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Phosphorus Fluorides

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Advances in the chemistry of compounds containing P–F bonds, published during the past three or four years, are surveyed. Methods of synthesising several novel and some previously known products containing phosphorus and fluorine are reported, together with their chemical properties and the results of structural investigations using optical spectroscopy, nuclear magnetic resonance spectroscopy, and electron diffraction. The Review covers recent investigations on the stereochemistry of fluorides of five-coordinated phosphorus, and also problems of the complexing power of P[III] and P[V] fluorides, which have been widely studied during recent years. Progress in the chemistry of the phosphorus fluorides will help to solve such important and continuing problems as the degree of hybridisation and the nature of the phosphorus-substituent bond in five-coordinated phosphorus compounds, the mechanism of chemical reactions involving phosphorus compounds of various coordination numbers, the possibility and the character of interference between substituents, etc. A list of 188 references is given.

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I. INTRODUCTION

In 1965 a review by Schmutzler appeared in the series "Advances in Fluorine Chemistry"[1], which surveyed the main results of investigations on the fluorides of phosphorus varying in coordination, made from the time of Moissan's discovery of phosphorus trifluoride to 1964 inclusive. The present Review is based on work published during 1965–1968, and reflects both the increasing intensity of research in this field and the shift in the centre of attention from fluorides of four-coordinated phosphorus P[IV] to compounds in which the coordination number of phosphorus is either three (P[III]) or five (P[V]). The latter feature depends upon the widespread possibilities of modern physicochemical methods for identifying and investigating structure. This has given the most significant results in the study of the stereochemistry of the molecules PF_5, CH_3PF_4, and $(CH_3)_2PF_3$, for which the previously suggested configuration of a trigonal bipyramid has been quite rigorously confirmed.

II. METHODS OF PREPARATION AND CHEMICAL PROPERTIES

1. Fluorides of Three-coordinated Phosphorus

Phosphorus trifluoride, mixed halides, and fluoride pseudohalides of P[III]. It has recently been proposed to prepare phosphorus trifluoride by double decomposition between the halides $PHal_3$ (Hal = Cl, Br) and salts of hexafluorosilicic acid[2], which are considerably more readily available than the fluorides of arsenic, antimony, lead, and calcium which are usually employed[1].

During this period, however, research workers have paid greater attention not to phosphorus trifluoride itself but to its derivatives XPF_2 (X = I, Br, Cl, CN, NCO, NCS), which open up possibilities for the preparation of interesting new compounds. In particular, immediately after Cavell's reported[3] preparation of phosphorus iodide difluoride by treating *NN*-dimethylphosphoramidous difluoride

with hydrogen iodide, publications appeared[4-6] confirming his results and developing the chemistry of phosphorus iodide difluoride. Reaction of the latter with mercury yielded the previously unknown tetrafluorodiphosphine[6], attempts to prepare which from tetrachloro- or tetraiodo-diphosphine had been unsuccessful[7]. The preparation of tetrafluorodiphosphine was conducted in a vacuum (residual pressure ~50 mmHg), since at higher pressures the initial phosphorus iodide difluoride disproportionates into the trifluoride and the tri-iodide of phosphorus.

Analysis of the mass spectrum of tetrafluorodiphosphine led to the conclusion[6] that the product contained pyrophosphorous tetrafluoride as impurity, which might have been formed by the hydrolysis of tetrafluorodiphosphine:

$$2\,P_2F_4 + H_2O \rightarrow 2\,PHF_2 + F_2POPF_2.$$

This compound has been prepared from phosphorus iodide difluoride and copper(I) oxide[6,8]. It is unstable, and at room temperature it decomposes slowly in conformity with the equation

$$F_2POPF_2 \rightarrow PF_3 + (POF)_n.$$

Phosphorus iodide difluoride reacts with cuprous cyanide to form phosphorus cyanide difluoride[6]:

$$IPF_2 + CuCN \rightarrow PF_2CN + CuI.$$

This compound is stable only below 0°C. Above −20°C it probably undergoes exchange interactions with the more stable phosphorus trifluoride and phosphorus tricyanide.

The previously unknown phosphorus di-isothiocyanate fluoride has been obtained, together with the difluoride $P(NCS)F_2$, by exchange between the tri-isothiocyanate and antimony trifluoride[9]:

$$2\,P(NCS)_3 + SbF_3 \rightarrow F_2P(NCS) + FP(NCS)_2 + Sb(NCS)_3.$$

The quite substantial difference in the boiling points reported[9,10] for phosphorus isothiocyanate difluoride indicates that the earlier investigation[10] had dealt not with $P(NCS)F_2$ but with a phosphorus fluoride of greater coordination number—most probably $SP(NCS)F_2$.

Fluorides of the type XPF_2 (where X = Br, I, H) exhibit an interesting peculiarity on reaction with hexafluoroacetone. Unlike most other P[III] derivatives, which form 1 : 2 adducts, in which the coordination number of the phosphorus is five, these fluorides give with hexafluoroacetone 1 : 1 adducts having the structure of phosphorodifluoridous esters of the type $(CF_3)_2CX.OPF_2$.[11] Quite recently Lustig[12] has obtained $(CF_3)_2C(CN)OPF_2$ by the reaction between phosphorus bromide difluoride and hexafluoroacetone in the presence of sodium cyanide. This involves the initial formation of $(CF_3)_2C(CN)O^-Na^+$, which then reacts with $BrPF_2$ to yield the final product.

Phosphorofluoridous amides and esters. Synthetic work in this field is distinguished by a broader study of the chemical properties of derivatives of phosphorofluoridous acids, which previously had hardly been investigated.

An interesting result is obtained from the reaction of phosphorodifluoridous esters and amides with primary amines. In both cases hydrides of P[V] are among the main products[13,14]:

$$XPF_2 + H_2NR \rightarrow XF_2PH(NHR) \quad (X=OR,\ NR_2),$$

Nevertheless, the phosphorus-31 nuclear magnetic resonance spectra indicate that no P[V] derivatives are formed in the reactions of amides R_2NPF_2 and esters $ROPF_2$ or $(RO)_2PF$ with alcohols. Only after prolonged heating of an alcohol and a phosphorofluoridous diester do signals from $(RO)_2POH$ appear in the spectra. Amides of phosphorodifluoridous acid react readily with alcohols even at room temperature, to form a series of P[III] derivatives, among which phosphorofluoridous diesters have been identified by their ^{31}P and ^{19}F n.m.r. spectra. When, however, the fluorides $ROPF_2$ are treated with secondary amines, at least three products—an amide R_2NPF_2, a phosphoramidous ester R_2NPFOR, and a diester $(RO)_2PF$—are formed. There are grounds for supposing that this reaction involves the initial formation of hydrides $RO(R_2N)PHF_2$, which at elevated temperatures may break down into R_2NPF_2 and $R_2N(RO)PF$, whereas the formation of diesters $(RO)_2PF$ may be a consequence of subsequent reactions in the phosphoramidous esters $R_2N(RO)PF$ in the multicomponent reaction mixture. The higher stability of hydrides containing an NHR group may be a consequence of intramolecular hydrogen bonding[13,14].

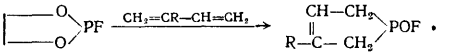
The addition of chlorine to phosphoramidous difluorides was first noted by Ivanova[15]. It has since been established[13,16,17] that chlorine and bromine form with these derivatives liquid 1 : 1 adducts, which in several cases can be distilled in a vacuum, their spectral characteristics indicating that they are P[V] derivatives. Furthermore, dimethylaminodichlorodifluorophosphorane has been obtained by treating the corresponding phosphoramidous difluoride with copper(II) chloride[16]:

$$(CH_3)_2NPF_2 + 2\,CuCl_2 \rightarrow \text{Complex} \rightarrow (CH_3)_2NPF_2Cl_2 + 2\,CuCl.$$

The formation of 1 : 1 adducts has been established also in the reactions of diamides $(R_2N)_2PF$ and amides $R(R_2N)PF$ with halogens, but the products are probably ionic, not pentacovalent structures[13,17]. It is obvious that 1 : 1 adducts are formed also in the initial stage of the interaction of P[III] fluorides with cyanogen bromide[13,18].

At temperatures up to 50–60°C amides and esters of phosphorofluoridous acids do not react with simple ketones. Nevertheless, the amides R_2NPF_2 and the diesters $(RO)_2PF$ react exothermally with hexafluoroacetone to form 1 : 2 adducts containing a five-coordinated phosphorus atom. Phosphorodifluoridous esters do not react with hexafluoroacetone under the same conditions[19]. As already mentioned, fluorides of the type XPF_2 (X = I, Br, H) form 1 : 1 adducts with hexafluoroacetone, which have been regarded as phosphorodifluoridous esters[11].

The condensation of cyclic phosphorofluoridous esters with diene hydrocarbons led to the isolation of four-coordinated phosphorus compounds[20], which are probably decomposition products of the initially formed P[V] fluorophospholens:



The first attempt to isolate difluorodihalogenophosphoranes of the type $ROPF_2X_2$ (X = Cl, Br) were unsuccessful[21], the reaction of phosphorodifluoridous esters with halogens yielding instead halide fluorides $XPOF_2$, which have since been proved[13] to be products of the rearrangement of the difluorodihalogenophosphoranes (P[V]):

$$ROPF_2 + Hal_2 \rightarrow ROPF_2Hal_2 \rightarrow HalPOF_2 + RHal \quad (Hal=Cl,\ Br).$$

More stable addition products are obtained from halogens and phosphorofluoridous esters containing ArO groups or the phosphorus atom in a five-membered phospholan ring.

Among work on the synthesis of phosphorofluoridous amides and esters themselves we must first note the development of a process for preparing the previously unknown

amides $RN(PF_2)_2$, which have been obtained in good yield by the reaction of their chlorine-containing analogues with antimony trifluoride[22]. The same type of reaction has been used to synthesise several new dialkylamides of phosphorodifluoridous acid[15] and cyclic phosphorofluoridous esters[20]. A previously unknown phosphorodifluoridous ester has recently been obtained by Lustig[12] by means of the reaction

$$BrPF_2 + OC(CF_3)_2 + NaOCN \xrightarrow{-CO} (CF_3)_2C{=}NC(CF_3)_2{-}OPF_2 .$$

Difluorophosphines and dialkylfluorophosphines. In 1965 Rudolph and Parry reported the synthesis of the first member HPF_2 of the series of difluorophosphines, by the reaction of phosphorus iodide difluoride with hydrogen iodide in the presence of mercury[23]:

$$F_2PI + Hg + IH \rightarrow HPF_2 + Hg_2I_2 .$$

Later the same workers noted[6] that difluorophosphine is formed by the reaction of tetrafluorodiphosphine with water or with hydrogen iodide:

$$2P_2F_4 + H_2O \rightarrow 2HPF_2 + F_2POPF_2$$
$$P_2F_4 + HI \rightarrow HPF_2 + IPF_2 .$$

Little work has yet been done on the chemical properties of difluorophosphine, although available information shows that they are unusual in the quite high lability of the P–H bond, as indicated both by the above reaction with hexafluoroacetone[11] and by the hydrolysis of difluorophosphine, the latter accompanied by the evolution of hydrogen[23]:

$$PHF_2 + H_2O \rightarrow HOPF_2 + H_2 .$$

A theoretical yield of hydrogen is not obtained, this being attributed[23] to secondary processes accompanying the cleavage of P–F bonds.

