(5.2 mmol) was refluxed in diethyl ether for 3–6 hr. The reaction mixture was then stripped of solvent by evaporation under vacuum, and the remaining oily red material was dissolved in a minimum of dichloromethane and chromatographed on Florisil. Elution with heptane gave a bright yellow band containing $(CO)_3MnB_8H_{13}$, which, if allowed to stand for several hours, showed very definite signs of decomposition.

A second band was eluted using dichloromethane, after preliminary experiments showed that mixtures of heptane and dichloromethane produced no further separations. Evaporation of the solvent and recrystallization from hot heptane produced reddish orange crystals of IV. Tetrahydrofuran removed the final product, which was isolated and identified as I. In addition, a brownish band was often left which could be eluted with acetone. However, this material was very unstable and no attempt was made to characterize it. Yields for a typical reaction were as follows: I, 0.2699 g (0.836 mmol), 15.9%; IV, 0.0106 g (0.03 mmol), 0.63%.

The mass spectrum for IV, 2-Et_2O-6-$Mn(CO)_3B_9H_{12}$, was quite similar to that for 2-THF-6-$Mn(CO)_3B_9H_{12}$. Mass envelopes were again observed at values corresponding to parent mass, P, P – 2(CO), P – 3(CO), and P – (Et_2O + CO). Below this value, envelopes characteristic of boron hydride fragmentation patterns were present. Exact *m*/*e* determination verified the identity of a parent fragment: calcd for $^{55}Mn(^{12}C^{16}O)_3{}^{11}B_9{}^1H_{12}\cdot{}^{16}O(^{12}C_2{}^1H_5)_2$, 324.1737; found, 324.1772. Other characterization data are in Tables IV–VI and Figure 5.

$[Me_4N]^+[6\text{-}(CO)_3\text{-}6\text{-}ReB_9H_{12}]^-$, V. The white $Re(CO)_5Br$, 1.960 g (4.83 mmol), was allowed to react in refluxing tetrahydrofuran with 0.995 g (6.62 mmol) of KB_9H_{14} for 3–6 hr. The solvent was evaporated and the residue chromatographed on Florisil. Two yellow materials were eluted using dichloromethane and THF. The covalent 2-THF-6-$(CO)_3$-6-ReB_9H_{12} was assumed to be the species eluted by dichloromethane. This material was extremely air and water sensitive, however, and has not been fully characterized. The THF eluent contained the 6-$(CO)_3$-6-$ReB_9H_{13}^-$ anion which was isolated as the tetramethylammonium salt in a yield of 1.0321 g (2.27 mmol), 47%. Characterization data are in Tables IV–VI.

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Registry No. I, 41729-34-4; II, 51801-39-9; III, 51801-38-8; IV, 51801-37-7; V, 51801-36-6; KB_9H_{14}, 39296-28-1; $Mn(CO)_5Br$, 14516-54-2; $Re(CO)_5Br$, 14220-21-4; ^{11}B, 14798-13-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2261.

Contribution from the Departments of Chemistry, the University of Michigan,
Ann Arbor, Michigan 48104, and the University of Utah, Salt Lake City, Utah 84112

Preparation and Structure of Trifluorophosphine-Trichloroalane and a Study of Related Acid-Base Systems

E. R. ALTON, R. G. MONTEMAYOR, and R. W. PARRY*

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Aluminum chloride reacts with an excess of trifluorophosphine under pressure to give a compound of formula $F_3P\cdot AlCl_3$. Molecular weight and nmr data support an ethane-like structure involving a P–Al bond. The compound undergoes halogen exchange to give PCl_3 and AlF_3. Evidence for interaction of $Al_2(CH_3)_6$ with both PF_3 and NH_3 was found, but all attempts to bring about reaction between $Al_2(CH_3)_6$ and CO were unsuccessful. No reaction could be detected between CO and Al_2Cl_6, or between PF_3 and BF_3. About 2.5 mole % of Al_2Cl_6 will dissolve in excess PCl_3 at 130°, but the solid precipitates out almost completely when the temperature is lowered to 25°. In agreement with observations of Holmes, we find no evidence for compound formation between PCl_3 and $AlCl_3$.

