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The Preparation and Fluorine-19 Nuclear Magnetic Resonance Investigation of the Phosphorus Chlorofluorides[1]

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A simplified procedure for the preparation of phosphorus(III) chlorofluorides is given. Low temperature chlorination of the latter is used to obtain PCl_4F, PCl_2F_3, and the new compound, PCl_3F_2. The pyridine adducts, $C_5H_5N \cdot PCl_3F_2$ and $C_5H_5N \cdot PCl_4F$, were characterized. A F^{19} n.m.r. investigation shows an upfield shift in the series PCl_xF_{3-x} with decreasing fluorine content and a downfield shift in the series PCl_xF_{5-x} with decreasing fluorine content. The F^{19} shift of the pyridine adducts follows the same order as that observed in the phosphorus(V) chlorofluorides. The data are used to show that PCl_4F and PCl_3F_2 most likely have a trigonal bipyramidal configuration similar to PCl_2F_3 and that the pyridine adducts are simple molecular addition compounds. The F^{19} shifts in the phosphorus chlorofluoride series are examined in relation to F^{19} data in other series.

Despite the frequent considerations of the trigonal bipyramid as an intermediate in SN1 substitution reactions of octahedral complexes[4] or SN2 displacement reactions of tetrahedral compounds,[5] bonding in molecules possessing a trigonal bipyramidal configuration is not understood to any great degree. Since most of the work reported[6] in the literature has been confined to the known pentafluorides and pentachlorides of phosphorus and antimony, the study of mixed chlorofluorides of phosphorus(V) provides a logical extension. Accordingly, the chlorofluorides of phosphorus(V) were prepared, formation of pyridine adducts was investigated, and a F^{19} n.m.r. study of both trivalent and pentavalent phosphorus chlorofluorides was undertaken.

It was found convenient to prepare the individual phosphorus(V) chlorofluorides by the low temperature chlorination of the separate phosphorus(III) chlorofluorides.[7,8] The phosphorus(III) chlorofluorides may be prepared by a procedure described by Booth and Bozarth.[9] Preliminary investigation indicated that their method could be greatly simplified and still achieve satisfactory results. Consequently, a modified procedure is described.

Experimental

Reagents.—Pyridine (Baker and Adamson reagent grade) was distilled and a middle fraction stored over KOH pellets, b.p. 112.8–113.0° (725 mm.), $n^{20}D$ 1.5100. $SbCl_5$ (Baker and Adamson reagent grade) was purified by vacuum distillation and middle fractions were collected. Tank chlorine (Matheson) was used directly. Other starting materials (Baker and Adamson, reagent grades) were used directly from freshly opened bottles.

Preparation of Phosphorus(III) Chlorofluorides.—Phosphorus dichloromonofluoride, phosphorus monochlorodifluoride, and phosphorus trifluoride were prepared by the fluorination of phosphorus trichloride by antimony trifluoride with the use of antimony pentachloride as a catalyst using a much simplified version of a procedure originally described by Booth and Bozarth.[9]

The final design of the apparatus is shown in Fig. 1. It was constructed so that the temperature of the reaction flask, the temperature of the reflux condenser, and the pressure in the system could be controlled. Since PCl_3, PCl_2F, $PClF_2$, and PF_3 differ in volatility, the boiling point decreasing in the series by about 60° as a chlorine atom is replaced by a fluorine atom, proper choice of the three controlled conditions allowed much of the desired product to boil away from the solution before it could be fluorinated further, thus limiting the amount of more fluorinated product produced. Less fluorinated products, thus higher boiling, were separated on the fractionating column, A, and returned to the reaction vessel. However, as Booth and Bozarth[9] point out, because the rate of fluorination increases in

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[1] Pentacoördinated Molecules. I. Abstracted from a thesis submitted by W. Patrick Gallagher in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology. Presented before the Inorganic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

[2] Bell Telephone Laboratories, Inc., Murray Hill, N. J.

[3] National Science Foundation Predoctoral Fellow, 1959–1961.

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

[5] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp. 316–322.

