1 mmole of PCl_3 was released. The ratio of $AlCl_3$ to reacted $(CH_3)_2NPCl_2$ was 1 to 0.84, presumably due to incomplete reaction. The reaction tube, when warmed to room temperature, contained a clear, fairly mobile liquid with a small amount of white solid, probably unreacted $AlCl_3$, suspended in it. After remaining at room temperature overnight, small amounts of volatile material were pulled from the reaction tube over a period of several days. After 8 days, 0.44 mmole of PCl_3 and 0.13 mmole of $(CH_3)_2NPCl_2$ were recovered.

An excess of $(CH_3)_3N$ (5.40 mmole) was condensed onto a 2.60 mmole sample of the above adduct at -196°C. The reaction tube was warmed to 0°C and held at this temperature about 18 hours. The volatile material was pulled

from the reaction tube and was passed through traps at -45°C and -196°C. The -45°C trap contained 1.61 mmole of $(CH_3)_2NPCl_2$ and the -196°C trap contained 2.09 mmole of $(CH_3)_3N$. This corresponds to an uptake of 3.31 mmole of $(CH_3)_3N$ giving a ratio of adduct to $(CH_3)_3N$ of 1 to 1.27, indicating that not all of the excess amine was recovered. In addition, only 62% of the dichloro ligand was recovered. Although the stoichiometry of this reaction was poor, probably due to insufficient pumping on the sample, it is quite clear that the reaction which took place was:

$$(CH_3)_2NPCl_2 \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + (CH_3)_2NPCl_2$$

Reaction of $[(CH_3)_2N]_2PCl$ with $AlCl_3$

$$2\,[(CH_3)_2N]_2PCl + AlCl_3 \longrightarrow \left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$$

In a typical reaction 3.83 mmole of $[(CH_3)_2N]_2PCl$ was condensed onto 0.78 mmole of $AlCl_3$ at -196°C in the vacuum system, warmed to room temperature and maintained at this temperature, with occasional stirring, for 18 hours. Pumping on the reaction mixture over a period of six days resulted in a continual, but decreasing, evolution of $[(CH_3)_2N]_2PCl$. A total of 1.99 mmole of monochloro ligand was recovered, giving an $AlCl_3$ to $[(CH_3)_2N]_2PCl$ ratio of 1 to 2.36. (In another experiment under essentially the same conditions, this ratio was 1 to 2.15.) Heating the reaction tube to 100°C for one half hour caused only a

negligible further evolution of $[(CH_3)_2N]_2PCl$. Difficulty in removing the excess monochloro ligand appears to be due to the solubility of the adduct in the free ligand, lowering the vapor pressure of the monochloro ligand to such an extent that it cannot be pumped from the adduct. To recover this excess ligand, several grams of n-hexane – in which the ligand is soluble but the adduct is not – were condensed onto the reaction mixture, stirred briefly, then pumped off. Fractionation of the material pumped from the reaction tube through traps at -45°C and -196°C allowed recovery of additional excess ligand in the -45°C trap. Repeated condensation of the hexane on the mixture, followed by rapid removal of the volatile material, coupled with repeated heating to 70°C, resulted in a final $AlCl_3$ to $[(CH_3)_2N]_2PCl$ ratio of 1 to 2.06. (A second experiment leveled off at 2.09).

When the adduct $\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$ was to be used for further study, such as for a molecular weight determination, melting point, or further reaction, the problem of excess ligand was avoided by combining the correct stoichiometric ratios of $AlCl_3$ and ligand. This resulted in a pure, dry adduct.

The melting point of the adduct was found to be 118-123°C in a sealed capillary. It decomposed above its melting point to a light yellow oil. It was soluble in methylene chloride and in chlorobenzene, although it

appeared to react in the latter. It was insoluble in benzene, hexane, chloroform, bromoform and carbon tetrachloride. The adduct reacts readily with moisture, fuming in moist air and reacting almost explosively when put in contact with liquid water.