Difluorophosphine is more basic than phosphine and phosphorus trifluoride towards borine. Its adduct $F_2PH.BH_3$ (b.p. 6.2°C) is stable to decomposition up to 25°C at a pressure of ~1 atm.[24] Under comparable conditions $F_3P.BH_3$ and $H_3P.BH_3$ will dissociate into the initial components.

The first alkyl(or aryl)difluorophosphines were described in 1959 by Kulakova and her coworkers[25]. However, owing to a misprint in this paper—the boiling point of $C_6H_5PF_2$ was printed 74–70°, whereas actually it is 74°C at 70 mmHg—the possibility of obtaining these compounds by reaction between their chloro-analogues and antimony trifluoride was open to doubt. A more detailed investigation of the reaction of alkyl(or aryl)dichlorophosphines with antimony trifluoride showed that, under certain conditions, it could be successfully used for the preparation of difluorophosphines. In particular, 80–85% yields of gaseous methyl- and ethyl-difluorophosphines are formed by the reaction of their chloro-analogues with the complex $SbF_3.2C_5H_5N$,[26,27] and high-boiling difluorophosphines can be obtained in 40–60% yield by exchange between the corresponding dichlorophosphines and antimony trifluoride in dialkylaniline in a vacuum[26,27].

The fluorophosphines CH_3PF_2[29] and $(CH_3)_2PF$[30] have been prepared by exchange between the chloro-analogues and the highly active potassium fluoride in a vacuum. Sodium fluoride has been successfully used in thiolan 1,1-dioxide medium for the preparation of $C_6H_5PF_2$.[31]

Fluorinated phosphines can be obtained also by the elimination of hydrogen fluoride from the hydrides $RPHF_3$[26,32] and R_2PHF_2.[33] Better results are given by heating the monohydride aryltrifluorophosphoranes with potassium fluoride[26,32], whereas alkyldifluorophosphines could not be obtained in this way[26]. The elimination of hydrogen fluoride from unsubstituted alkyltrifluorophosphoranes and dialkyldifluorophosphoranes can be accomplished by means of tertiary amines[26,33], but the yields of the final compounds are low, since the reaction is accompanied by secondary processes.

In assessing existing methods for the preparation of fluorophosphines, we note that, in order to obtain gaseous compounds, it is advisable to use the reaction of chlorophosphines with the complex $SbF_3.2C_5H_5N$, which requires only simple apparatus and ensures high yields of the final products. For the preparation of high-boiling fluorophosphines it is more convenient to use the reaction between chlorophosphines and sodium fluoride in thiolan 1,1-dioxide, since in this case the purest fluorophosphines are obtained.

The study of the chemical properties of alkyldifluorophosphines has revealed that the reaction of three-coordinated phosphorus fluorides with reagents of the type H–X (where X = NHR, OR, F, Cl) may yield hydrides containing five-coordinated phosphorus[27,30,34-42]. The resulting hydrides $RPHF_2X$ vary greatly in thermal stability depending on the structure of the radical X. In particular, the hydrides $RPHF_2NHR$[37,38], $RPHF_2OR$[34-36], and $RPHF_3$[39,40] can in several cases be distilled even at atmospheric pressure, whereas the hydrides in which X = NR_2, Cl[42] possess far lower thermal stability. Formation of the hydride $CH_3PHF_2SC_2H_5$ in a mixture of CH_3PF_2 and C_2H_5SH could not be detected at temperatures between –30° and +20°C by means of the ^{31}P n.m.r. spectra[41].

Both alkyl- and aryl-difluorophosphines add chlorine and bromine to form alkyl(or aryl)difluorodihalogenophosphoranes RPF_2Hal_2, which are extremely unstable even below 0°C, with a tendency to intermolecular exchange of ligands[13]. With rise in temperature the exchange processes become more intense, so that it is possible to isolate from the reaction mass alkyl(or aryl)tetrafluorophosphoranes and crystalline products approximating closely in composition to alkyl(or aryl)fluorotrihalogenophosphoranes[13,17].

Alkyl(or aryl)phosphonofluoridous amides and O- and S-esters. Compounds of this type have been described quite recently, and their chemical properties have not yet been adequately studied. The most detailed investigations have been made on alkyl(or aryl)phosphonofluoridous amides, rather less work has been done on O-alkyl alkylphosphonofluoridites, and the *S*-alkyl analogues of the latter have been the least studied.

It has been noted above that at low temperatures alkyldifluorophosphines form with secondary amines the hydrides $RPHF_2NR'_2$[42], which, with rise in temperature to 50–60°C in the presence of excess of the amine, eliminate hydrogen fluoride to give 40–60% yields of *NN*-dialkylamides of alkylphosphonofluoridous acids. The same compounds can be obtained by treating the amides $RPClNR'_2$[38,43] with antimony trifluoride or pentafluoride in an inert solvent (ether, benzene), but the results were more satisfactory when this exchange interaction was accomplished in a dialkylaniline, the products containing phosphorus and fluorine being distilled off under a vacuum[38]. Prolonged heating of the hydrides $RPHF_2NHR'$ with tributylamine gives 10–15% yields of monoalkylamides of alkylphosphonofluoridous acids[44]. The single example has also been reported of the synthesis of the *NN*-dibutylamide of methylphosphonofluoridous acid from methylchlorofluorophosphine

and dibutylamine[38]. Most of the above reactions are suitable also for the synthesis of arylphosphonofluoridous amides. However, it has been noticed[28] that, although the products of the interaction of aryldifluorophosphines with secondary and even with primary amines contain signals from arylphosphonofluoridous amides in their ^{31}P n.m.r. spectra, vacuum distillation enables only their adducts with hydrogen fluoride to be isolated (the structure of the latter was not investigated).

Amides of alkyl(or aryl)phosphonofluoridous acids are relatively stable compounds: in sealed ampoules they can be kept for several months without any signs of change in structure. In air the substances are slowly oxidised to the corresponding alkyl(or aryl)phosphonofluoridic amides. Prolonged heating with antimony trifluoride oxidises them to alkyl(or aryl)trifluoroaminophosphoranes[38]. Like the phosphorofluoridous amides they form liquid 1 : 1 adducts with chlorine and bromine, which as a result of intermolecular exchange of ligands yield the trifluorophosphoranes $RPF_3NR'_2$, and on hydrolysis form the amides $RPOFNR'_2$ [17,45]. Hydrogen chloride causes rupture of the P–N bond in alkyl(or aryl)phosphonofluoridous amides with the formation of alkyl(or aryl)chlorofluorophosphines[27,38,46]. With α-diketones the alkylphosphonofluoridous amides form 1 : 1 products, which on the basis of spectral investigations are regarded as dioxophospholens containing a five-coordinated phosphorus atom[47].

O-Alkyl (or aryl) alkylphosphonofluoridites were first reported in 1968.[35,41] They can be obtained by—(1) treating the hydrides $RPHF_2OR'$ with ammonia or a tertiary amine[35,41], (2) the reaction of alkyldifluorophosphines with sodium alkoxides[48], or (3) exchange interaction between alkylphosphonochloridous esters and antimony trifluoride[48]—but in all cases the yields are low, since the reactions are accompanied by secondary reactions. The purest products are formed from difluorophosphines and sodium alkoxides[48].

Alkylphosphonofluoridous esters are oxidised comparatively easily by oxygen, and add sulphur to form the corresponding phosphonofluoridates[48]. In the presence of alkyl halides[49] or of halogens[50] they undergo a Michaelis–Arbuzov type of rearrangement, with the formation of dialkylphosphinic fluorides and alkylphosphonofluoridic halides respectively. Like other compounds containing a three-coordinated phosphorus atom, alkylphosphonofluoridous esters react with trifluoromethyl azide to form phosphazo-compounds $R(R'O)PF : NCF_3$.[51]

The only *S*-alkyl alkylphosphonofluoridite known at present has been obtained by the reaction of methyldifluorophosphine with butanethiol in the presence of triethylamine[52].

Complex compounds containing fluorides of three-coordinated phosphorus as ligands. In the general development of the chemistry of complex compounds comprehensive investigations have been made during recent years on a series of complexes containing fluorides of three-coordinated phosphorus as ligands. Methods of preparation, chemical and physical properties, structure, and spectroscopic results, as well as theoretical aspects of the problem of transition metal–PF_3 (ligand) complexes, have been discussed in a review by Kruck[53], who covered work published up to 1967 inclusive. Schmutzler's review[1] considers the same aspects of the chemistry of complex compounds containing other phosphorus-containing ligands as well as the trifluoride. We recommend that the reader, who wishes to be fully informed on this research, refer first to these two reviews[1,53], and the small amount of work not covered by them will be discussed below.

To estimate the electron-donor capacity of difluorophosphine Rudolph and Parry[24] studied its reaction with diborane to form the complex $HPF_2.BH_3$, which does not decompose below 25°C. The same complex can be obtained by substituting HPF_2 for the phosphorus-containing ligand in the complexes $F_3P.BH_3$ and $H_3P.BH_3$. Substitution of the PF_3 ligand takes place even between –78° and –45°C, whereas replacement of the PH_3 ligand requires considerably more severe conditions. From these results it was concluded[24] that HPF_2 is more basic than PF_3 and PH_3 towards the Lewis acid BH_3. This fact was explained on the hypothesis that difluorophosphine contains an intramolecular hydrogen bond (FHF interaction).

Tetrafluorodiphosphine reacts at 25°C with diborane to form the complex $P_2F_4.BH_3$. At room temperature this decomposes slowly in conformity with the equation[54]

$$F_2P{-}PF_2 \cdot BH_3 \rightarrow F_3P \cdot BH_3 + (PF)_n.$$

Deewer and Ritter[55] have recently been able to obtain the relatively stable complex $B_2H_4(PF_3)_2$ by the reaction of B_3H_7 with PF_3. The reaction was conducted in dimethyl ether at –15°C under pressure (35 atm). The adduct $B_3H_7.O(CH_3)_2$, formed initially, then reacted with PF_3 to give diborane–bistrifluorophosphine. Hydrogenation of the latter yielded $BH_3.PF_3$.

Complexes of fluorides of three-coordinated phosphorus with zerovalent nickel NiL_4 are usually obtained from the corresponding phosphorus fluoride and tetracarbonylnickel[1,53,56]. A disadvantage of this method for obtaining NiL_4 complexes is the necessity of isolating them from a mixture of products of all degrees of substitution, which in several cases is a difficult task. A more convenient method in this respect is that proposed by Nixon, who prepared several such complexes by the reaction of π-dicyclopentadienylnickel with fluorides of three-coordinated phosphorus[57]:

$$\pi\text{-}(C_5H_5)_2Ni + 4X_nPF_{3-n} \rightarrow Ni(X_nPF_{3-n})_4 + (2\cdot C_5H_5)$$
$$X{=}F,\ CCl_3,\ (C_2H_5)_2N,\ C_5H_{10},\quad n=1;\ X{=}CF_3,\ n=1.\ 2$$

In order to prepare $Ni(PF_3)_4$ and $Pd(PF_3)_4$ Kruck et al.[58] used the direct reaction of the metals with phosphorus trifluoride in the presence of iodine as catalyst. Under the same conditions platinum gives only traces of $Pt(PF_3)_4$ with phosphorus trifluoride. When cobalt was treated under pressure with a mixture of phosphorus trifluoride and hydrogen, the hydride $HCO(PF_3)_4$ was obtained.