[6] (a) D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961); (b) J. W. George, *Progr. Inorg. Chem.*, **2**, 33 (1960).

[7] PCl_4F has been prepared by the thermal decomposition of $PCl_4^+PF_6^-$: L. Kolditz, *Z. anorg. allgem. Chem.*, **286**, 307 (1956).

[8] (a) PCl_2F_3 was first prepared in 1885: H. Moissan, *Ann. Chim. Phys.*, **6**, 433 (1885). (b) More recently the properties of PCl_2F_3 have been studied: T. Kennedy and D. S. Payne, *J. Chem. Soc.*, 1228 (1959). (c) PCl_3F_2 was suspected by Booth and Bozarth[9] but not identified.

[9] H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **61**, 2927 (1939).

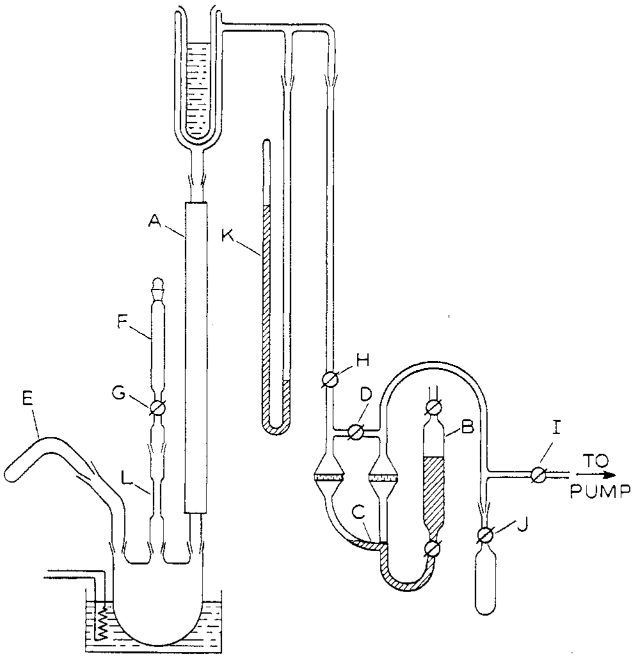

Fig. 1.—Fluorination apparatus for the preparation of phosphorus(III) chlorofluorides.

the series, PCl_3, PCl_2F, $PClF_2$, and because the fractionation of the product gases is not complete, the product of every run is a mixture of the phosphorus(III) chlorofluorides.

The fluorination apparatus was all glass, with different sections connected by standard-taper joints. Dow Corning high vacuum silicone grease was used on all joints and stopcocks. The fractionating column was an asbestos jacketed glass tube, 70 cm. long, 11 mm. i.d., packed with 0.25 in. glass helices. The condenser was constructed from a dewar form. A removable tube that fit in the condenser was filled with a bath of the desired condenser temperature which was checked and adjusted regularly during the runs. A small amount of a low freezing liquid mixture, 50% CCl_4–50% $CHCl_3$, was put between the bath tube and the condenser to provide for better heat transfer. The reaction vessel temperature was controlled by regulating the temperature of a bath around the outside of the flask. Stirring of the reaction mixture was accomplished by use of a strong Alnico horseshoe magnet rotating below the bath vessel to spin a 0.5 in. glass covered magnetic stirring bar in the flask.

Pressure regulation was achieved by the use of an adjustable mercury manostat. The pressure of the air above the mercury in the reservoir, B, was adjusted so that when the pressure exceeded that desired, the gas would bubble through the mercury at C until the excess pressure was removed. A stopcock D allowed the manostat to be by-passed while evacuating the system. Fritted disks prevented the mercury from entering the system when the system was at low pressures. An ampoule fitted with a stopcock was cooled with liquid nitrogen for collection of the product after it bubbled through the manostat. Because of the high toxicity of the product gases, the apparatus was used only in the laboratory hood.