The reaction between PF_3 and B_2H_6 gives the well-known compound $F_3P\cdot BH_3$ even though inductive effect arguments suggest that PF_3 should not be a significant Lewis base.[1] Theoretical hyperconjugation type arguments[2] which were advanced to explain the stability of F_3PBH_3 suggested that a study of the system F_3P-Al_2Cl_6 would be of interest. Such a study, completed in this laboratory, has resulted in the preparation and characterization of the compound $F_3P\cdot AlCl_3$ as a monomeric, presumably ethane-like structure with a P–Al bond. Inasmuch as recent work[3] has shown that $[(CH_3)_2N]_2PCl$ reacts with $AlCl_3$ to give an ionic species containing the $AlCl_4^-$ anion, the ethane-like structure here is significant.

The System Aluminum Chloride-Phosphorus Trifluoride

Freshly prepared, scrupulously dry aluminum chloride reacts with phosphorus trifluoride at 8 atm pressure in a sealed glass bomb. At room temperature and the conditions used in this study the reaction was essentially quantitative after 4 hr (Table I). Shorter periods of time or lower pressures usually produced incomplete reaction. Longer periods of time or certain still incompletely defined impurities promoted a halide shift. The overall equation is

$$F_3P(g) + Al_2Cl_6(s) \rightarrow F_3P\cdot AlCl_3(s) \rightarrow AlF_3(s) + PCl_3(l)$$

The halide shift occurs spontaneously and fairly rapidly above −20° when the large excess of PF_3 is removed. Excess PF_3 above the solid seems to have an inhibitory effect on halogen transfer. One of the most reasonable possibilities for an intermediate in the halogen-transfer process would involve possible P–F–Al and P–Cl–Al bridge structures in which the aluminum assumes coordination numbers of 5 or 6 in the activated complex.[4] If this model is assumed, the

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* To whom correspondence should be addressed at The University of Utah.

(1) R. W. Parry and T. C. Bissot, Jr., *J. Amer. Chem. Soc.*, 78, 1524 (1956).

(2) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, 12, 266 (1958).

(3) M. G. Thomas, R. L. Kopp, C. W. Schultz, and R. W. Parry, submitted for publication in *J. Amer. Chem. Soc.*

inhibitory role of excess PF_3 can be attributed to the loose blocking of these open coordination sites on the aluminum through coordination of PF_3 molecules. Under these conditions halogen-bridge formation would be inhibited and halogen exchange retarded. At low temperatures (below $-25°$) the complex $F_3P{\cdot}AlCl_3$ is a white solid; because of rapid halogen exchange it converts to a heterogeneous paste as it warms toward room temperature.

The phosphorus trifluoride in $F_3P{\cdot}AlCl_3$ can be displaced from the complex by dimethyl and diethyl ethers and by trimethylamine. In each case the expected new aluminum chloride coordination compound is formed. Solubility problems complicated molecular weight measurements. Solvents which froze above $-25°$ were ruled out by halogen-exchange processes. Solvents such as ethers, amines, alcohols, etc., were ruled out as a result of easy PF_3 displacement. Successful molecular weight measurements were achieved, however, by using liquid PF_3 as a solvent at $-112°$. Vapor pressure depression techniques gave an experimental molecular weight of 202 which is in fair agreement with the theoretical value of 221.4. The deviation of about 10% may be explained by experimental difficulties which were extreme. Observations on solubility also provided interesting information about $F_3P{\cdot}AlCl_3$. While $F_3P{\cdot}AlCl_3$ is soluble in excess liquid PF_3 at $-112°$, all of its decomposition products, Al_2Cl_6, PCl_3, and AlF_3, are insoluble in liquid PF_3. It was also noted that very slow halogen exchange to generate AlF_3 occurred in liquid PF_3 at $-112°$. While excess PF_3 vapor retards halogen exchange in the solid, it cannot block exchange completely in the liquid.