A large number of complexes of the type $Ni(CO)_nL_{4-n}$ ($n = 0-3$), $Mo(CO)_3L$ [$L = RPF_2$, $ROPF_2$, R_2NPF_2, $(RO)_2PF$, R_2PF, $R(R_2N)PF$, $(R_2N)_2PF$], and $Mn_2(CO)_n(PF_3)_{10-n}$ ($n = 7-9$) have been obtained by replacing carbonyl groups in the complexes $M(CO)_4$ (M = Ni, Mo) and $Mn_2(CO)_{10}$ by the appropriate phosphorus-containing ligands[56,57,59–61].

2. Fluorides of Four-coordinated Phosphorus

Phosphoryl fluoride, mixed halides and fluoride pseudohalide, phosphorofluoridic esters, and their derivatives. Fluorides of the type ZPF_nX_{3-n} (where Z = O, S; X = Cl, Br, NCO, NCS; $n = 1-3$) are usually obtained by double decomposition between ZPX_3 and the metal fluorides[1]. Phosphoryl and thiophosphoryl fluorides can also be obtained by the

reaction of P_2O_5 and P_2S_5 with CaF_2, SF_4, HF, or IF_5.[1] These methods have been somewhat developed during recent years. In particular, the possibility has been reported of using fluorosilicates in the exchange reaction with the halides $ZPHal_3$ (Z = O, S) in order to obtain phosphoryl and thiophosphoryl fluorides. In view of the accessibility of the starting materials, this method can probably be used on an industrial scale. A 40% yield of phosphoryl fluoride has been obtained by heating a mixture of P_2O_5 and NF_3 (1 : 2) in a nickel autoclave to 480°C. However, the reaction is complicated by secondary processes leading to the formation of $NOPF_6$.[62]

Useful results have been obtained in the search for new methods of synthesising halide fluorides POF_2Hal (where Hal = Cl, Br), which will be convenient in laboratory practice. All three new reactions which can be used to obtain these compounds provide good yields and require only simple apparatus, so that the choice of method of synthesis in the laboratory may be governed merely by the availability of particular starting materials:

$$(1)\ ROPF_2 \xrightarrow{Hal_2} OPF_2Hal + RHal\ ^{21}$$

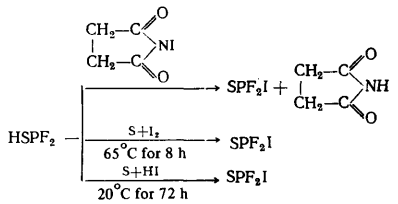
$$(2)\ F_2POOOPF_2 \xrightarrow{PHal_5\ или\ MHal_3} OPF_2Hal\ ^{63}\ (Hal=Cl,\ Br;\ M=Al)$$

$$(3)\ HOPOF_2 \xrightarrow{PHal_5} OPF_2Hal + OPHal_3 + HHal\ ^{63}.$$

An attempt to prepare $OPIF_2$ by reaction (1) was unsuccessful. Nor was this product obtained on treating phosphorodifluoridic amides with hydrogen iodide. Although this compound is probably formed in the initial stages, only phosphorodifluoridous acid can be isolated, which, like $HSPF_2$ obtained in a similar manner, contains a four-coordinated phosphorus atom[64,65]:

$$ZPF_2(NR_2) + 3\,HI \rightarrow ZPF_2H + R_2NH \cdot HI + I_2\ \ (Z=O,S).$$

Charlton and Cavell[66] have since reported that $SPIF_2$ can be obtained by treating phosphorodifluoridothious acid with the following reagents:



Thiophosphoryl iodide difluoride, unlike PIF_2, is thermally stable, and can be distilled at atmospheric pressure almost without decomposition. Only 5% of the substance had decomposed after the sample had been heated at 150°C for 4 days[66].

Treichell and his coworkers[67] reported that phosphorodifluoridous acid is formed also as a result of interaction between tetrafluorophosphorane and glass.

The chemistry of pseudohalide fluorides of P[IV] has been considerably extended during recent years. Roesky[63,68-70] investigated the chemical properties of the tetrafluoride of pyrophosphoric acid, and found a convenient method of synthesising OPF_2NCS, $OPF(NCO)_2$, and OPF_2NCO, which consisted in reaction of the tetrafluoride with potassium isothiocyanate and isocyanate respectively. It was found that phosphoryl di-isothiocyanate fluoride is formed by disproportionation of the initially formed OPF_2NCS:

$$F_2POOOPF_2 \xrightarrow[25°C\ for\ 12\ h]{KNCS} OPF_2(NCS)\ \ (yield\ 50\%)$$

$$2\,OPF_2(NCS) \xrightarrow[65°C\ for\ 1\ h]{} OPF(NCS)_2 + OPF_3.$$

Treatment of thiophosphoryl tri-isothiocyanate with antimony trifluoride at elevated temperatures yields thiophosphoryl fluoride isothiocyanates[9,68]:

$$SP(NCS)_3 + SbF_3 \rightarrow SPF_2(NCS) + SPF(NCS)_2 + Sb(NCS)_3$$

and phosphoryl fluoride isocyanates have been obtained[71] by the reaction

$$OPCl(NCO)_2 \xrightarrow{SbF_3} OPF(NCO)_2 + OPF_2(NCO).$$

An interesting method for obtaining OPF_2NCO, consisting in the reaction at elevated temperatures of silicon tetraisocyanate with phosphoryl trifluoride, has been proposed by Glemser and his coworkers[72], and a good yield of the di-isothiocyanate $SPF(NCS)_2$ is given by the reaction between $SPFCl_2$ and potassium isothiocyanate[73].

It should be noted that the boiling point given in Ref. 9 for SPF_2NCS is identical with that reported previously[10] for PF_2NCS, so that doubt is cast on the three-coordinated structure of the latter compound.

The new fluorides OPF_2OSO_2F and $OPF(OSO_2F)_2$, which are essentially mixed anhydrides of fluorosulphuric acid and the corresponding acids of phosphorus, have been obtained by heating $OP(OSO_2F)_3$ to 100°C for 2 h.[74]

Investigation of the chemical properties of P[IV] fluoride pseudohalides has shown that they react with alcohols and amines primarily at the NCO or NCS group[71,73]:

$$OPF(NCO)_2 \xrightarrow{ROH} OPF(NHCOOR)_2$$
$$\xrightarrow{RNH_2} OPF(NHCONHR)_2$$

$$RO(S)PF(NCS) \xrightarrow{RNH_2} RO(S)PF(NHCSNHR).$$

NN'-Dialkoxy(or aroxy)carbonylphosphorodiamidic fluorides are able to react further with alcohols and phenols to give the corresponding phosphorodiamidate esters.

Phosphoryl difluoride isocyanate reacts similarly to the monofluoro-derivative with alcohols and amines. The resulting difluorides $OPF_2NHCONHAr$ on treatment with phosphorus pentachloride form *N*-difluorophosphonyl-*N'*-aryl-*C*-chloroformamidines. Similar treatment of $OPFClNHCONHAr$ yields *N*-chlorofluorophosphonyl-*N'*-aryl-*C*-chloroformamidines[75]. These compounds are hydrolysed to phosphoric acid, although phosphorofluoridic acids may be formed at an intermediate stage:

$$ArNHC(=NPOF_2)Cl + 5\,H_2O \rightarrow ArNH_2 \cdot NF + NH_3 \cdot NCl + HF + CO_2 + H_3PO_4.$$

Study of the chemical properties of phosphoryl and thiophosphoryl fluorides has shown that they react with alkali-metal fluorides to form salts containing the anions $[PO_2F_2]^-$ and $[PS_2F_2]^-$. The salt KPS_2F_2 can be obtained also, together with potassium hexafluorophosphate, by the reaction between thiophosphoryl chloride and potassium fluoride[76]:

$$2\,MF + 2\,ZPF_3 \rightarrow MPZ_2F_2 + MPF_6\ \ (M=Cs,\ K;\ Z=O,\ S)$$

$$8\,KF + 2\,SPCl_3 \rightarrow KPS_2F_2 + KPF_6 + 8\,KCl.$$

The caesium salt $CsPS_2F_2$ has been used for the preparation of $(C_6H_5)_4AsPS_2F_2$ and $[(C_6H_5)_3P]_2NPS_2F_2$. Onium compounds of nitrogen, phosphorus, and arsenic containing the anion $[POSF_2]^-$ can be obtained by the reaction[77]

$$SPF_3 + (R_3R'Z)OH \rightarrow [R_3R'Z]^-[POSF_2]^-\ \ (Z=N,\ P,\ As).$$

Ammonium salts containing the anions $[POSF_2]^-$ and $[PO_2SF]^{2-}$ have been obtained by treating with hydrogen fluoride salts containing the anions $[POSNH_2]^-$ and $[PO_2SNH_2]^{2-}$.[78] In water P_4S_{10} reacts with sodium fluoride[79] to form a salt containing the doubly charged anion $[S_2PF-S-PS_2F]^{2-}$.

An interesting reaction takes place between phosphoryl fluoride and difluorocarbene. The latter acts as both reducing and fluorinating agent, first adding to the P=O bond and then forming OCF_2 and PF_3 or F_4PCOF. It is assumed[80] that the latter compound is formed by migration of a fluorine atom from the carbonyl carbon to the phosphorus atom in the initially formed trifluorophosphorane



accompanied by cleavage of the P–O bond.

Among work on phosphorofluoridates the greatest interest attaches to the synthesis of the silyl esters and to the study of their chemical properties. Bistrialkyl(or aryl)-silyl phosphorofluoridates have been obtained by the reaction between silver phosphoromonofluoridate and the corresponding chlorosilanes[81]:

$$2\,R_2R'SiCl + Ag_2PO_3F \rightarrow (R_2R'SiO)_2POF + 2\,AgCl.$$

An analogous type of reaction has been used for the synthesis of silylene diphosphorodifluoridates[82]:

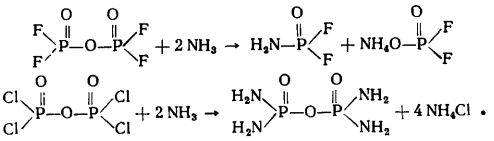
$$RR'SiCl_2 + 8\,NH_4PO_2F_2 \rightarrow RR'Si[OP(O)F_2]_2 + RR'Si[OP(O)F_2]F + RR'SiF_2.$$

It is interesting that with alkali-metal alkoxides silylene diphosphorodifluoridates yield salts of phosphorodifluoridic acid. The hydroloysis of silyl phosphorofluoridates is accompanied by the formation of fluorosilanes, disiloxanes, and $[PO_3F]^{2-}$ anions[81,82].

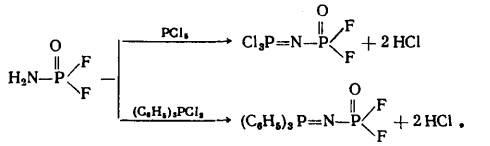
Several new phosphorofluoridates have been obtained by Roesky by the widely applied reaction of mixed halide fluorides of four-coordinated phosphorus with alcohols or thiols in the presence of tertiary amines[63].

Canadian workers[83] have described a new synthesis of dialkyl phosphorofluoridates based on cleavage of the P–N bond in phosphoroamidates by means of hydrogen fluoride. Phosphorofluoridates $(RO)_2PZF$ (where Z = O, S) can be obtained[84] by the reaction of salts of phosphorodithioic and the corresponding *SS'*-diethyl acids with aromatic and heterocyclic fluorides.