An excess of $(CH_3)_3N$ (3.84 mmole) was condensed onto 1.49 mmole of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ at -196°C. The system was warmed to 0°C and maintained at this temperature, with occasional stirring, for two days. The volatile material was then pulled from the reaction tube and passed through traps held at -45°C and -196°C. The -45°C trap contained 1.20 mmole of $[(CH_3)_2N]_2PCl$ and the -196°C trap contained 3.32 mmole of $(CH_3)_3N$, indicating an uptake of 0.52 mmole of amine. Since this obviously corresponded to an incomplete reaction, the $(CH_3)_3N$ was condensed back onto the adduct at -196°C and pulled off three more times. The final results indicated that 1.16 mmole of $(CH_3)_3N$ was retained and 2.03 mmole of $[(CH_3)_2N]_2PCl$ was released. This represents a ratio of adduct to amine of 1 to 0.78 and a recovery of 68% of the $[(CH_3)_2N]_2PCl$ according to the equation:

$$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot AlCl_3 + 2\,[(CH_3)_2N]_2PCl$$

The molecular weight of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ was determined by vapor pressure lowering of a CH_2Cl_2 solution

(Table VI).

Table VI

Molecular Weight of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$

p, mm	ΔP, mm	ΔP/P	$n_{solvent}$, mole	Mol. Wt. = Wt. solute x (1-ΔP/P) / (ΔP/P x $n_{solvent}$)
(1) 147	0.7	0.00476	0.152	399 ± 60
(2) 147	0.8	0.00544	0.113	462 ± 60

Solute: (1) 0.291 g.

(2) 0.286 g.

Solvent: CH_2Cl_2

Temperature: 0°C

Reaction of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ with $[(CH_3)_2N]_3P$

$$[(CH_3)_2N]_2PCl \cdot AlCl_3 + [(CH_3)_2N]_3P \longrightarrow [(CH_3)_2N]_3P \cdot [(CH_3)_2N]_2PCl \cdot AlCl_3$$

A 5.12 mmole sample of $[(CH_3)_2N]_3P$ was condensed onto 1.45 mmole of $[(CH_3)_2N]_2PCl \cdot AlCl_3$ at -196°C. The system was warmed to room temperature and allowed to remain at this temperature for 5 days. Pumping on the reaction mixture over a period of two days resulted in the recovery of 3.57 mmole of $[(CH_3)_2N]_3P$ only. An infrared spectrum of the recovered liquid showed no peaks in the P-Cl region,

400-600 cm^{-1}. The 1.55 mmole of $[(CH_3)_2N]_3P$ retained corresponds to an adduct to $[(CH_3)_2N]_3P$ ratio of 1 to 1.07.

This double adduct neither reacts with nor is soluble in diethyl ether.

Reaction of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ with PCl_3

A large excess of PCl_3 (4.617 g., 33.61 mmole) was condensed onto 3.00 mmole of $\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$ at -196°C. The system was warmed to room temperature and stirred, whereupon the solid slowly reacted to form a liquid layer above the PCl_3. This reaction appeared complete in about 30 minutes. After about 24 hours the volatile material was pulled from the reaction tube and passed through traps held at -45°C and -196°C. The -45°C trap contained 4.93 mmole of $(CH_3)_2NPCl_2$ and the -196°C trap contained 30.82 mmole of PCl_3. These data correspond to an uptake of 2.79 mmole of PCl_3, giving a ratio of adduct to reacted PCl_3 to evolved $(CH_3)_2NPCl_2$ of 1 to 0.93 to 1.65. Although the reaction was incomplete and the $(CH_3)_2NPCl_2$ formed was not completely pulled from the reaction tube, the reaction observed may be written as:

$$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl \cdot AlCl_3 + 2\ (CH_3)_2NPCl_2$$