The structure of the complex was finally established from nmr measurements using a solution of $F_3P{\cdot}AlCl_3$ in $CDCl_3$. This solvent dissolved enough of the complex for study, while separate studies showed that it did not displace any PF_3. The ^{31}P nmr spectrum (Figure 1) of $F_3P{\cdot}AlCl_3$ in $CDCl_3$ at $-30°$ showed a 1:3:3:1 quartet at δ -104.4 ppm (orthophosphoric acid standard) with a J_{FP} of 1392 ± 5 Hz. Uncoordinated PF_3 in $CDCl_3$ appears at δ -104.0 ppm (OPA) with a J_{FP} of 1410 Hz. The phosphorus in the related $F_3P{\cdot}BH_3$ appears at δ -107 ppm (OPA).[5] The existence of the 1:3:3:1 quartet shows clearly that the integrity of the F_3P unit has been maintained in coordination. This fact suggests a P-Al bond.

The ^{19}F spectrum of $F_3P{\cdot}AlCl_3$ at $-50°$ showed a 1:1 doublet at δ 31.5 ± 0.1 ppm from $CFCl_3$. Because the doublet was very close to that expected for free F_3P in $CDCl_3$ solution, it was essential to show that a complex was being measured and not free PF_3 resulting from slow displacement of PF_3 by the solvent. This fact was demonstrated by placing 0.3 mmol of $F_3P{\cdot}AlCl_3$ and 1.0 mmol of excess PF_3 in an nmr tube containing enough $CDCl_3$ to give a homogeneous solution. At $-50°$ two sets of doublets could be clearly seen; one was at δ 31.3 ppm; the second was again at 31.5 ppm. Figure 2a shows one member of this doublet; the area of the free PF_3 peak is very close to 3 times the area of the $F_3P{\cdot}AlCl_3$ peak. Another test of the same point was made by adding 0.52 mmol of $F_3P{\cdot}AlCl_3$ and 0.53 mmol of F_3P to an nmr tube containing $CDCl_3$ as a solvent. At $-50°$ two sets of doublets of equal area were found. One member of this doublet is shown in Figure 2b. In an independent experiment a 0.50-mmol sample of PF_3 was dissolved in $CDCl_3$ in a comparable nmr tube. A doublet at δ 31.2 with J_{PF} of 1430 Hz was observed. It is significant that the ^{19}F nmr shows only one kind of fluorine atom in $F_3P{\cdot}AlCl_3$. This fact also argues strongly for an Al-P rather than a halogen-bridged or ionic structure.

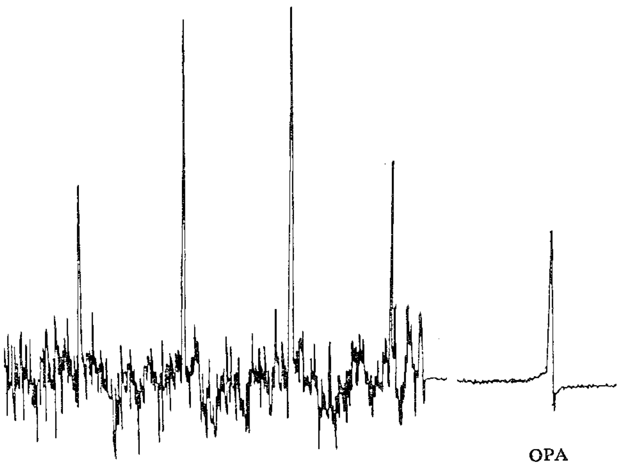


Figure 1. ^{31}P nmr spectrum of $PF_3{\cdot}AlCl_3$ in $CDCl_3$ at $-30°$. δ -104.5 ppm; J_{PF} = 1392 Hz.