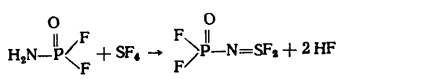
Heating the compound OPF_2OPOF_2 with ammonia leads to the formation of phosphoramidic difluoride and the salt $[NH_4]^+[PO_2F_2]^-$: i.e. the reaction involves cleavage of a P–O bond which has been weakened by the displacement of electrons towards the highly electronegative fluorine atoms[85]. This explanation for the rupture of a P–O bond in OPF_2OPOF_2 appears to be sound, since the compound $OPCl_2OPOCl_2$ reacts with ammonia without cleavage of such a bond[86,87]:



The compound H_2NPOF_2 obtained in this way has been used for the synthesis of phosphazophosphoryl fluorides[85]:



Glemser and his coworkers[88] obtained the compound $OPF_2N:SF_2$ from H_2NPOF_2 and sulphur tetrafluoride:



The previously unknown aroxydifluorophosphazoiminoaryls[89] and alkoxydifluorophosphazosulphonylaryls[90] have been obtained by the reaction of phosphorodifluoridic esters with *N*-chloroarenamines and with dichloroamides of arenesulphonic acids respectively. The P–N bond in the first group of compounds is ruptured by the action of water, to give arenesulphonamides, and treatment with aqueous potassium carbonate yields the salts $ArSO_2NKPFOOR$, which can also be obtained by replacing a fluorine atom by an alkoxy-radical in potassium arenesulphonylamidophosphorodifluoridates[90].

Several new phosphorofluoridates of the type $(CF_3)_2CXOPZF_2$ (X = CN, N_3 and Z = O, S) have recently been obtained by Lustig[12] by the reactions

$$ZPF_2Br + [(CF_3)_2C(CN)O]^-Na^+ \rightarrow (CF_3)_2C(CN)-O-P(Z)F_2 + NaBr$$
(Z=O, S; yield 60–87%)

$$OPF_2Br + [(CF_3)_2CO + NaN_3] \rightarrow (CF_3)_2C(N_3)-O-P(O)F_2 + NaBr.$$
(yield 64%)

The above compounds have been characterised by nuclear magnetic resonance using the ^{31}P and ^{19}F nuclei, by their infrared spectra, and by their mass spectra; there is no doubt about their structure.

A recent paper by Shreeve[91] records the preparation of $SPIF_2$ by the addition of sulphur to PIF_2 at 80–90°C (duration of contact of reactants 1 h). The yield of the final product was ~50%, which is extremely surprising in view of the tendency of PIF_2 to disproportionate at elevated temperatures.

Fluorides of four-coordinated phosphorus containing a C – P bond. Here we must first note the development of new syntheses of mixed halides of alkylphosphonic acids and the investigation of their chemical properties. Good yields of CH_3POClF, C_6H_5POClF, and also several previously unknown chloride fluorides have been obtained by the reaction of alkylphosphonofluoridic esters with the chlorides $XPCl_4$ (X = Cl, R_2N, C_6H_5):[92]

$$RPOF(OR') \xrightarrow{PCl_5} RPOFCl + R'Cl + POCl_3$$
$$RPOF(OR') \xrightarrow{R''_2NPCl_4} RPOFCl + R''_2NPOCl_2 + R'Cl$$
$$RPOF(OR') \xrightarrow{C_6H_5PCl_4} RPOFCl + C_6H_5POCl_2 + R'Cl.$$

When phosphorus pentachloride is used, the temperature of the reaction mass must be kept between 30° and 40°C, since considerable quantities of the dichlorides $RPOCl_2$ are formed at higher temperatures. Under laboratory conditions the choice of a particular chloride $XPCl_4$ is governed not only by its accessibility but also by the relative boiling points of the phosphorus-containing products formed. In particular, it is inadvisable to use phosphorus pentachloride to obtain chloride fluorides RPOClF whose boiling points are close to that of phosphoryl chloride, which would make it difficult to separate the final products by distillation.

The same workers[92] have used the reaction

$$RPSF(OR') + Cl_2 \rightarrow RPOFCl + SCl_2 + R'Cl$$

to obtain alkylphosphonic chloride fluorides. This probably involves the intermediate formation of the dichlorofluorophosphorane $RPCl_2FOR'$ (as is observed in the reaction of the amides R_2NPSF_2 with chlorine), which, being unstable, splits off R'Cl to form RPOClF.

Under the influence of thionyl chloride, phosphorus pentachloride, or phosphorus pentabromide alkylphosphonofluoridic acids, like phosphorodifluoridic acid[63], are able to replace their hydroxyl by Cl or Br, to form the

corresponding mixed halides RPOHalF, among which the bromine-containing products can be obtained also by treating alkylphosphonofluoridous esters with bromine[50,92]:

$$RPOF(OH) \xrightarrow{SOCl_2} RPOFCl$$
$$RPOF(OH) + PBr_5 \rightarrow RPOFBr + HBr + OPBr_3$$
$$RPF(OR') + Br_2 \rightarrow [RPFBr_2(OR')] \rightarrow RPOFBr + R'Br.$$

On hydrolysis all the fluorides RPOHalF (where Hal = F, Cl, Br) produce initially alkylphosphonofluoridic acids, these being followed by alkylphosphonic acids[50]. The differing activities of the halogen atoms in alkylphosphonic chloride fluorides have been used in the preparation of the previously unknown alkylphosphonisocyanatidic and alkylphosphon(isothiocyanatidic) fluorides[92]:

$$RPOFCl \begin{cases} \xrightarrow{NaOCN} RPOF(NCO) + NaCl \\ \xrightarrow{KSCN} RPOF(NCS) + KCl. \end{cases}$$

The yield of alkylphosphon(isothiocyanatidic) fluorides exceeds 50% in this reaction, whereas, among the considerably more unstable derivatives containing an isothiocyanato-group, only $CH_3PO(NCS)F$ has been isolated, in 10% yield.

Trichloromethylphosphonisocyanatidic fluoride has been obtained by double decomposition between $CCl_3PO(NCO)Cl$ and antimony trifluoride. The use of excess of the latter reagent makes it possible to conduct the reaction so that it yields exclusively trichloromethylphosphonic difluoride[93] (the latter is formed as a byproduct in the reaction of Cl_3CPCl_4 with antimony trifluoride).

Investigation of the chemical properties of the alkylphosphonisocyanatidic and alkylphosphon(isothiocyanatidic) fluorides has shown that their reactions with primary amines and alcohols involve firstly the NCO and NCS groups[92,93]:

$$RPOF(NCO) \begin{cases} \xrightarrow{ArNH_2} RPOF(NHCONHAr) \\ \xrightarrow{R'OH} RPOF(NHCOOR') \end{cases}$$
$$RPOF(NCS) \xrightarrow{ArNH_2} RPOF(NHCSNHAr).$$

An interesting synthesis of alkyl methylphosphonofluoridates has been suggested recently by Boter and Berg[94], who used the reaction between the ammonium salts $[(C_6H_{11})_2NH_2]^+[CH_3PSOOR]^-$ and fluorotrinitrobenzene:

$$[(RO)CH_3POS]^- [H_2N(C_6H_{11})_2]^+ + 2\,O_2N{-}C_6H_3(NO_2){-}F \rightarrow$$
$$\rightarrow CH_3POF(OR) + (C_6H_{11})_2NH \cdot HF + S\left(C_6H_3(NO_2)_2\right)_2$$

This method has been successfully used[94] to prepare t-butyl methylphosphonofluoridate, which is difficult to obtain by other methods, since it decomposes appreciably even at room temperature.

Several new phosphonofluoridates containing P–O–El bonds (where El = Si, Ge, As) have been obtained by the reaction of methylphosphonic difluoride with oxides of the type $R_nEl{-}O{-}ElR_n$.[95]

3. Fluorides of Five-coordinated Phosphorus

Phosphorus pentafluoride and the mixed halides $PHal_nF_{5-n}$ ($n = 1 - 4$). Phosphorus pentafluoride is usually obtained[1] by double decomposition between the pentachloride and such fluorides as AsF_3, HF, AgF, and C_6H_5COF. In the laboratory it is convenient to use the reaction between phosphorus pentachloride and antimony pentafluoride, which guarantees a relatively high yield of the final product[13]. The recently patented[2] preparation by treating phosphorus pentachloride with salts of hexafluorosilicic acid is evidently a promising method for industrial application.

Phosphorus trifluoride is readily oxidised[1] to the pentafluoride by elementary fluorine, molybdenum hexafluoride, and O_2F_2. Lustig showed[96] that difluorohydrazine also reacts under comparatively mild conditions (room temperature for 17 h) with phosphorus trifluoride to form the pentafluoride. It is interesting that phosphoryl fluoride can also be converted into phosphorus pentafluoride by the action of difluorohydrazine:

$$PF_3 + N_2F_2 \rightarrow PF_5 + N_2$$
$$OPF_3 + N_2F_2 \rightarrow PF_5 + N_2 + O_2.$$

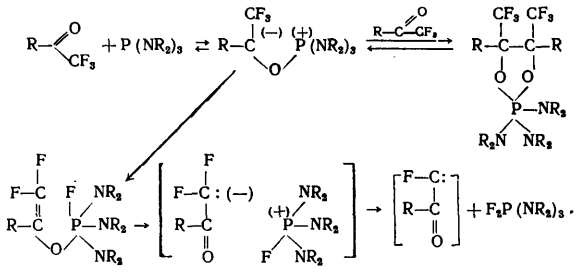
Among the mixed halides $PHal_nF_{5-n}$ those in which n has the values 1 and 4 have been the least studied. Only in 1965 did Carter and Holmes[97] obtain $PClF_4$ by the reaction of PCl_2F_3 with antimony trifluoride. Phosphorus chloride tetrafluoride is a gas having an extrapolated boiling point of –43.4° and a melting point of –132°C. When kept at room temperature, it slowly decomposes to form a solid deposit on the walls of the vessel together with gaseous phosphorus pentafluoride and phosphorus dichloride trifluoride. It has since been shown[13,98] that $PClF_4$ and $PBrF_4$ can be obtained from dialkylaminotetrafluorophosphoranes and the corresponding hydrogen halides. It has not proved possible to obtain PIF_4 by this method.

Phosphorus tetrachloride fluoride was first obtained by Kolditz[99] by the vacuum sublimation of $[PCl_4]^+[PF_6]^-$. The product exists in two forms—covalent and ionic $[PCl_4]^+F^-$—and the former can be converted into the latter merely when allowed to warm to room temperature from –40° to –50°C, at which the covalent form is preserved for quite a long time. The compound was obtained directly in the ionic form by Kesavadas and Payne[100] by the gas-phase reaction of phosphorus trichloride with fluorine in nitrogen. The structure $[PCl_4]^+F^-$ is supported by X-ray examination.