Reaction of $[(CH_3)_2N]_3P$ with $AlCl_3$

$$[(CH_3)_2N]_3P + AlCl_3 \longrightarrow [(CH_3)_2N]_3P \cdot AlCl_3$$

In a typical reaction 8.15 mmole of $[(CH_3)_2N]_3P$ was condensed onto 2.11 mmole of $AlCl_3$ at -196°C. The system was warmed to room temperature and the contents allowed to remain in contact, with occasional stirring, for 18 hours. Pumping on the reaction mixture resulted in the recovery of 5.96 mmole of $[(CH_3)_2N]_3P$. The 2.19 mmole of $[(CH_3)_2N]_3P$ retained corresponds to an $AlCl_3$ to $[(CH_3)_2N]_3P$ ratio of 1 to 1.04.

Unlike the other $AlCl_3$ adducts studied, $[(CH_3)_2N]_3P \cdot AlCl_3$ is not soluble in an excess of the free ligand. Thus if an excess of the ligand, over a 1 to 1 ratio, is present, the reaction tube contains a liquid, the free phosphorus ligand, and a solid, the adduct, with no apparent solution, even with a large excess of ligand. The melting point of the adduct was 105-112°C in a sealed capillary. It decomposed to a dark brown solid when heated above its melting point.

An excess of $(CH_3)_3N$ (2.68 mmole) was condensed onto 1.62 mmole of $[(CH_3)_2N]_3P \cdot AlCl_3$ at -196°C. The system was warmed to 0°C and maintained at this temperature for 36 hours. The volatile material was pulled from the reaction tube and passed through traps held at -45°C and -196°C. The -45°C trap contained 1.30 mmole of $[(CH_3)_2N]_3P$, and the

-196°C trap held 1.33 mmole of $(CH_3)_3N$. The latter corresponds to an uptake of 1.35 mmole of amine. Since this corresponded to an incomplete reaction, the $(CH_3)_3N$ was recondensed onto and pulled from the adduct two more times. The final results showed that 1.43 mmole of $(CH_3)_3N$ was retained and 1.35 mmole of $[(CH_3)_2N]_3P$ was recovered, corresponding to an 88% complete reaction according to the equation:

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot AlCl_3 + [(CH_3)_2N]_3P$$

The molecular weight of $[(CH_3)_2N]_3P\cdot AlCl_3$ was determined by the vapor pressure lowering of a CH_2Cl_2 solution (Table VII).

Table VII

Molecular Weight of $[(CH_3)_2N]_3P\cdot AlCl_3$

	P, mm	ΔP, mm	ΔP/P	$n_{solvent}$, mole	Mol. Wt. $\frac{\text{wt. solute} \times (1-\Delta P/P)}{\Delta P/P \times n_{solvent}}$
(1)	147	1.1	0.00748	0.127	340 ± 60
(2)	147	1.3	0.00884	0.127	297 ± 50

Solute: (1) 0.326 g.

(2) 0.334 g.

Solvent: CH_2Cl_2

Temperature: 0°C

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with $[(CH_3)_2N]_2PCl$

$$[(CH_3)_2N]_3P\cdot AlCl_3 + [(CH_3)_2N]_2PCl \longrightarrow [(CH_3)_2N]_2PCl\cdot [(CH_3)_2N]_3P\cdot AlCl_3$$

A 1.40 mmole sample of $[(CH_3)_2N]_2PCl$ was condensed onto 1.53 mmole of $[(CH_3)_2N]_3P\cdot AlCl_3$ at -196°C. After contact at room temperature for one week, only a few milligrams of volatile material could be pulled from the reaction tube, indicating the formation of the double adduct $[(CH_3)_2N]_2PCl\cdot [(CH_3)_2N]_3P\cdot AlCl_3$.