The fluorination procedure was as follows. A weighed amount of SbF_3 was powdered in the laboratory drybox and transferred to the right angle solid addition tube, E. The addition tube then was attached to the fluorination apparatus which had been thoroughly dried and filled with dry nitrogen. PCl_3 was measured out volumetrically in the drybox and put into an addition funnel, F. Approximately 0.5-ml. quantities of $SbCl_5$ used as a catalyst were sealed in thin-walled glass ampoules. One of these was lowered into the reaction flask with tweezers.

After the manostat was adjusted to give the required pressure, the apparatus was evacuated, stopcocks D, H, I, and J all being open. The condenser bath and reaction vessel bath then were adjusted to the desired temperature. Stopcocks D and I were closed and a liquid nitrogen bath was placed on the collection ampoule. The magnetic stirring was started and after the $SbCl_5$ ampoule was broken, PCl_3 was added. The passage of PCl_3 through the addition funnel stopcock results in attack and weakening of the stopcock grease. Hence, this section of the apparatus was sealed off at L immediately after the addition. After the PCl_3 had come to temperature equilibrium with the surrounding bath, addition of SbF_3 was initiated by rotation of the solid addition tube. The reaction was continued until evolution of gas ceased, which was evidenced by the failure of gas to bubble through the manostat.

Conditions and yields for several fluorination runs are given in Table I. The yields given are in volume %, *i.e.*, ml. of product/ml. of PCl_3. They are estimates of the crude fractions.

Table I

Experimental Conditions for Fluorination Runs

	Starting materials			Conditions			Solid addition completed	Length of run	
Product	PCl_3, ml.	SbF_3, g.	$SbCl_5$, ml.	reaction temp., °C.	condenser temp., °C.	pressure, mm.	hr.: min.	hr.: min.	Yield estd.
$PFCl_2$	15	20	0.4	40°	11°	125[a]	0:20	1:05	35%
$PFCl_2$	23	30	.5	42°	10°	125	:20	1:05	40%
PF_2Cl	30	30	.5	[b]	−78°	250	1:04	3:40	30%
PF_3	By-product of above run								35%
PF_2Cl	50	67	2	30°	−78°	280	0:40	4:10	40%

[a] Manual manipulation of stopcock to control pressure on this run. [b] 0° for 2 hr. 40 min., 25° for 1 hr.

Purification of the crude materials was accomplished by repeated low temperature vacuum fractionations. Using a train of traps cooled to various low temperatures it was found that $PFCl_2$ would pass through a −85° trap and be retained at −98°; PF_2Cl passed a −119° trap and was retained at −150°; PF_3 passed a −150° trap and was collected at −196°. After sufficient recycling the products were virtually tensiometrically homogeneous. Resulting vapor pressures are: PCl_2F, 446.7 mm. at 0° (lit.[10] 448 mm. at 0°); $PClF_2$, 148.0 mm. at −80.0° (lit.[10] 150.7 mm. at −80.0°); PF_3, 206.7 mm. at −119° (lit.[10] 232 mm. at −119°). Vapor density measurements yielded the following molecular weights: PCl_2F, 120.9 (calcd., 120.89); $PClF_2$, 104.1 (calcd., 104.43); PF_3, 88.1 (calcd., 87.975). F^{19} n.m.r. spectra of samples of PCl_2F and $PClF_2$ (Table II) indicated that only one specie was present in each case. Although no quantitative estimate was made of the maximum amount of impurity which would give a minimum observable signal, samples of PCl_2F and $PClF_2$ which were not properly fractionated would show the presence of F^{19} signals of PCl_2F, $PClF_2$, and PF_3.

Preparation of Phosphorus(V) Chlorofluorides.—The chlorination reaction $PCl_AF_{3-A} + Cl_2 = PCl_{2+A}F_{3-A}$ was utilized for the preparation of phosphorus tetrachloromonofluoride, phosphorus trichlorodifluoride, and phosphorus dichlorotrifluoride, using a glass mercury-free vacuum system.