Many papers have appeared during recent years on the donor–acceptor properties of phosphorus pentafluoride and some of its derivatives. Investigation of the reaction of the pentafluoride with secondary amines has confirmed the initial formation of 1 : 1 adducts, which at high temperatures yield dialkylaminotetrafluorophosphoranes[101]. With excess of the secondary amine bisdialkylaminotrifluorophosphoranes can also be obtained[13,101]. The original conclusion reached by Brown and his coworkers[102], that only bisdimethylaminotrifluorophosphorane can be obtained in this way, is incorrect, since the corresponding bisdiethylamino-derivative has been obtained by heating a mixture (1 : 4) of phosphorus pentafluoride and diethylamine from –180° to 110–130°C.[13]

As a consequence of the sharp decrease in electron-acceptor power on passing from phosphorus pentafluoride to bisdialkylaminotrifluorophosphoranes, the latter do not react with secondary amines even at 100–120°C.[13,101] The triaminodifluorophosphoranes which might be expected in this reaction have been obtained in a different way—by treating the amides $(R_2N)_3P$ with fluorinated ketones[103,104]—the initially formed 1 : 1 adducts being able below 0°C to add a further molecule of the ketone to form dioxophospholans containing a five-coordinated phosphorus atom.

Above 100°C the 1 : 1 adducts undergo reduction and defluorination to yield trisdialkylaminodifluorophosphoranes:



The adducts formed by phosphorus pentafluoride with trimethylamine and acetonitrile, as well as the adducts $AsF_5.CH_3CN$ and $SbF_5.CH_3CN$, are electrically conducting, this being explained[105] by self-ionisation:

$$2AF_5 \cdot L \rightleftarrows AF_4L_2^+ + AF_6^- \quad (A=P, Sb, As).$$

From a study of the ^{19}F nuclear magnetic resonance spectra, however, Tebbe and Muetterties concluded[106] that no appreciable self-ionisation occurs in these systems. Their results seem to be convincing, and the electrical conductivity of the complexes investigated by Kolditz and Rehak was probably due, not to self-ionisation, but to ionisation resulting from the initial formation of an F^- ion (this may be caused by partial hydrolysis of the complexes), which attacks the complexes by an S_N1 or S_N2 mechanism.

Phosphorus pentafluoride forms an adduct with thiolan. Determination of the molecular weight of the adduct has shown that ~50% of the pentafluoride is bound into a 1 : 1 complex. The ^{19}F n.m.r. spectrum indicates complete loss of P–F splitting in this complex, which may be due to partial ionisation of the pentafluoride with rapid exchange of ligands between ionised and non-ionised forms[107].

The adducts $(CH_3)_2O.PF_5$ and $(CH_3)_2S.PF_5$ both undergo rearrangement even at room temperature in conformity with the equation[108]

$$3(CH_3)_2O \cdot PF_5 \rightarrow 2[(CH_3)_3O]^+[PF_6]^- + POF_3$$
$$3(CH_3)_2S \cdot PF_5 \rightarrow [(CH_3)_3S]^+[PF_6]^- + [(CH_3)_2SSCH_3]^+[PF_6]^- + PF_3.$$

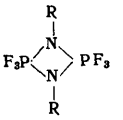
Several properties of the resulting saltlike compounds have been studied[108]. The oxonium compound $[(CH_3)_3O]^+[PF_6]^-$ reacts with acetone and dimethylformamide. It dissolves satisfactorily in acetonitrile, but in time reacts even with this solvent. It reacts with water with the evolution of hydrogen fluoride. The n.m.r. spectra of a rapidly cooled acetonitrile solution indicate the formation of a saltlike product $[(CH_3)_2CN]^+[PF_6]^-$.

Aminofluorophosphoranes and aminofluorohalogenophosphoranes. It has already been noted that dialkylaminotetra- and bisdialkylaminotri-fluorophosphoranes have been obtained by the reaction between phosphorus pentafluoride and secondary amines[101], and trisdialkylaminodifluorophosphoranes by interaction of the corresponding phosphorous amides with $(CF_3)_2CO$ or $CF_3COC_6H_5$.[103,104] Dialkylaminotetrafluorophosphoranes are formed also as a result of intermolecular exchange of ligands in the difluorodihalogenophosphoranes $R_2NPHal_2F_2$ (where Hal = Cl, Br).[13,45] Treatment of the latter with antimony pentafluoride in a solvent while the temperature is gradually raised from −30° to 20–25°C may give 30–70% yields of the dialkylaminotetrafluorophosphoranes[13]. The quite considerable fluctuations in the yield of the final products are probably associated with the thermal stability of the initial dialkylaminodifluorodihalogenophosphoranes, which increases appreciably on passing from the brominated to the chlorinated products, and reaches a maximum in the fluorophosphoranes



(the fluorophosphoranes $R_2NPF_2Cl_2$, where R = CH_3, C_2H_5, C_4H_9, are less stable at corresponding temperatures).

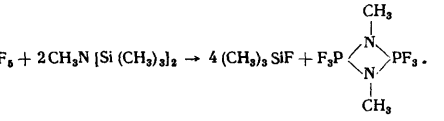
A more detailed investigation of the interaction between phosphorus pentafluoride and primary amines has recently been reported[109]. Compounds $RNHPF_4$ cannot be isolated or even detected here, cyclic derivatives of the type



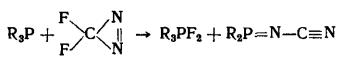
and salts $[RNH_3]^+[PF_6]^-$ being formed. Dehydrofluorination of the adduct $NH_3.PF_5$ by means of triethylamine gives a low yield of phosphonitrile fluoride, the main product being a partly dehydrofluorinated oil.

The reaction of dialkylaminodifluorodihalogenophosphoranes with secondary and primary amines gives the corresponding triaminodifluorophosphoranes[13]. The trifluorophosphoranes $(R_2N)_2PF_3$ or R_2NPF_3NHR' were also isolated, their formation evidently being a consequence of intermolecular exchange of ligands either in the final triaminodifluorophosphoranes during distillation or in the intermediate chlorodifluorophosphoranes $(R_2N)_2PClF_2$ or R_2NPClF_2NHR'. The trifluorophosphoranes R_2NPF_3NHR' can be obtained also by the reaction between dialkylaminotetrafluorophosphoranes and primary amines.

The reaction of phosphorus pentafluoride with silazanes can be successfully used to obtain aminofluorophosphoranes. Dimethyl- and diethyl-aminotetrafluorophosphoranes have been obtained in this way[110,111]. The reaction involves intermediate formation of a 1 : 1 adduct stable at −78°C. At room temperature the adduct breaks down into R_2NPF_4 and R_3SiF. 2,2,2,4,4,4-Hexafluoro-1,3-dimethyl-1,3-diazadiphosphetan can easily be obtained by a reaction of similar type[110]:

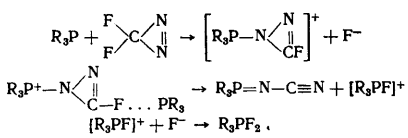


A large number of fluorophosphoranes, including some containing R_2N, RO, RS, and mixed functional groups attached to the phosphorus atom, have been obtained by reaction of the corresponding P[III] derivatives with difluorodiazirine[112]:

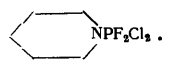


where R = Alk, Ar, RO, RS, R_2N. The amide $[(CH_3)_2N]_3P$ reacts the most easily with difluorodiazirine (at −78°C), with the formation of $[(CH_3)_2N]_3PF_2$ (the same worker[112] obtained the product by the reaction of $[(CH_3)_2N]_3P$ with tetrafluorohydrazine). Compounds containing more electronegative substituents react under more severe conditions with difluorodiazirine. The reaction is assumed to

have an ionic mechanism, in conformity with the probable scheme



The fact that phosphorodifluoridous amides are able to add chlorine to form adducts, which can be converted by sulphur dioxide into phosphorodifluoridic amides, was first noted by Ivanova[15]. Later work has established that both chlorine and bromine, in a solvent at low temperatures, react with the amides R_2NPF_2 [13,16,17], $(R_2N)_2PF$ [13,17,45], and $RPFNR_2$ [13,17,45] to give 1:1 adducts, in most cases liquid and soluble in the usual organic solvents, among which the chlorinated adducts $(CH_3)_2NPCl_2F_2$, $(C_2H_5)_2NPCl_2F_2$, and

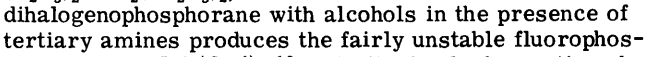


have been isolated in the pure state by distillation[13,17]. The phosphorus-31 n.m.r. spectra confirm the pentacovalent structure of the adducts $R_2NPHal_2F_2$ (Hal = Cl, Br), but saltlike structures of the type $[X_2PHalF]^+Hal^-$ are more probable in the case of the adducts $(R_2N)_2PHal_2F$ and $RPHal_2FNR_2$.

All the above addition products can be kept satisfactorily only below 0°C. At room temperature they undergo intermolecular exchange of ligands, with the formation of both mixed fluorohalogenophosphoranes and phosphoranes containing only one halogen. The fluorine-19 n.m.r. spectra have shown[45] that diethylaminodibromodifluorophosphorane forms the bromotrifluorophosphorane $(C_2H_5)_2NPBrF_3$ and the tetrafluorophosphorane $(C_2H_5)_2NPF_4$ as a result of exchange. The adducts $RPHal_2FNR_2$ gradually form trifluorophosphoranes RPF_3NR_2 and probably the halides $RPHal_3NR_2$ even below 0°C. Exchange processes are appreciably accelerated by raising the temperature to 40–60°C, and at 100–150°C phosphorus(III) halides in particular are formed, evidently as a result of redox reactions.

Emeléus and Onak have recently proposed[113] a new synthesis of aminofluorohalogenophosphoranes, consisting in the reaction of P[III] fluorides with compounds containing a nitrogen–chlorine bond. They have obtained the previously unknown fluorohalogenophosphoranes $(CF_3)_2NPClF_3$ and $(CF_3)_2NPCl_2F_2$ by the reaction of *N*-chlorobistrifluoromethylamine with phosphorus trifluoride and phosphorus chloride difluoride.

Several investigations have shown[13,16,17,113] that the hydrolysis of aminofluorodihalogenophosphoranes results in formation of the corresponding phosphorofluoridic amides. The same products result from the interaction of these phosphoranes with carboxylic anhydrides. The reaction of $(C_2H_5)_2NPClF_2$ with ethanethiol in the presence of triethylamine yields the difluorophosphorane $(C_2H_5)_2NPF_2(SC_2H_5)_2$, and interaction of the same difluorodihalogenophosphorane with alcohols in the presence of tertiary amines produces the fairly unstable fluorophosphoranes $R_2NPF_2(OR')_2$.[13] Monitoring both reactions by means of the n.m.r. spectra revealed also partial formation of the amides R_2NPXF_2 (X = O, S), which may be due to rearrangement of the products of the first stage of substitution:



On treatment with antimony trifluoride, adducts of all types form either tetra- or tri-fluorophosphoranes[13]. The same type of interaction has been used[13] for the synthesis of $(C_2H_5)_2NPF_3CN$ from $(C_2H_5)_2NPBrF_2CN$, and Clune and Cohn[18] have isolated $(CH_3)_2NPF_3CN$, formed by the disproportionation of $(CH_3)_2NPBrF_2CN$.

Fluorophosphoranes containing a C – P bond. The most widely used syntheses of fluorophosphoranes containing a carbon–phosphorus bond have been described in Schmutzler's reviews[1,114]. However, immediately after publication of these reviews Treichel and Goodrich proposed[115] a new and extremely promising synthesis of alkyltetrafluorophosphoranes based on the reaction between phosphorus pentafluoride and tetra-alkyl stannates. Yields of 15–19% of methyltetrafluorophosphorane are obtained when the duration of the reaction is 1–2 days. Increasing the time of contact of the initial reactants increases the yield to 60–70%. This synthesis of alkyltetrafluorophosphoranes is attractive in that the initial phosphorus-containing compound used is the readily available phosphorus pentafluoride, not the alkyldichlorophosphines from which alkyltetrafluorophosphoranes are usually obtained.