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with $(CH_3)_2NPCl_2$

A 3.00 mmole sample of $(CH_3)_2NPCl_2$ was condensed onto 1.22 mmole of $[(CH_3)_2N]_3P\cdot AlCl_3$ at -196°C. The system was warmed to room temperature and the contents of the reaction tube were allowed to remain in contact for two days. The volatile material pulled from the reaction tube consisted of 1.88 mmole of $(CH_3)_2NPCl_2$. This value indicates an uptake of 1.12 mmole of dichloro ligand and a ratio of adduct to $(CH_3)_2NPCl_2$ of 1 to 0.92.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_2NPCl_2 \longrightarrow \{[(CH_3)_2N]_2PCl\}_2\cdot AlCl_3$$

Reaction of $[(CH_3)_2N]_3P\cdot AlCl_3$ with PCl_3

A large excess of PCl_3 (4.530 g., 32.98 mmole) was condensed onto 2.11 mmole of $[(CH_3)_2N]_3P\cdot AlCl_3$ at -196°C in the vacuum system. The reaction mixture was warmed

quickly to room temperature with constant stirring. In about 30 minutes the suspension of solid adduct in liquid PCl_3 had changed to two liquid layers, with the PCl_3 on the bottom. After room temperature contact for three days the volatile material was pulled from the reaction tube and fractionated through traps held at -45°C and -196°C. The -45° trap contained 1.76 mmole of $(CH_3)_2NPCl_2$ and the -196°C trap contained 30.98 mmole of PCl_3. This corresponds to an uptake of 2.00 mmole of PCl_3. The ratio of adduct to PCl_3 retained to $(CH_3)_2NPCl_2$ evolved was 1 to 0.95 to 0.84, indicating the reaction

$$[(CH_3)_2N]_3P\cdot AlCl_3 + PCl_3 \longrightarrow [(CH_3)_2N]_2PCl\cdot AlCl_3 + (CH_3)_2NPCl_2$$

Reaction of $(CH_3)_2NPCl_2$ with $(C_2H_5)_2O\cdot AlCl_3$

Ether Solvent Reaction

A 1.63 mmole sample of $AlCl_3$ was dissolved in 4.265 g. (57.54 mmole) of $(C_2H_5)_2O$. Condensed onto this solution at -196°C was 7.48 mmole of $(CH_3)_2NPCl_2$. The reactants were warmed to room temperature and stirred for about two hours, after which the total volatile material was pulled off and passed through traps held at -63°C and -196°C. The -196°C trap contained 56.82 mmole of diethyl ether, corresponding to a retention of 0.72 mmole of ether. The contents of the -63°C trap were passed through traps held at -45°C and -196°C. The -45°C trap contained 6.85

mmole of $(CH_3)_2NPCl_2$ and the -196°C trap contained less than 0.07 mmole of PCl_3. This corresponds to a retention of 0.63 mmole of $(CH_3)_2NPCl_2$. Thus less than 50% of the ether coordinated to the $AlCl_3$ was replaced by the dichloro ligand according to the equation

$$(C_2H_5)_2O \cdot AlCl_3 + (CH_3)_2NPCl_2 \longrightarrow (CH_3)_2NPCl_2 \cdot AlCl_3 + (C_2H_5)_2O$$

Direct Reaction

A 5.79 mmole sample of $(CH_3)_2NPCl_2$ was condensed onto 5.79 mmole of solid $(C_2H_5)_2O \cdot AlCl_3$ at -196°C. Warming to room temperature resulted in the ether adduct very rapidly dissolving in the phosphorus ligand. After contact at room temperature overnight, the volatile material was pulled from the reaction tube. Fractionation of this material through traps held at -63°C and -196°C produced 0.62 mmole of $(C_2H_5)_2O$ in the -196°C trap and 5.16 mmole of $(CH_3)_2NPCl_2$ and a trace of PCl_3 in the -63°C trap. Thus only a very small proportion of ether was displaced in the absence of ether solvent and with a smaller proportion of $(CH_3)_2NPCl_2$.