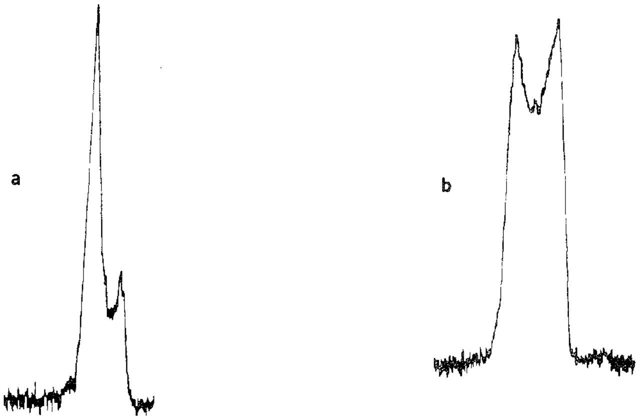
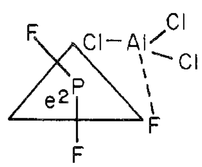


Figure 2. ^{19}F spectra: (a) 1.03 mmol of PF_3, 0.32 mmol of $PF_3{\cdot}AlCl_3$ in $CDCl_3$; (b) 0.53 mmol of PF_3, 0.52 mmol of $PF_3{\cdot}AlCl_3$ in $CDCl_3$.

While the idea of an Al-P bond is strongly supported by these data, several unattractive but real possibilities cannot be ruled out completely. For example one might suggest a halogen-bridge structure such as $Cl_2AlCl{\cdot}PF_3$. In terms of geometry, a five-coordinate phosphorus atom with an electron pair as one of the stereochemically active coordinated units would be demanded. Such a structure would then be required.



Because of the open site on the aluminum, bridging of the equatorial (or axial) fluorine to the aluminum would be expected, thus differentiating at least two kinds of fluorine atoms (and perhaps even three for an axial bridge). All fluorine atoms are the same experimentally. One might argue that pseudorotation in this structure with the Cl^- as the fixed equatorial unit could equalize all fluorines, but such pseudorotation would have to be carried out with Al-

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(4) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 81, 1084 (1959).

(5) R. W. Rudolph, Doctoral Dissertation, University of Michigan, 1966.

F bridge breaking and with movement of the electron pair to an axial position. In our judgment, such a dynamic model is quite improbable in view of the nature of an Al-F interaction, but it is not completely excluded.

Similarly one might postulate a structure $F_2PF \cdot AlCl_3$. Again in a stable structure of this type one fluorine would differ from the other two. In order to see nmr equivalence in such a case, rapid formation and dissociation of the complex would be required, and nonequivalence of fluorine at low temperatures, where one sees differences between free and coordinated PF_3, might be expected. Such differences were not observed. Again we believe that a model containing only a fluoride bridge is quite improbable but not completely eliminated. Certainly the evidence argues most easily for an Al-P linkage.

The ^{19}F spectrum of the mixture of $F_3P \cdot AlCl_3$ and F_3P is temperature dependent. At −60° distinct ^{19}F signals corresponding to $F_3P \cdot AlCl_3$ and free PF_3 are clearly visible at a separation of 17 Hz. At about −35° the separation is 2 Hz suggesting an exchange process involving fluorine atoms with an activation energy of about 2.0 kcal.[6] Two types of exchange might be considered. One involves exchange between complexed and free PF_3 molecules; the second would involve exchange of fluoride ions between free and bound PF_3 under the influence of the coordinated $AlCl_3$. In the first case where PF_3 units are exchanging, P-F coupling would be retained. In the second, where exchange of fluorides on phosphorus occurs, the P-F coupling would be expected to collapse. Since P-F coupling is retained in all experiments, exchange of PF_3 molecules is indicated. Exchange of PF_3 molecules could be easily carried out at the low temperatures (−40° and up) and with the very low activation energy (2.0 kcal[6]) found, by simple expansion of the coordination number of aluminum to 5 or 6 rather than the 4 of the original $Cl_3Al \cdot PF_3$.[7] The resulting transition-state species $[Cl_3Al \cdot 2PF_3]$ might well resemble the stable and well-established five-coordinate complex of aluminum $H_3Al(N(CH_3)_3)_2$.[8] The exchange study continues. It is worthwhile to point out an interesting fine point here which relates to the exchange process. We saw quite clearly that the reaction between $Al_2Cl_6(s)$ and $PF_3(g)$ or $PF_3(soln)$ does not seem to be reversible. The complex is formed slowly at room temperature and decomposes slowly. In this process PF_3 must displace another $AlCl_3$ unit, bound by two bridge bonds. This is quite a different process from the displacement of one PF_3 by another through the temporary expansion of the coordination number of aluminum to 5.