The reaction of phosphonothionic and phosphinothionic halides with antimony trifluoride has been proposed[116] for the preparation of alkyl(or aryl)tetra- and dialkyltri-fluorophosphoranes. A reaction of similar type had previously[114] been used for the synthesis of trialkyldifluorophosphoranes. The possibility of converting thione derivatives of four-coordinated phosphorus into fluorophosphoranes is of the greatest value for the synthesis of dialkyltrifluorophosphoranes, which are mostly obtained by the reaction of antimony trifluoride with dialkylchlorophosphines, these being considerably less readily available substances than their thione derivatives.

Triphenyldifluorophosphorane has been obtained by the reaction of triphenylphosphine with dinitrogen tetrafluoride[117], perfluoropiperidine, and nitrogen trifluoride[118]. The reaction between diphenylphosphine and tetrafluorohydrazine might be expected to yield the hydride $(C_6H_5)_2PHF_2$, but diphenyltrifluorophosphorane is said[117] to be formed (though in a later patent[119] the same workers state that reaction of the appropriate phosphines with tetrafluorohydrazine yields the hydrides R_2PHF_2).

It has not proved possible to isolate alkyl(or aryl)difluorodihalogenophosphoranes in the pure state[13,45]. Thermally the compounds are considerably less stable than their analogues[1] containing perfluoroalkyl radicals, and their formation in the reaction of alkyl(or aryl)difluorophosphines with chlorine or bromine has been detected[13] by means of the low-temperature fluorine-19 n.m.r. spectra. Even below 0°C they form, as a result of intermolecular ligand exchange, fluorophosphoranes $RPHalF_3$, RPF_4, and solids, insoluble in most organic solvents, whose composition is close to that of alkyl(or aryl)fluorotrihalogenophosphoranes (on treatment with antimony trifluoride the latter also give RPF_4).[13] Trichlorofluorotrifluoromethylphosphorane CF_3PCl_3F has been obtained as the desired product by Griffiths[120] by the addition of chlorine fluoride to dichlorotrifluoromethylphosphine.

During the past three or four years a large amount of work has been done on alkyl(or aryl)mono(or di)alkylaminofluorophosphoranes, among which the trifluorophosphoranes $ArPF_3NR_2$ were reported originally[121], and then other members of the series of alkyl(or aryl)aminotrifluorophosphoranes[40,122–126]. Alkyldiaminodifluorophosphoranes have recently been obtained[127] by the reaction of

trifluorophosphoranes RPF_3NR_2 or RPF_3NHR with primary or secondary amines. Alkyl(or aryl)mono(or di)alkylaminotrifluorophosphoranes have been synthesised by the following methods:

(1) $RPF_4 + 2\,H_2NR' \rightarrow RPF_3(NHR') + HF \cdot H_2NR'$[40,123–124]

(2) $2\,RPF_4 + 2\,HNR'_2 \rightarrow RPF_3(NR'_2) + [R_2NH_2]^+[RPF_5]^-$[122,123,125]

(3) $RPF_3Cl + 2\,HNR'_2 \rightarrow RPF_3(NR_2) + HCl \cdot HNR_2$[121,125]

(4) $RPHal(N<) \xrightarrow{SbF_3} RPF_3(N<)$ (Hal=Cl, F)[40,122,123,125]

(5) $RPF_4 + (CH_3)_3Si{-}NR'_2 \rightarrow RPF_3(NR'_2) + (CH_3)_3SiF$[122,123,126]

Arylaminotrifluorophosphoranes are most conveniently obtained by reaction (3), since the initial arylchlorotrifluorophosphoranes can easily be prepared by treating aryltrifluorophosphoranes with chlorine, the latter being comparatively readily available compounds. Reaction (4) is advisable for the preparation of alkyldialkylaminotrifluorophosphoranes, and reaction (1) for their monoalkylamino-derivatives.

Study of the hydrolysis of alkyl(or aryl)aminotrifluorophosphoranes by means of the ^{19}F n.m.r. spectra has shown[13,128] that the addition even of catalytic quantities of water results in formation of the anion $[RPF_5]^-$, whose concentration initially increases as fresh portions of water are added, reaches a maximum at a ratio of the initial reactants of ~1 : 1, and then diminishes until signals due to $[RPF_5]^-$ have completely disappeared from the spectrum. Ultimately, as had been noted previously[121], hydrolysis yields the salts $[HN<]^+[RPO_2F]^-$, which can be obtained also by the direct reaction between alkylphosphonofluoridic acids and amines[13].

In a series of papers Schmutzler and Reddy have shown[129–131] that on storage the fluorophosphoranes $C_6H_5PF_3N(CH_3)_2$ and $CH_3PF_3N(CH_3)_2$ undergo rearrangement accompanied by formation of the ionic compound $[RPF(N(CH_3)_2)_2]^+[RPF_5]^-$. Other workers have found[13,128] that the anions $[RPF_5]^-$ are formed also on the storage of most fluorophosphoranes RPF_3NHR, although the formation of cations containing phosphorus has not been established in this case.

The first attempts to obtain the trifluorophosphoranes RPF_3OR' from tetrafluorophosphoranes and siloxanes did not give the results expected[1,114]: instead of compounds of five-coordinated phosphorus, the phosphonic fluorides $RPOF_2$ and RPFOOR' were isolated, among which at least the former product might be formed by the rearrangement

$$RPF_3(OR') \rightarrow RPOF_2 + R'F.$$

Investigation of the reaction of methyl- and ethyl-tetrafluorophosphoranes with siloxanes by means of the low-temperature ^{19}F n.m.r. spectra has shown the actual formation in this case of the trifluorophosphoranes RPF_3OR', which are stable only at subzero temperatures. On warming up to room temperature the signals from the trifluorophosphoranes disappeared, and signals appeared from the phosphonic fluorides $RPOF_2$ and RPFOOR'. Formation of the latter compounds may be due either to reaction of the difluorides $RPOF_2$ with the siloxanes or to rearrangement of alkyldialkoxydifluorophosphoranes

$$RPF_3(OR')_2 \rightarrow RPOF(OR') + R'F,$$

which may be formed both by interaction of the trifluorophosphoranes RPF_3OR' with siloxanes and as a consequence of intermolecular exchange in the alkylalkoxytrifluorophosphoranes themselves

$$2\,RPF_3(OR') \rightarrow RPF_3(OR')_2 + RPF_4.$$

The relatively stable difluorophosphoranes $RPF_2(OC_6H_5)_2$ and $(C_6H_5)_2PF_3OC_6H_5$ have recently been obtained by reaction of the corresponding tetra- and tri-fluorophosphoranes with siloxanes[132]. Fluorophosphoranes containing alkylthio- or arylthio-groups attached to the phosphorus atom have been described[13,132,133].

The attention of research workers has long been attracted to the acceptor properties of fluorophosphoranes. Alkyl(or aryl)tetrafluorophosphoranes are weaker acceptors of electrons than is phosphorus pentafluoride, but nevertheless they exhibit this property quite distinctly. Thus phenyltetrafluorophosphorane forms relatively stable complexes with dimethylformamide and with pyridine. The temperature variation in the parameters of the ^{19}F n.m.r. spectra observed in solutions of these complexes may be due to the partial dissociation[134]

$$C_6H_5PF_4.Donor \rightleftharpoons C_6H_5PF_4 + Donor.$$

According to Muetterties and Mahler[134] donor–acceptor interaction is not observed in solutions of phenyltetrafluorophosphorane in acetonitrile and triethylamine. Alkyltetrafluorophosphoranes undergo an exothermic interaction with many organic bases, but at room temperature the resulting complexes are in considerable measure dissociated. According to their acceptor power the fluorides of five-coordinated phosphorus form the sequence[134]

$$PF_5 > ArPF_4 > AlkPF_4 \gg R_2PF_3 > R_3PF_2$$

which reflects the diminution in the relative positive charge on the phosphorus atom when the fluorine atom is replaced by less electronegative substituents. Steric factors probably play an important part also.

Phenyltetrafluorophosphorane forms with dimethyl sulphoxide a complex, which at 25°C dissociates with increase in the electrical conductivity of the solution. Spectroscopic investigation indicates that the reversible process

$$C_6H_5PF_4 \cdot OS(CH_3)_2 \rightleftarrows C_6H_5PF_4 + (CH_3)_2SO$$

is accompanied in the solution by another interaction involving formation of the anion $[RPF_5]^-$ and of $RPOF_2$ (the role and the fate of the dimethyl sulphoxide in this process have not been ascertained)[134].

Alkyltetrafluorophosphoranes react irreversibly with dimethyl sulphoxide. The products contain the anions $[RPF_5]^-$ and alkylphosphonic difluorides. The ^{19}F n.m.r. spectrum of these anions varies with temperature, this being attributed to exchange with F^- ions[134].

It has come to be accepted[1,114,134] that the donor properties of fluorides of five-coordinated phosphorus may be due either to ionisation $PX_5 \rightleftharpoons PX_4^+ + X^-$ or to the presence of lone pairs of electrons on the atoms attached to the phosphorus. All derivatives of phosphorus pentafluoride possess donor properties, although it is unknown which of the above causes is operative. Alkyl- and aryl-tetrafluorophosphoranes form colourless crystalline 1 : 1 complexes with strong acceptors such as boron trifluoride, antimony pentafluoride, and phosphorus pentafluoride. The complexes of dialkyltrifluorophosphoranes with the same acceptors are usually more stable than those of alkyltetrafluorophosphoranes [the dissociation pressure for the complex $PF_5.(CH_3)_2PF_3$ is less than 1 mm at 25°C, whereas for $CH_3PF_4.PF_5$ it is ~10 mm at –61°C][134].

Hydrides of five-coordinated phosphorus. The first hydrides containing a five-coordinated phosphorus atom were described in 1961 [135,136]: tetra- and tri-fluorophosphorane were obtained by the reaction of orthophosphorous and hypophosphorous acids with hydrogen

fluoride, and treatment of aryldichlorophosphines with potassium hydrogen fluoride gave aryltrifluorophosphorus monohydrides. Treichell and his coworkers have since found[67] that the hydrides HPF_4 and H_2PF_3 can be obtained by the gas-phase reaction of phosphorus pentafluoride with trimethylstannane [the deuteriated derivatives DPF_4 and D_2PF_3 have been prepared by the use of $(CH_3)_3SnD$]. Available data indicate[67,137,138] that both compounds are monomeric in the vapour state, whereas in the liquid state the H_2PF_3 molecules are in considerable measure associated. The chemical properties of these compounds have not been studied. It is known only that HPF_4 reacts with glass or quartz to form the unstable phosphorodifluoridous acid[67].

The hydrides methyl- and ethyl-trifluorophosphorane were first described in the patent literature[39]. Their synthesis and also several chemical properties have since been reported[13,35,38,40,139-141]. Both alkyl- and aryltrifluorophosphoranes (monohydrides) can be obtained in 80–90% yield by the low-temperature reaction between the halides $RPHal_2$ (where Hal = Cl, Br, F) and hydrogen fluoride[13,39,40,140,141]. The reaction of methyl- and ethyltetrafluorophosphoranes with trimethylstannane has also been used to prepare the alkyl derivatives[139].