Reaction of $[(CH_3)_2CH]_2O$ with $AlCl_3$

A 3.88 g. (37.96 mmole) sample of $[(CH_3)_2CH]_2O$ was condensed onto 1.45 mmole of $AlCl_3$ at -196°C. The resulting suspension was stirred for six hours at room temperature, after which the excess ether was pulled off. Retained was

1.45 mmole of $[(CH_3)_2CH]_2O$, leaving a dry, white solid. After three days at room temperature about 2 mg of $[(CH_3)_2CH]_2O$ was the only volatile material which could be pulled from the tube. An infrared spectrum of the material showed no trace of $(CH_3)_2CHCl$.

In other reactions of this ether with $AlCl_3$, some decomposition of the adduct invariably occurred. The time required for noticeable decomposition — as indicated by the formation of a yellow or red-brown color — ranged from less than an hour, even before the excess ether was removed, to several days, well after the dry, white adduct was isolated. Apparently, varying amounts of impurities, probably water, in the reactants and/or the reaction tube caused the decomposition.

Attempted Reaction of $(CH_3)_2NPCl_2$ with $[(CH_3)_2CH]_2O$

A 4.58 mmole sample of $(CH_3)_2NPCl_2$ was condensed onto 4.62 mmoles of $[(CH_3)_2CH]_2O$ at -196°C, warmed to room temperature, and left in contact for 18 hours. A quantitative separation of the mixture was made by passing the mixture through traps held at -45°C and -196°C. The infrared spectrum of a portion of the vapor above the more volatile (ether) fraction showed no trace of $(CH_3)_2CHCl$.

Reaction of $(CH_3)_2NPCl_2$ with $[(CH_3)_2CH]_2O \cdot AlCl_3$

Ether Solvent Reaction

A 7.07 mmole sample of $(CH_3)_2NPCl_2$ was condensed onto a suspension of 1.24 mmole of $AlCl_3$ in 4.69 g (45.90 mmole)

of $[(CH_3)_2CH]_2O$ at -196°C. The resulting suspension changed to a clear solution in less than one hour with stirring at room temperature. The total volatile material was pulled from the reaction tube after 3 hours contact. Fractionation of this material with traps at -45°C and -196°C resulted in the recovery of 4.66 grams of material in the -196°C trap and 6.00 mmole of $(CH_3)_2NPCl_2$ in the -45°C trap. An infrared spectrum of the vapor above the material in the -196°C trap showd that, besides the ether, small amounts of $(CH_3)_2CHCl$ and PCl_3 were present. The retention of 1.07 mmoles of $(CH_3)_2NPCl_2$ indicates that, ignoring side reactions, 86% of the ether was displaced. (In another experiment using essentially the same conditions, 90% of the ether was displaced.) The unreacted $(CH_3)_2NPCl_2$ was condensed back into the reaction tube without the ether, warmed to room temperature, and left in contact overnight. The volatile material was removed and fractionated through traps at -45°C and -196°C. In the -196°C trap was collected 0.11 g of a mixture consisting mostly of $(CH_3)_2$-CHCl and a small amount of $[(CH_3)_2CH]_2O$, and a large amount of PCl_3. In addition, 1.18 mmole of additional $(CH_3)_2NPCl_2$ was retained, giving an original $AlCl_3$ to total $(CH_3)_2NPCl_2$ ratio of 1 to 1.8. (Another experiment gave a ratio of 1 to 1.96).

Direct Reaction

In a typical reaction 7.81 mmole of $(CH_3)_2NPCl_2$ was condensed onto 7.87 mmole of $[(CH_3)_2CH]_2O \cdot AlCl_3$ at -196°C,

warmed to 0°C and stirred at this temperature for 7 hours. A light yellow-brown color developed in the reaction mixture at this point. (All reactions attempted showed some color formation at this stage, from very light yellow to dark red-brown.) The volatile material pulled from the reaction tube consisted of mostly $(CH_3)_2CHCl$, at least 7.8 mmole, possibly more, and a small amount of $[(CH_3)_2CH]_2O$ as shown by the infra-red spectrum of the material. (Other reactions showed small amounts of PCl_3 evolved, especially if an excess of $(CH_3)_2NPCl_2$ was used.) No $(CH_3)_2NPCl_2$ was recovered.