In a typical reaction, tank chlorine was slowly led into the evacuated system *via* a glass tube 1 m. long. The tube was packed with potassium hydroxide, Drierite, and beads coated with phosphorus pentoxide to remove hydrogen chloride and water impurities. The chlorine was condensed on the appropriate phosphorus(III) chlorofluoride present at liquid nitrogen temperatures in an ampoule attached to the system. The addition of chlorine was continued until an excess appeared to be present. Reaction was allowed to take place in the liquid phase by replacing the liquid nitrogen bath surrounding the ampoule with a warmer bath (−78° in the case of PCl_4F and PCl_3F_2 and −127° in the case of PCl_2F_3). If the yellow color of Cl_2 disappeared, the liquid nitrogen trap was replaced, more Cl_2 condensed on the reaction mixture, and the warming procedure repeated. In

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(10) Calculated from equations by Booth and Bozarth.[9]

every case that the yellow color of Cl_2 disappeared, it did so within 2 min. of the melting of the ampoule contents indicating that the reactions are quite rapid.[11]

To ensure completeness of the reaction, the system was held at the reaction temperature for 0.5 hr. Afterward, excess chlorine was removed by vacuum fractionation in a series of U traps. A bath temperature of −36° retained PCl_4F, −78° retained PCl_3F_2, and −95° retained PCl_2F_3; the chlorine passed through in each case and was trapped at −196°. Several recyclings were necessary to obtain completely colorless products.

To establish the composition and purity of the products, the melting points, the phosphorus analyses (halogen analyses proved unsatisfactory except for the least volatile member, PCl_4F), and the F^{19} n.m.r. spectra were obtained. The melting points were determined by a dropping weight apparatus and calibrated thermometer. Melting points are as follows: PCl_4F, −59.0° (lit.[7] −63°); PCl_3F_2, −63.0°; PCl_2F_3, −124° (lit.[8b] −130 to −125°).

Anal. Calcd. for PCl_4F: P, 16.15; Cl, 73.94. Found: P, 16.52; Cl, 73.90. Calcd. for PCl_3F_2: P, 17.67. Found: P, 17.92. Calcd. for PCl_2F_3: P, 19.49. Found: P, 18.76.

The F^{19} spectra (Table II) showed the presence of only one type of fluorine environment in each case, indicating homogeneity of the samples.

TABLE II

F^{19} NUCLEAR MAGNETIC RESONANCE DATA

Compound	Chemical shift[a] from CF_3COOH, p.p.m.	P–F coupling constant, c.p.s.
PF_5	−5.0	930
PCl_2F_3	−108.0	1048
PCl_3F_2	−191.8	1045
PCl_4F	−220.0	996
PF_3	−43.4	1400
$PClF_2$	−39.9	1390
PCl_2F	−20.7	1320
$C_5H_5N{\cdot}PCl_3F_2$	−101.8	983
$C_5H_5N{\cdot}PCl_4F$	−140.0	1049
POF_3	15.8	1055
$POClF_2$	−30.4	1120
$POCl_2F$	−69.0	1175
CF_4	−11.9	
$CClF_3$	−48.7	
CCl_2F_2	−72.3	
CCl_3F	−88.6	
CF_4	−11.9	
CHF_3	6.3	
CH_2F_2	69.0	
CH_3F	198.1	

[a] F^{19} shifts for PF_5, PF_3, $POCl_xF_{3-x}$, CCl_xF_{4-x}, and CH_xF_{4-x} (all as liquids) are those of Gutowsky and co-workers [ref. 22 and *J. Chem Phys.*, **21**, 279 (1953)]. The chemical shifts for the latter two series have been converted to trifluoroacetic acid as a reference by subtracting +11.9 from the shifts listed in ref. 22.

In agreement with previous investigations,[8,12] the liquid phosphorus(V) chlorofluorides were observed to change slowly to white solids at 25° on standing under vacuum. Visually, extensive solidification was observed to occur in about 25 to 30 hr. for samples of PCl_4F and PCl_2F_3 while about 2 to 3 days was required for PCl_3F_2. Evidence[8b,12] indicates that the solids from liquid PCl_4F and PCl_2F_3 are ionic in nature.[8b,12] Samples of all the phosphorus(V) chlorofluorides could be stored at −78° for extended periods of time without any noticeable conversion. This was determined by observing whether any solid was present immediately after warming samples to room temperature.