All the trifluorophosphorus monohydrides investigated are relatively low-boiling liquids, which distil satisfactorily in an atmosphere of nitrogen, are easily hydrolysed, and react with glass. The compounds can be stored for a long time in vessels of an inert material (quartz, polyethylene, polytetrafluoroethylene). With tertiary amines they form alkyl(or aryl)difluorophosphines and salts $[NHR_3]^+[R'PHF_4]^-$ [26,38,40,141]. By the action of sodium alkoxides on aryltrifluorophosphoranes (monohydrides) the fluorine atom can be replaced by an alkoxy-group[35,141,142], and the action of primary amines on the corresponding alkyl monohydrides yields the alkyl-alkylaminodifluorophosphoranes $RPHF_2NHR'$ [38,41,141]. The latter compounds, as well as the hydrides $AlkPHF_2OR$, can also be obtained by the reaction of alkyldifluorophosphines with alcohols and with primary amines respectively[13,34-38,141,143]. The hydrides $AlkPHF_2NR_2$ are formed also in the first stage of interaction between alkyldifluorophosphines and secondary amines[13,42]. However, these compounds break down at high temperatures to form alkylphosphonofluoridous amides, and it proved extremely difficult to isolate them in the pure state by distillation.

Somewhat obscure results have been obtained for the reaction of aryldifluorophosphines and aryltrifluorophosphoranes with primary and secondary amines[38]. The formation of amides $ArPFN\langle$ in these cases is established by the ^{31}P n.m.r. spectra, whereas on distillation only their adducts with hydrogen fluoride, corresponding formally in composition to the hydrides $ArPHF_2N\langle$, can be isolated.

The previously unknown hydrides $ROPHF_2NHR'$ and R_2NPHF_2NHR' have been obtained from the corresponding fluorides XPF_2 and primary amines[14]:

$$XPF_2 + H_2NR' \rightarrow XPHF_2(NHR') \quad (X=OR, NR_2)$$

and the hydrides R_2PHF_2 (R = Alk, Ar) by reaction of the halides R_2PCl and R_2PF with hydrogen fluoride[13,107].

The above cases of the formation of hydrides of five-coordinated phosphorus by the reaction of fluorides of three-coordinated phosphorus with alcohols, amines, and hydrogen halides have several common features, which suggest that the initial step in this process is the reaction of a weak *n*-base with an acid HX (where X = F, Cl, OR, NHR, NR_2). The driving force in this stage of the reaction should be the high electronegativity of X. Where the electronegativity of X is small, systems may be formed containing a hydrogen bond $\rangle P:\ldots H:X$, the strength of which depends on the state of the lone pair of electrons of the base. When, however, X is strongly electronegative, and the phosphorus is combined with substituents of low electronegativity, the H–X bond may be ruptured with formation of the ion-pair $[\rangle PH]^+X^-$. The presence on the phosphorus atom of highly electronegative substituents, tending to lower the energy and localise the *d*-orbitals, is evidently a necessary condition for conversion of the initially formed system $\rangle P:\ldots H:X$ into a hydride of five-coordinated phosphorus.

It may be supposed then that the hydrides HPF_3X (where X = F, Cl, OR, NHR, etc.) will be fairly difficult to obtain by direct reaction of the compounds HX with phosphorus trifluoride, owing to the weak donor power of the latter. This conclusion is supported by the well known experimental fact that the hydride PHF_4 is not formed as a result of contact between phosphorus trifluoride and hydrogen fluoride. Replacement of one of the fluorine atoms in phosphorus trifluoride by a less electronegative substituent is sufficient for the compound to react exothermally with HX to form, as is shown experimentally, hydrides of five-coordinated phosphorus. On the whole it is obvious that, in the series PF_3, YPF_2, Y_2PF, and Y_3P (where Y is a substituent other than fluorine), the last compound will react most easily with the acid HX. However, if the reaction can produce a five-coordinated molecule thanks to the presence of highly electronegative substituents in the compounds YPF_2 and to a less extent Y_2PF, such possibilities should be limited in the latter compounds. This conclusion also is supported by the experimental results available at present. In particular, the fluorophosphines RPF_2 and R_2PF form with hydrogen fluoride hydrides of five-coordinated phosphorus, whereas the products of the interaction of hydrogen fluoride with trialkyl(or aryl)phosphines have a clearly ionic structure[144].

III. PHYSICOCHEMICAL INVESTIGATIONS

The wide use of modern physicochemical methods of investigation, primarily n.m.r. spectroscopy, has had an exceptionally fruitful influence on the development of the chemistry of the fluorides of phosphorus. The most significant result has been obtained from a combined study (by electron diffraction, and n.m.r. and vibrational spectroscopy) of the structure of P[V] compounds, which are in most cases found to have a trigonal–bipyramidal configuration.

Another important result of work done during recent years is the evaluation of the true parameters of the ^{31}P and ^{19}F n.m.r. spectra for the fluorides of three-coordinated phosphorus, and in particular for derivatives of alkylphosphonofluoridous acids, which exhibit abnormally small chemical shifts δ_P.

Particular attention will be paid here to the results of n.m.r. and vibrational spectroscopy, and also to the investigation of the structure of the fluorides of phosphorus by electron diffraction.

1. Phosphorus-31 and Fluorine-19 n.m.r. Spectra

^{31}P and ^{19}F n.m.r. spectra of the fluorides of three-coordinated phosphorus. The fluorides C_2H_5PFX (where X = F, Cl, iso-OC_3H_7) were among the first organophosphorus compounds to be investigated by means of the ^{31}P n.m.r. spectra. Unfortunately, the relevant paper[145] contained a mistake, these compounds being attributed the spectral characteristics of more highly coordinated fluorides of phosphorus. Only eight years later[146] was the error in the original results demonstrated, and subsequently the true parameters of the ^{31}P and ^{19}F n.m.r. spectra have been determined[26-29,33,41,49,52,147] for these types of compounds (see Table 1), which were found to possess abnormally low δP values, disproving the theory of "group shifts"[145].

Quite a large amount of experimental information has now accumulated providing knowledge of the values of δP, δF, and J_{P-F} for about a hundred phosphorus(III) fluorides. However, it has not yet proved possible to use this information in developing theoretical aspects of the problem of screening and spin-spin interaction in the series of compounds considered. Solution of these problems is complicated by the absence of any well-developed regularities in the variation of these parameters with the structure of the compounds. Only in narrow series of closely related derivatives, where the variation in structure seemingly does not involve substantial variation in angles and bond lengths, is it possible to detect a more or less well defined inverse relation (e.g. for compounds 15-19 in Table 1) and occasionally even a direct relation (compounds 8-10, 12, and 13) between the values of δP and the aggregate electronegativities of the substituents. However, when broader series of compounds are considered, e.g. fluorides of the type XPF_2 (compounds 1-13, Table 1) and XYPF (compounds 14-24), this relation breaks down, probably because of the considerable fluctuations in the valency angles within series of these compounds.

Not only δP but also the chemical shifts of the ^{19}F nuclei vary over a wide range. Thus for compounds of the type RPFX (Table 1, compounds 12-19) the range of variation in δP is ~90 ppm, while the chemical shifts δF vary over the range 522-626 ppm. The screening of the ^{31}P nuclei changes with the nature of X in the sequence $F < Cl < OR \simeq SR < R < NR_2$, which differs from the sequence of variation in δF in the same compounds (the screening of ^{19}F nuclei varies in the sequence $OR < F < NR_2 < SR < R$). The constants J_{P-F} increase in the sequence $R < NR_2 < SR < Cl < OR < F$, which differs from both δP and δF sequences.

It must be noted in conclusion that ^{31}P nuclei are usually considerably less screened in P[III] fluorides than in the corresponding derivatives containing P[IV] or P[V], whereas ^{19}F nuclei, on the other hand, are more screened in P[III] fluorides than in the P[IV] compounds. In virtue of these facts phosphorus(III) fluorides can often be easily identified by means of the ^{31}P and ^{19}F n.m.r. spectra not only in the pure state but also when mixed with more highly coordinated phosphorus compounds.

Phosphorus-31 and fluorine-19 n.m.r. spectra of complex compounds. An interesting paper appeared recently[60] on the investigation by means of the ^{31}P and ^{19}F n.m.r. spectra of complex compounds containing P[III] fluorides as ligands. It contains extensive experimental results, and makes an analysis of possible factors influencing the variation in the parameters of the n.m.r. spectra on passing from the free ligands to the complex compounds. In the complexes the ^{31}P nuclei are deshielded in comparison with the free ligands ($\Delta\delta P$ = 6-55 ppm); the ^{19}F nuclei also become less well screened ($\Delta\delta F$ = 17-46 ppm). The constants J_{P-F} are, with rare exceptions, smaller in the complexes than in the free ligands. It has also been noted that, the better screened are the ^{31}P nuclei in the free ligands and complexes, the smaller is $\Delta\delta F$ accompanying complex formation.

Analysis of these results led to the conclusions[60] that complex formation is accompanied by an increase in the paramagnetic contribution to the screening constants of the ^{31}P and ^{19}F nuclei, and this contribution is greater in molybdenum complexes than in nickel complexes. Part of this contribution is due to $d_\pi-d_\pi$ bonding between the phosphorus atom and the metal. The change in hybridisation of the phosphorus atom accompanying complex formation should also play an important part. However, the absence of data on valency angles and bond lengths, both in the initial phosphorus-containing compounds and in the complexes, prevents serious discussion of this problem. It is clear only that a diminution in the *s*-character of the phosphorus-fluorine bond, which should be observed on complex formation, will lead to a decrease in the J_{P-F} constants in the complexes (and this is actually observed in the vast majority of compounds investigated). In the opinion of the authors, polarisation of the lone pair of electrons on the

Table 1. Parameters of ^{31}P and ^{19}F n.m.r. spectra for various groups of three-coordinated phosphorus compounds*.

No.	Compound	δ_P, ppm	δ_F, ppm	J_{P-F}, c/s	Σ_κ	Refs.	No.	Compound	δ_P, ppm	δ_F, ppm	J_{P-F}, c/s	Σ_κ	Refs.
1	PF_3	−97	464	1405	11.7	1	14	$CH_3PF(NR_2)$	~−165	~540	~920	~8.53	33,38
2	$ROPF_2$	−110	~479	~1290	~10.3	1	15	$(CH_3)_2PF$	−185	626	823	8.44	30,33
3	CCl_3PF_2	−131	518	1285	10.64	1	16		(−187)		(830)		
4	$CNPF_2$	−140	519	1267	11.64	6	17	$CH_3(C_2H_5)PF$	−182	—	820	8.45	33
5	R_2NPF_2	−144	495	1194	10.16	1,14	18	$CH_3(OR)PF$	~−214	~530	~1120	8.70	33,35,41
6	CF_3PF_2	−158	536	1250	11.26	1	19	$CH_3(SR)PF$	~−214	~580	~960	8.56	33,42
7	$ClPF_2$	−176	468	1390	10.80	1		$CH_3(Cl)PF$	−240	—	1040	9.17	33
8	$ClC_6H_4PF_2$	−197	—	1118	—	26	20	$(RO)_2PF$	~−130	495	1215	~8.96	1,14
9	$CH_3C_6H_4PF_2$	−206	521	1099	10.24	26	21	$RO(R_2N)PF$	~−151	~500	~1125	~8.80	14
10	$C_6H_5CH_2PF_2$	−224	527	1191	—	26	22	$(R_2N)_2PF$	~−151	~530	~1050	~8.60	14
11	F_2P-PF_2	−226	—	1130	—	6	23	Cl_2PF	−224	487	1320	9.90	1
12	$C_2H_5PF_2$	−245	533	1162	10.08	33	24	Br_2PF	−255	500	1301	9.30	148,149
13	CH_3PF_2	−251	522	1157	10.07	1,29							

* Chemical shifts δP given relative to H_3PO_4, and δF relative to F_2.

central atom of the free ligand by the unsymmetrical field of the substituents should promote descreening of the ^{31}P nuclei in the compounds XPF_2 and X_2PF. This effect should be considerably weaker in the complexes, since the "lone" pair in them is already bound, and therefore less subject to polarisation.