The System Phosphorus Trichloride-Aluminum Trichloride

The system PCl_3-Al_2Cl_6 was first studied by Holmes,[9] who found no evidence of stable compound formation. The conclusion of Holmes has been confirmed here. Extreme care was used in applying those techniques which had previously produced $F_3P \cdot AlCl_3$. No identifiable compound was ever found. At 130° about 2.5 mole % of Al_2Cl_6 dissolves in liquid PCl_3 in a sealed tube; when the tube is cooled to 25°, all except traces of the dissolved Al_2Cl_6 precipitates out. Certainly no PCl_3 complex comparable to $F_3P \cdot AlCl_3$ forms at room temperature.

The System Aluminum Chloride-Carbon Monoxide

In view of the known similarities in the coordination chemistry of PF_3 and CO, an attempt was made to prepare an $AlCl_3 \cdot CO$ adduct through the use of those techniques which had been successful for $F_3P \cdot AlCl_3$. No reaction was ever observed even though high-purity freshly prepared Al_2Cl_6 was used under pressures ranging from 9 to 87 atm. Temperatures of the experiments ranged from 25 to 100°.

Other Systems

1. **Aluminum Trimethyl-Phosphorus Trifluoride.** When PF_3 and $Al_2(CH_3)_6$ were allowed to mix at room temperature under PF_3 pressures ranging up to 12 atm, evidence for interaction *was* obtained. The liquid products appeared to be a complex mixture containing alkylphosphines, but the mixture was not resolved. Hydrolysis experiments after reaction yielded only a fraction of the methane expected from the original $Al_2(CH_3)_6$ used. Complex formation to give unstable $F_3P \cdot Al(CH_3)_3$ followed by exchange of fluorines and methyl groups is suggested by analogy to the known $F_3P \cdot AlCl_3$ case.

2. **Aluminum Trimethyl-Carbon Monoxide.** This system gave no evidence for reaction under temperatures ranging up to 100° and pressures ranging up to 12 atm of CO. Starting materials were recovered unchanged.

3. **Ammonia-Aluminum Trimethyl.** Ammonia and aluminum trimethyl reacted at −78° to give a compound of formula $[(CH_3)_3AlNH_3]_n$. Molecular weight measurements in liquid ammonia indicated that $n = 1$. A species with C_{3v} geometry was suggested from the formula only.

4. **Boron Trifluoride-Phosphorus Trifluoride.** No reaction was observed using PF_3 partial pressures of 8 atmospheres.

Discussion

The existence of $F_3P \cdot AlCl_3$ indicates that not all of the coordination chemistry of PF_3 can be rationalized through $d\pi$-$d\pi$ bond formation. The data cited here support earlier arguments[10] to the effect that the lone pair of electrons on PF_3 is available for σ bonding if subjected to a high field at short metal-phosphorus bond distances. The phosphorus-metal distance is frequently determined by the size of the distortion energies required to convert the Lewis acid into a bonding configuration. In BF_3, distortion energies of BF_3 are high, and close approach of F_3P and BF_3 is effectively blocked. No $F_3P \cdot BF_3$ complex forms. In $AlCl_3$, because of the larger size of the aluminum, the required four-coordination number is easily obtained; in fact, it exists in Al_2Cl_6 itself before reaction and part of the problem involves $AlCl_3$ displacement. Higher coordination numbers of aluminum are also quite common. Thus a relatively low distortion energy of $AlCl_3$ would be required to place it in a bonding configuration where close approach of P and Al would be possible. The foregoing arguments are also useful in postulating five-coordinate aluminum as a transitory species for PF_3 exchange processes.

The failure of PCl_3 to bond to $AlCl_3$ could be related to the larger size of the chlorides and to chloride-chloride repulsion which prevents the short Al-P distances needed for bonding. In terms of size and repulsion arguments, $(CH_3)_3Al$ and Cl_3Al are roughly comparable (van der Waals

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(6) This is an order of magnitude value which approaches the limit of the method used.

(7) Muetterties and Phillips[4] found activation energies of about 4 kcal for processes involving fluoride exchange in a number of chalcogen and halogen fluorides.