Preparation of Pyridine Adducts.—The liquid phase reaction of excess pyridine with PCl_4F in the vacuum system took place readily at −25° producing a white solid. In a typical preparation a sample of PCl_4F which had been stored at −78° was transferred to a weighed ampoule containing a glass stirring rod. The ampoule and contents were weighed quickly, then cooled again, so that the slow conversion to the solid form that takes place at room temperature would be minimized. After approximately a 2:1 mole ratio excess of pyridine had been condensed on the PCl_4F in the ampoule, the mixture was warmed to −25° and reaction occurred. The mixture was stirred for 15 min. and then warmed to 0° for 1 hr. On removal of the excess pyridine, a white solid was present having a ratio of 1.03 mole of C_5H_5N to 1.00 mole of PCl_4F. The solid was thermally unstable and began to liquefy at 63° with decomposition.

Anal. Calcd. for $C_5H_5N{\cdot}PCl_4F$: N, 5.17; Cl, 52.35. Found: N, 5.15; Cl, 51.84.

The reaction of PCl_3F_2 with excess pyridine at −36° was carried out analogously. Again a 1:1 reaction was demonstrated in the vacuum line giving a white solid having the formula $C_5H_5N{\cdot}PCl_3F_2$. The behavior of this compound on heating was analogous to that of $C_5H_5N{\cdot}PCl_4F$, and no reproducible melting point could be obtained.

Anal. Calcd. for $C_5H_5N{\cdot}PCl_3F_2$: P, 12.16; N, 5.50. Found: P, 11.59; N, 6.08.

Using the method described for the preparation of $C_5H_5N{\cdot}PCl_4F$, it was found that PCl_2F_3 reacted with excess pyridine at −36° to give a white solid having the composition $3C_5H_5N{\cdot}2PCl_2F_3$. This compound, perhaps analogous to the compound $3C_5H_5N{\cdot}2SbCl_5$ reported by Hutton and Webb,[13] was determined to be soluble in nitrobenzene. No further work was done with it.

F^{19} Nuclear Magnetic Resonance.—The instrument used in all determinations was a Varian Associates Model VR-60 high resolution spectrometer. Sweeping of the magnetic field was done with the slow sweep of the Varian superstabilizer, and the spectra were recorded on a Varian G-10. For all determinations the samples were externally referenced using trifluoroacetic acid sealed under vacuum in glass capillary tubes. The frequency scale was determined by the side-band technique.

The high vapor pressures of the phosphorus trihalides and the tendency of the phosphorus pentahalides to disproportionate made it necessary to make determinations below room temperature (−15°). For the separate pure liquid samples of PCl_2F, $PClF_2$, PCl_4F, PCl_3F_2, and PCl_2F_3 and nitrobenzene solutions of $C_5H_5N{\cdot}PCl_4F$ and $C_5H_5N{\cdot}PCl_3F_2$, the spectrum of each consisted of one doublet. No secondary-splitting of any of the doublet peaks was observed when examined under resolution that would have made a splitting of 2 c.p.s. evident. Data derived from the spectra of these compounds appear in Table II.

The P^{31} spectrum of PCl_4F was recorded. It consisted of a sharp doublet with chemical shift − 56 ± 2 p.p.m. relative to 85% H_3PO_4 and a coupling constant of 1010 ± 25 c.p.s.

Discussion

The somewhat lower yields obtained in the preparation of the phosphorus(III) chlorofluorides (~40%) compared to the yields of Booth and Bozarth[9] (~65%) are amply compensated by the simplification in equipment and procedure reported here. The low temperature chlorination of the separate phosphorus(III) chlorofluorides was found to proceed smoothly in each case, giving the liquid products PCl_4F, PCl_2F_3, and PCl_3F_2, the latter characterized for the first time.