Excess $(CH_3)_3N$ (over 7 mmole) condensed into the reaction tube resulted in the release of small amounts of $(CH_3)_2CHCl$ and $[(CH_3)_2CH]_2O$ and 0.89 mmole of $(CH_3)_2NPCl_2$. The latter was conclusively identified by its vapor pressure (3 mm at 0°C, 6 mm at 25°C) and its infrared spectrum. Thus only about 11% of the $(CH_3)_2NPCl_2$ was recovered. (All other reactions produced from 0 to 25% of the dichloro ligand.) The amount of $(CH_3)_3N$ retained in this particular reaction was not measured, but other reactions which were run indicate a 1:1 pick up of amine. (Three different reactions gave ratios of adduct to $(CH_3)_3N$ of 1:1.2, 1:0.8, and 1:1.1).

Since it was quickly found qualitatively that relative amounts of products varied from reaction to reaction, depending on the purity of the original ether-adduct — determined by the degree of color developed during

the reaction – the reaction time, and the relative proportions of reactants, no consistant efforts were made to separate the $(CH_3)_2CHCl$, $[(CH_3)_2CH]_2O$, and PCl_3 which usually came off during the course of each reaction. Estimates of the relative amounts for the above and later reactions were made by observations on the vapor pressure above the mixture, and the relative peak intensities of the individual species in an infrared spectrum of the mixture.

Reaction of $[(CH_3)_2N]_2PCl$ with $[(CH_3)_2CH]_2O \cdot AlCl_3$

A 3.63 mmole sample of $[(CH_3)_2N]_2PCl$ was condensed onto 3.53 mmole of $[(CH_3)_2CH]_2O \cdot AlCl_3$ at -196°C. A very light yellow color developed slowly as the reaction mixture stood, with occasional stirring, over about 18 hours at room temperature. The volatile material was pulled from the reaction tube and passed through traps held at -45°C and -196°C. The -196°C trap contained mostly $[(CH_3)_2CH]_2O$, roughly 2.5 mmole, with some $(CH_3)_2CHCl$. Only a trace of $[(CH_3)_2N]_2PCl$ was recovered in the -45°C trap.

A second reaction produced essentially the same results except that the reaction was a yellow-brown color and a higher proportion of $(CH_3)_2CHCl$ was obtained.

Reaction of $[(CH_3)_2N]_3P$ with $[(CH_3)_2CH]_2O \cdot AlCl_3$

A 1.53 mmole sample of $[(CH_3)_2N]_3P$ was condensed onto 1.52 mmole of $[(CH_3)_2CH]_2O \cdot AlCl_3$ at -196°C. The mixture was

stirred at room temperature for 5 hours and the volatile material pumped off. No yellow color developed in this reaction. The final product was a dry, white solid. Fractionation of the volatile material through traps held at -45°C and -196°C produced 1.50 mmole of $[(CH_3)_2CH]_2O$ in the -196°C trap, and a trace of $[(CH_3)_2N]_3P$ in the -45°C trap. Thus a straightforward base displacement reaction occurred in this case.

$$[(CH_3)_2N]_3P\cdot AlCl_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot AlCl_3 + [(CH_3)_2N]_3P$$

Reaction of PCl_3 with $[(CH_3)_2CH]_2O\cdot AlCl_3$

A 3.14 mmole sample of PCl_3 was condensed onto 3.10 mmole of $[(CH_3)_2CH]_2O\cdot AlCl_3$ at -196°C. The mixture, which consisted of a white solid and a clear colorless liquid, was maintained with some stirring at 0°C for about 18 hours. The volatile material was pulled from the reaction tube over a period of 5 hours. Fractionation of this material through traps held at -45°C and -196°C produced 3.38 mmole of $(CH_3)_2CHCl$. Very small amounts of $(CH_3)_2CHCl$ were still being evolved at this time.