(8) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, 2, 508 (1963).

(9) R. R. Holmes, *J. Inorg. Nucl. Chem.*, 12, 266 (1960).

(10) R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, 89, 1621 (1967).

radius: CH_3, ~2.0; Cl, ~1.80; F, ~1.35).[11] The interaction of both with PF_3 to form a complex such as $F_3P{\cdot}AlCl_3$ is reasonable. In contrast, the data from these studies indicate that CO will not react with either $AlCl_3$ or $Al(CH_3)_3$. This fact suggests that CO is a significantly weaker σ-bond forming ligand than is PF_3.

Experimental Section

Materials Used. 1. Aluminum Chloride. Anhydrous, high-purity aluminum chloride was prepared by burning high-purity commercial aluminum (reagent grade) in reagent grade dry chlorine gas. An all-glass apparatus with no internal joints was used; the Al_2Cl_6 was condensed in a cooled bulb containing predried glass wool. The entire glass reaction apparatus was weighed before reaction. After reaction was completed and the Al_2Cl_6 had condensed, the bulb was sealed off. The remaining pieces were cleaned up and weighed along with the bulb. From these values the weight of the pure Al_2Cl_6 in the bulb could be calculated.[12] At no point was the Al_2Cl_6 handled in the air or even in a drybox.

2. Phosphorus trifluoride was prepared by literature methods[13] from PCl_3 and ZnF_2. To eliminate mixed chlorofluorides and HCl or HF the PF_3 was passed through dilute NaOH solution before condensation at −196°. It was then distilled from a trap at −150° to a trap at −196°. The PF_3 vapor pressure was 374 ± 1 mm at 112°.

3. Aluminum trimethyl was prepared by the reaction of reagent grade aluminum with methyl iodide. Details are available.[9] Hydrolysis of a sample gave more than 98% of the expected methane gas. The vapor pressure was 17 mm at 26°. The vacuum line was equipped with mercury float valves for all manipulations of aluminum trimethyl.

4. Other Reagents. All other reagents were commercial products of the highest purity. Drying was conducted before use when required.

Instrumental Methods. All ^{19}F nmr spectra were run on a Varian HR-56-60 spectrometer. ^{31}P nmr spectra were run on a Varian HR-100. Infrared measurements were made on a Beckman IR-10 and on a Beckman IR-20.

Synthesis of Trifluorophosphine–Trichloroalane. A heavy-walled glass bomb tube (15 mm; open top) was attached to the vacuum line by a side arm containing a constriction which could later be sealed. The sealed bulb containing aluminum chloride was placed in the bomb tube through the open top. A magnetic hammer to be used in subsequent breaking of the bulb was added. Then a vacuum break-off tip with a 19/35 standard taper joint was sealed on top of the bomb tube to close it off. The system was then evacuated and exposed to the vacuum pumps overnight with occasional gentle warming. With the $AlCl_3$ bulb and the bomb tube at room temperature, the Al_2Cl_6 bulb was broken with the magnetic hammer. Any residual gases from the bulb were pumped out rapidly. Then a measured amount of PF_3 sufficient to give a final pressure of 8–10 atm at 25° was condensed into the system with liquid N_2. The tube was sealed off at the side arm and the system was allowed to warm to a desired reaction temperature defined by a slush bath. After reaction, the system was frozen down with liquid N_2, the vessel was attached to the tube breaker with DeKhotinsky cement, and the line was evacuated. The tube was then opened to the vacuum line through the break-off tip. The reaction tube was surrounded with a CS_2 slush (−112°) and the excess PF_3 was removed and measured.

Displacement reactions were carried out by condensing the appropriate reagent in on the product and measuring the PF_3 evolved (after purification).

In determining molecular weight in PF_3 solution the bomb tube containing the pure F_3PAlCl_3 was cooled to −196° and flooded with N_2. The tube was removed from the line; a magnetic stirrer was placed in the reactor which was transferred as rapidly as possible to the molecular weight apparatus where vapor pressure depression of the solution was determined. After about 2 hr in liquid PF_3 at −112° some evidence for halogen exchange (small amount AlF_3 precipitate) appeared. After removal of PF_3 and warming to 25°, PCl_3 could be separated from the system in 98% yield: $Cl_3Al{\cdot}PF_3 \rightarrow AlF_3 + PCl_3$. Representative data are in Table I.