Physical properties such as volatility and low melting point indicate that these substances are molecular. The observance of but one type of fluorine from the

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[11] J. N. Wilson, *J. Am. Chem. Soc.*, **80**, 1338 (1958), observed a much faster rate in the liquid phase compared to the gas phase.

[12] On standing, liquid PCl_4F slowly changes to an ionic solid, reported as $PCl_4{}^+F^-$: L. Kolditz, *Z. anorg. allgem. Chem.*, **293**, 147 (1957).

[13] J. C. Hutton and H. W. Webb, *J. Chem. Soc.*, 1523 (1931).

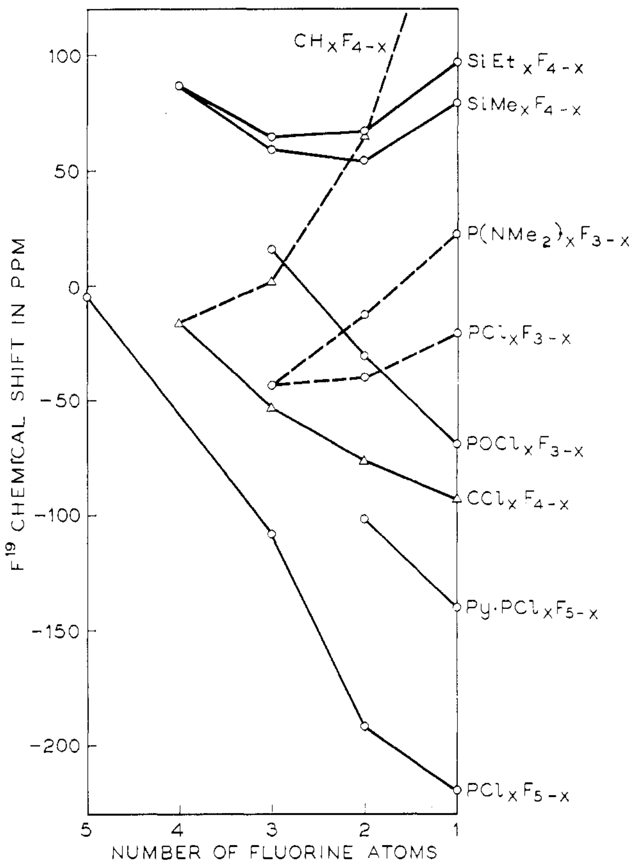

Fig. 2.—F^{19} chemical shift *vs.* number of fluorine atoms.

F^{19} n.m.r. spectra of each compound coupled with the presence of a doublet character shows that all the fluorine atoms are attached to phosphorus. The P^{31} n.m.r. spectrum of PCl_4F (doublet) shows only one type of phosphorus atom with a P–F coupling constant approximately the same as that observed in the F^{19} spectrum. Further, the systematic variation in F^{19} n.m.r. absorption (Fig. 2) supports a common structural model.

The structure of gaseous PCl_2F_3 has been reported[14] to be the same as that of gaseous PF_5, a trigonal bipyramid. Such a structure is the most reasonable one to assume for PCl_4F and PCl_3F_2 as well. The presence of only a single sharp doublet in the F^{19} n.m.r. spectrum at $-15°$ for each of the compounds, PCl_4F, PCl_3F_2, and PCl_2F_3, might indicate that only one stereoisomer of each results from the preparative methods used and that in each compound all fluorine atoms are equivalent; however, the very small chemical shift, 0.07 p.p.m., observed[15] for the difference between the apical and equatorial fluorine atoms in CF_3PF_4 and the lack of any observable[15,16] difference in PF_5 itself calls for postponement of a more detailed assignment.