Treatment of the clear viscous liquid in the reaction tube with excess $(CH_3)_3N$ resulted in the release of small amounts of $[(CH_3)_2CH]_2O$, $(CH_3)_2CHCl$, and a large amount of a liquid with a room temperature vapor pressure of about 1 mm. The infrared spectrum of this liquid was essentially

that of $(CH_3)_2CHPOCl_2$ (45).

Reaction of $[(CH_3)_2N]_2PCl\cdot BH_3$ with $(CH_3)_3N$

A 2.43 mmole sample of $(CH_3)_3N$ was condensed into a U-tube at -196°C adjacent to one containing a 2.82 mmole sample of $[(CH_3)_2N]_2PCl\cdot BH_3$, prepared by the direct combination of $[(CH_3)_2N]_2PCl$ and B_2H_6. As the amine warmed slowly to room temperature, the stopcock separating the two reactants was opened and the adduct was stirred with a magnetic stirrer. The pressure in the system increased slowly until all of the amine had vaporized, then decreased slowly and steadily over a period of about two hours, at which time it leveled off at about 10 mm. More $(CH_3)_3N$ (4.13 mmole) was condensed into the system at -196°C and then slowly warmed to room temperature. Again the pressure increased as the amine warmed up and again it decreased after all of it had vaporized. After a total contact time of about 8 hours the volatile material was pulled from the reaction tube and fractionated through traps held at -45°C and -196°C. The -196°C trap held 3.84 mmole of $(CH_3)_3N$ and the -45°C trap contained a clear, colorless liquid and white, easily sublimable, needle-like crystals. The liquid was identified as $[(CH_3)_2N]_2PCl$ by its infrared spectrum. The crystals were $(CH_3)_3N\cdot BH_3$. The ratio of adduct to amine picked up was 1 to 0.96, indicating an essentially complete reaction according to the equation:

$$[(CH_3)_2N]_2PCl\cdot BH_3 + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot BH_3 + [(CH_3)_2N]_2PCl$$

APPENDIX

Chemical Shifts

Compound	^1H Shift, p.p.m. (relative to TMS)	^{31}P Shift, p.p.m. (relative to H_3PO_4)
PCl_3	—	-219
$(CH_3)_2NPCl_2$	-2.82	-166 (34)
$(CH_3)_2NPCl_2 \cdot AlCl_3$	-3.57	-322
$[(CH_3)_2N]_2PCl$	-2.65 (54)	-160 (34)
$[(CH_3)_2N]_2PCl \cdot AlCl_3$	-3.25	-268
$[(CH_3)_2N]_3P$	-2.43 (54)	-123 (34)
$[(CH_3)_2N]_3P \cdot AlCl_3$	-2.62 (multiplet at -2.69)	-56 or -98
$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$	H_{end} -2.90	PCl_{end} -119
	H_{bridge} -2.78	PCl_{bridge} -50

Coupling Constants

Coupled Atoms	Coumpound	Value of J, c.p.s.
$\underline{P}NC\underline{H}$	$(CH_3)_2NPCl_2$	12.6 (54)
	$(CH_3)_2NPCl_2 \cdot AlCl_3$	13.2
	$[(CH_3)_2N]_2PCl$	12.1 (54)
	$[(CH_3)_2N]_2PCl \cdot AlCl_3$	11.0
	$[(CH_3)_2N]_3P$	8.8 (54)
	$[(CH_3)_2N]_3P \cdot AlCl_3$	10.5
$\underline{P}NC\underline{H}_{end}$	$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$	9.5
$\underline{P}NC\underline{H}_{bridge}$	$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$	12.0
$\underline{P}PNC\underline{H}_{end}$	$\{[(CH_3)_2N]_2PCl\}_2 \cdot AlCl_3$	~1

$\underline{P}PN\underline{C}\underline{H}_{bridge}$	$\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$	3.5
$\underline{P}Al\underline{P}$	$\left\{[(CH_3)_2N]_2PCl\right\}_2 \cdot AlCl_3$	349

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