Table I

Amt, mmol					
Al_2-Cl_6	PF_3 used	PF_3: Al_2Cl_6	Pressure, atm	Time	Remarks
0.735	1.44	1.96:1	8.1	2 weeks	PCl_3 formed
0.855	1.70	1.99:1	8.1	4 days	PCl_3 formed
1.16	2.42	2.08:1	8.0	4.5 hr	No PCl_3 initially
1.18	1.25	1.06:1[a]	8.9	1 hr	Reaction incomplete[a]
1.10	1.54	1.40:1[a]	5.7	3 hr	Reaction incomplete[a]
1.02	2.05	2.00:1	8	4 hr	No PCl_3; used in mol wt study[b]
0.86	1.72	2.00:1	8	4 hr	Same as above

[a] Ratio determined by reactants used. [b] Molecular weight study: run 1, 0.454 g of $F_3P{\cdot}AlCl_3$, 23.0 mmol of PF_3, −112°, $\Delta P/P = 2.24$, mol wt 202; run 2, 0.381 g of $F_3P{\cdot}AlCl_3$, 42.0 mol of PF_3, −112°, $\Delta P/P = 1.89$, mol wt 202.

Table II

Amt, mmol				
Al_2-$(CH_3)_6$	PF_3 used	Time	PF_3 pressure, atm	Remarks
0.37	0.28	4 hr	8	Tube warmed to 25°; gave liquid with odor of phosphine
0.73	0.84	1.5 days	8	Liquid product
0.64	0.47	4 days	9	Liquid product at 25°; hydrolysis with dilute HCl gave 2.1 mmol of CH_4 + little ppt
0.64	1.64	3 days	12	Liquid product; hydrolysis gave 1.55 mmol of CH_4

Other Systems. All other systems were run using a technique similar to that described above. Details of reactions which gave only starting materials [$AlCl_3$–CO, $(CH_3)_3Al$–CO, $AlCl_3$–PCl_3, and F_3B–PF_3] are available elsewhere[9] but are not given here. The system $(CH_3)_3Al$–PF_3 gave the data shown in Table II.

The System Ammonia-$Al_2(CH_3)_6$. A ring of excess NH_3 was frozen with liquid N_2 in a reaction tube; then a ring of $Al_2(CH_3)_6$ was frozen over the top of it. The system was closed and the temperature allowed to rise to −78° where it was held for 14 hr. When 1.0 mmol of $Al_2(CH_3)_6$ was used along with 5.72 mmol of NH_3, 1.85 mmol of ammonia was used to give an NH_3:$Al(CH_3)_3$ ratio of 0.93:1. The product $H_3N{\cdot}Al(CH_3)_3$ was a solid which did not melt below 235°. In a second run the ratio NH_3:$Al(CH_3)_3$ was 1.09:1. The molecular weight of the product, measured by vapor depression of liquid ammonia, was 74.0 at a concentration of 1.75 formula weights/1000 g of NH_3, 76 at 1.35 formula weights/1000 g of NH_3, and 83 at 0.54 formula weight/1000 g of NH_3. The value of the molecular weight extrapolated to infinite dilution is 87. This compares favorably with the value of 89.1 expected for the monomer.

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Registry No. F_3P, 7783-55-3; Al_2Cl_6, 13845-12-0; $F_3P{\cdot}AlCl_3$, 51830-74-1; $Al_2(CH_3)_6$, 15632-54-9; $NH_3{\cdot}Al(CH_3)_3$, 20775-95-5.

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(11) F. A. Cotton and G. Wilkinson, "Advances in Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 120.

(12) Details of these and all subsequent procedures are found in the Ph.D. dissertation of E. R. Alton, University of Michigan, Ann Arbor, Mich., 1960.

(13) A. A. Williams, *Inorg. Syn.*, **5**, 95 (1957).