One might speculate on the positions of the fluorine atoms by the following consideration: The melting points of PCl_4F, PCl_3F_2, and PCl_2F_3 are $-59°$, $-63°$, and $-124°$, respectively. If we assume that the lattice energies are equal for all the compounds and that the melting points of the compounds vary as they do because the symmetry group of the first two is the same, and different from that of the latter, then some slight support to the structures for PCl_4F and PCl_3F_2 in which the fluorine atoms are all equatorial results.[17]

The presence of only one sharp doublet in the F^{19} n.m.r. spectra of both $C_5H_5N \cdot PCl_4F$ and $C_5H_5N \cdot PCl_3F_2$ in nitrobenzene solution (the doublet arising from spin–spin coupling with the phosphorus atom) serves to show that the fluorine atoms remain attached to phosphorus and argues against a possible ionization process involving fluorine. It is noted that the F^{19} shifts of the adducts relative to the respective phosphorus(V) chlorofluorides (Table II) are of similar magnitude and are in the direction of increased field, that expected as a result of electron pair donation from nitrogen to phosphorus. Accordingly, the adducts are best regarded as formed by simple Lewis acid–base action.

F^{19} Chemical Shifts.—Figure 2 represents F^{19} chemical shifts (relative to trifluoroacetic acid taken as the zero reference point) for the series of compounds listed in Table II. Also included are data for the series $Si(CH_3)_xF_{4-x}$,[18] $Si(C_2H_5)_xF_{4-x}$,[18] and $P[N(CH_3)_2]_xF_{3-x}$.[19]

The theory as outlined by Saika and Slichter[20] ascribes F^{19} chemical shifts principally to changes in the paramagnetic contribution to the local nuclear screening. The contribution, which results in a shift to low field, should be zero for the spherically symmetrical fluoride ion and should increase, *i.e.*, should result in a greater shift to low field, as the ionic character of the bond to fluorine decreases. Satisfactory agreement with the theory has been observed for F^{19} shifts in binary fluorides.[21]

In Fig. 2 data for series showing a negative slope, *i.e.*, F^{19} shift decreasing with decreasing electronegativity of the group bonded to the fluorine atom, may seem at variance with the theory.

In accounting for the trends in the alkyl fluorosilanes[18] and the CCl_xF_{4-x}[22] series, it has been speculated that π-bonding involving fluorine atoms may be an important factor. Since π-bonding in these series may be interpreted as back bonding involving donation of p-electrons of fluorine to certain vacant orbitals of the central atom, less magnetic shielding around the fluorine atom is expected with a resultant increase in the paramagnetic contribution. To achieve qualitative agreement with the theory, the π contribution must be assumed to increase per central atom–fluorine bond as the number of fluorine atoms per molecule decreases in a

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[14] L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 1836 (1938).

[15] W. Mahler and E. L. Muetterties, *J. Chem. Phys.*, **33**, 636 (1960).

[16] S. Berry, *ibid.*, **32**, 936 (1960), discusses the possibility of an intramolecular exchange process to account for the spectroscopic equivalence of fluorine atoms in PF_5. No evidence for such an exchange was observed in CF_3PF_4.[15]

[17] Kolditz[12] was led to believe that the fluorine atom in PCl_4F is located in an equatorial position in order to explain an activation energy of 10.6 kcal./mole for the conversion of liquid PCl_4F to its solid modification.

[18] E. Schnell and E. G. Rochow, *J. Am. Chem. Soc.*, **78**, 4178 (1956).

[19] R. W. Parry, private communication.

[20] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

[21] H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

[22] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

particular series. In view of the demonstrated importance of π-bonding in boron trifluoride, it has been suggested[23] that the latter is the case in interpreting F^{19} chemical shifts in the series[24] RBF_2 and R_2BF (R = Cl, Br). Lack of adequate evidence regarding the changes in π-bonding for the series under consideration prevents a definite correlation with the negative slopes in Fig. 2.

Furthermore, closer examination of the F^{19} shifts in Fig. 2 indicates a more complicated situation. The trend in F^{19} shift in the phosphorus(III) chlorofluorides opposite to that in the phosphorus(V) chlorofluorides is particularly puzzling. If it is assumed that changes in π-bonding predominate in the PCl_xF_{5-x} and $POCl_xF_{3-x}$ series, it might be expected that this effect should be important in the PCl_xF_{3-x} series also. One might make the additional speculation that the presence of a readily available source of electrons, the lone electron pair, in the latter series may be "influential" in accounting for the opposite trends.

Explanations used in attempting to account for F^{19} shifts in fluorocarbon derivatives of metals[25] and organic fluorine compounds[26] have little applicability in accounting for the trends in the phosphorus chlorofluorides.

Additional studies of F^{19} shifts in series involving other central atoms should prove helpful in allowing more definitive correlations.

Acknowledgment.—Appreciation is expressed to the National Science Foundation for a grant supporting this work.

[23] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

[24] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

[25] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *ibid.*, **36**, 124 (1962), recently made calculations on the availability of low-lying excited states and concluded that the paramagnetic term should increase in the order H < F < Cl. This agrees qualitatively with the trend in F^{19} shifts in the series, CH_xF_{4-x} and CCl_xF_{4-x}, but does not predict the opposite trends in F^{19} shift in the PCl_xF_{3-x} series compared to the PCl_xF_{5-x} series.

[26] G. V. D. Tiers, *J. Am. Chem. Soc.*, **78**, 2914 (1956), invoked a "repulsive unshielding" effect attributed to the presence of bulky groups in causing a downfield shift in F^{19} resonance. While steric effects in a trigonal bipyramidal model (PCl_xF_{5-x} series) might be slightly greater than those in a pyramidal model (PCl_xF_{3-x} series), no appreciable change in steric requirements is expected for the series $POCl_xF_{3-x}$ compared to the series PCl_xF_{3-x} with increasing chlorine substitution. In both series, $POCl_xF_{3-x}$ and PCl_xF_{5-x}, the F^{19} shift trends downfield with similar slopes as x increases.

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The Relative Acceptor Properties of Phosphorus(V) Chlorofluorides and Antimony Pentachloride. A Calorimetric Investigation[1,2]

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The heats of solution of phosphorus trichlorodifluoride, phosphorus tetrachloromonofluoride, and antimony pentachloride in nitrobenzene were determined calorimetrically. The heats of reaction of these halides and phosphorus pentachloride with pyridine in nitrobenzene were measured calorimetrically. Comparing these values with similar data on the boron halides, the ordering of Lewis acid strengths toward pyridine obtained was: $BBr_3 > BCl_3 \sim SbCl_5 > PCl_3F_2 > BF_3 \overline{>} PCl_4F > PCl_5$. Heats of reaction of $SbCl_5$ with monoalkylpyridines were determined. Substitution of a methyl group in the 2-position of pyridine reduced the stability of the complex. Substitution in the 4-position enhanced the stability. Changes in structure of the alkyl group (ethyl or isopropyl) in the 4-position had little further effect on the stability of the complexes. The result of such changes in the 2-position suggested the presence of reactions other than simple complex formation. The 1:1 complexes of antimony pentachloride and alkylpyridines were prepared and characterized.

Introduction

Previous literature[1,5-7] shows that the pentahalides of phosphorus and antimony exhibit acceptor properties in that they form 1:1 complexes with a variety of Lewis bases. In the case of PF_5·base complexes a F^{19} n.m.r. study[7] supports an octahedral model with no observable dissociation occurring except in the case of complexes containing weak or hindered bases such as 2,4,6-trimethylpyridine.

In a continuation of our study of pentacoördinated molecules[1] it was decided to investigate the coördination tendencies of members of group V and if possible compare such data with the coördination tendencies of the boron halides reported[8] earlier.

Since the relative acceptor strengths of the boron halides were determined calorimetrically by measuring their heats of reaction with pyridine in nitrobenzene solution, a direct comparison would be possible only if

[1] Pentacoördinated Molecules. II. Previous paper: R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[2] Abstracted from theses submitted by W. Patrick Gallagher and Richard P. Carter in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology. Presented before the Inorganic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, California, April, 1963.

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[5] R. R. Holmes and E. F. Bertaut, *J. Am. Chem. Soc.*, **80**, 2980 (1958).

[6] (a) S. Johnson, Ph.D. Thesis, Purdue University, 1953; (b) R. R. Holmes, Ph.D. Thesis, Purdue University, 1953.

[7] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

[8] H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).