Nuclear magnetic resonance of fluorides of four-coordinated phosphorus. Until recently data on the parameters of the ^{31}P and ^{19}F n.m.r. spectra of P[IV] fluorides were extremely limited (a 1965 review[1] gave the spectral characteristics of forty compounds). Shortly after this the characteristics of about eighty more compounds were recorded, including the thiophosphoryl derivatives SPF_nX_{3-n} ($n = 1-3$ and X = Cl, Br, NCS, H, NR_2, SR, OR) [12,64,68,150-152], isocyanates and isothiocyanates of phosphorofluoridic acids[68], phosphazofluorides[153,154], the mixed halides XPOHalF (X = R, NR_2, Hal and Hal = Cl, Br) [14,50,155], and also a large number of phosphorofluoridates[66,147,148] and phosphonofluoridates[156,157].

A paper[156] giving the spectral characteristics of about thirty compounds of the type XYPOF, some new and many which had been investigated previously, noted that all the compounds can be divided into three groups, within each of which the chemical shifts δP and δ_F increase linearly with the sum of the electronegativities of the substituents X and Y. The first group comprises molecules in which X and Y ≠ F, Cl, or OH (Table 2, compounds 1-18); in the second group X = F, Cl, OH (compounds 20-27); and in the third group X and Y = F, Cl, OH (compounds 28-30). In each group δP and δ_F vary in the same sense, the dialkylphosphinic fluorides constituting an exception. The occurrence of such groups may be due to a slight variation in valency angles within each series of compounds.

On the whole, methods at present available for the quantum-chemical calculation of the parameters of the ^{31}P and ^{19}F n.m.r. spectra do not provide quantitative estimates of δP and δ_F. Moreover, there is no generally accepted view on the main factors responsible for the variation in the chemical shifts in these compounds[158-161].

Nuclear magnetic resonance of fluorides of five-coordinated phosphorus. Among phosphorus compounds the P[V] fluorides are some of the most interesting subjects for investigation by n.m.r. spectroscopy on ^{31}P and ^{19}F nuclei. However, theoretical aspects of screening and spin-spin interaction are still less developed for these compounds than for P[III] and P[IV] fluorides, which makes it important to seek purely empirical rules for the variation in the parameters of the spectra for different groups of these compounds.

The number of P[V] fluorides which have been investigated by the n.m.r. method now exceeds a hundred. They include most of the structures from XPF_4 to X_4PF which are conceivable in practice, the spectral data for which, with rare exceptions, are satisfactorily interpreted on the basis of a trigonal-bipyramidal model. Such exceptions include in particular the spectral characteristics of certain adducts of P[III] fluorides with halogens (Table 3), which have been investigated quite recently[13,16,17,45,162].

In spite of the formal similarity in structure, these compounds (Table 3) give an extraordinarily wide range of variation in δP (from +110 to -80 ppm); the majority have very low values of δ_F, and the constants J_{P-F} are unusually large for axial fluorine atoms. However, the low-temperature ^{19}F n.m.r. spectra proved the trigonal-bypyramidal configuration (with an axial conformation of the two fluorine atoms) of compounds 1 and 2 [162] and 3-13 [13] (Table 3) (an axial arrangement of the fluorine atoms was confirmed for compounds of the type $R_2NPF_2Hal_2$ by examining the ^{19}F n.m.r. spectra of compounds 5 and 11 at various temperatures). In view of the closeness of the spectral characteristics, compounds 21-31 can also be assigned to the same molecular model. Compounds 14-20 most probably have an ionic structure, especially in view of their very low δP values.

Another unexpected result, which at first glance seems to contradict the trigonal-bipyramidal model of the molecules, has been obtained for the structure of the trifluorophosphoranes RPF_3NHR' [13,40,125,128,163]. As was first shown for methylisobutylaminotrifluorophosphorane[40], the

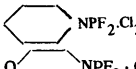
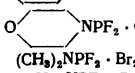
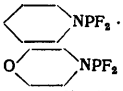
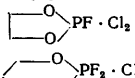
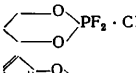
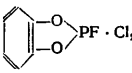
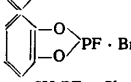
Table 2. Parameters of ^{31}P and ^{19}F n.m.r. spectra for compounds of type $\begin{matrix} X \\ \diagdown \\ \diagup \\ Y \end{matrix}$POF in comparison with sum of electronegativities of X and Y*.

No.	Compound X	Compound Y	δP, ppm	δ_F, ppm	J_{P-F}, c/s	$\kappa_X + \kappa_Y$
			R_2POF			
1	CH_3	CH_3	-66.7	495	968	4.54
2	CH_3	C_4H_9	-65.2	502	975	4.55
3	C_2H_5	C_6H_5	-53.4	507	1014	4.77
4	C_3H_7-*i*	C_3H_7-*i*	-78.2	529	1069	4.56
5	C_6H_5	C_6H_5	-40.5	—	1020	4.98
			R(RO)POF			
6	CH_3	C_3H_7O	-26	490	1035	~4.8
7	C_2H_5	CH_3O	-32.9	501	1078	4.96
8	C_2H_5	C_2H_5O	-33.1	498	1056	4.81
9	CH_2=CH	*i*-C_4H_9O	-15.5	497	1031	~4.9
10	C_6H_5	C_2H_5O	-14.9	495	1031	5.02
			R(RS)POF			
11	CH_3	C_2H_5S	-61.5	472	1064	4.66
12	C_2H_5	CH_3S	-67.0	484	1066	4.73
13	C_3H_7-*i*	C_2H_5S	-74.0	—	1107	4.67
			$(RO)_2POF$, RO(RS)POF, $(R_2N)_2$ POF			
14	C_2H_5O	C_2H_5O	9.2	512	963	5.06
15	*i*-C_4H_9O	*i*-C_4H_9O	9.0	513	969	—
16	C_6H_5O	C_6H_5O	20.3	509	997	5.36
17	C_2H_5O	C_2H_5O	-26.6	—	1127	4.92
18	$(CH_3)_2N$	$(CH_3)_2N$	-23.9	—	954	4.80
			Hal(R)POF, Hal(RO)POF, Hal(R_2N)POF, Hal_2POF			
19	F	CH_3	-27.4	491	1093	6.17
20	F	C_2H_5	-29.2	—	1130	6.18
21	F	$ClCH_2$	-12.0	—	1142	6.37
22	Cl	$ClCH_2$	-32.0	490	1014	5.47
23	OH	CH_3	-32.2	490	1014	5.78
24	F	C_2H_5O	20.9	—	1015	6.43
25	F	C_6H_5O	27.1	—	1030	6.58
26	Cl	CH_3O	5.4	477	1110	5.68
27	F	$(C_2H_5)_2N$	3.6	—	1004	6.26
28	F	F	35.5	523	1080	7.80
29	F	Cl	15.0	477	1138	6.90
30	OH	OH	8.0	504	954	7.02

*Chemical shifts δP given relative to H_3PO_4, and δ_F relative to F_2. Data taken from Ref. 156.

^{19}F n.m.r. spectra of compounds of this type have a pattern indicating the magnetic non-equivalence of all three fluorine atoms in the molecule, whereas the fluorine resonance spectra of the trifluorophosphoranes X_2PF_3 investigated previously indicated interaction of phosphorus nuclei with two magnetically equivalent (axial) ^{19}F nuclei and one ^{19}F nucleus differing from them. A more detailed investigation of the ^{19}F and ^{31}P n.m.r. spectra of the trifluorophosphoranes RPF_3NHR' showed[13,125,128,163] that the signals from these compounds in the fluorine resonance spectra can also be divided into signals from an equatorial and two axial fluorine atoms, because of the fact that under normal conditions the ^{31}P nuclei do not "sense" the non-equivalence of the two less well screened (axial) fluorine atoms, and preserve the normal pattern of the ^{31}P n.m.r. spectrum.

Table 3. Parameters of ^{31}P and ^{19}F n.m.r. spectra of 1 : 1 adducts of phosphorus(III) fluorides with halogens.

No.	Compound	δ_P^*, ppm	$\delta_{F_{ax}}^*$, ppm	$\delta_{F_{eq}}^*$, ppm	$J_{P-F_{ax}}$, c/s	$J_{P-F_{eq}}$, c/s	$J_{F-F'}$, c/s	Refs
1	$PF_3 \cdot Cl_2$	—	364	472	1023	1085	142	162
2	$PF_3 \cdot Br_2$	—	327	465	1141	1143	124	162
3	$(CH_3)_2NPF_2 \cdot Cl_2$	+44	381	—	960	—	—	16,17
4	$(C_2H_5)_2NPF_2 \cdot Cl_2$	+42	375	—	962	—	—	17
5**		—	378/383	—	945	—	—	13
6		+48	388	—	970	—	—	13
7		+46	—	—	950	—	—	13
8	$(CH_3)_2NPF_2 \cdot Br_2$	+103	354	—	1020	—	—	17
9	$(C_2H_5)_2NPF_2 \cdot Br_2$	+108	356	—	1025	—	—	17
10	$(C_4H_9)_2NPF_2 \cdot Br_2$	—	355	—	1030	—	—	13
11**		—	352/356	—	1050	—	45	13
12		—	353	—	1050	—	—	13
13		+110	—	—	1030	—	—	17
14***	$[(CH_3)_2N]_2PF \cdot Cl_2$	−40	480	—	1135	—	—	13,17
15***	$[(CH_3)_2N]_2PF \cdot Br_2$	−32	489	—	1130	—	—	13,17
16***	$(CH_3)_2N[(C_2H_5)_2N]PF \cdot Br_2$	—	491	—	1130	—	—	13
17***	$CH_3[(C_2H_5)_2N]PF \cdot Cl_2$	—	479	—	1122	—	—	13,17
18***	$C_6H_5[(C_2H_5)_2N]PF \cdot Cl_2$	−67	486	—	1150	—	—	13,17
19***	$CH_3[(C_2H_5)_2N]PF \cdot Br_2$	−80	473	—	1164	—	—	13,17
20***	$C_6H_5[(C_2H_5)_2N]PF \cdot Br_2$	−57	—	—	1200	—	—	13,17
21	$CH_3OPF_2 \cdot Cl_2$	—	378	—	960	—	—	13,21
22	$C_6H_5OPF_2 \cdot Cl_2$	—	376	—	910	—	—	13,21
23	$C_6H_5OPF_2 \cdot Cl_2$	+35	374	—	1020	—	—	13,21
24	$C_6H_5OPF_2 \cdot Br_2$	+96	345	—	1025	—	—	13,21
25		—	375	—	915	—	—	13,21
26		—	373	—	930	—	—	13,21
27		—	379	—	940	—	—	13,21
28		—	345	—	975	—	—	13,21
29	$CH_3PF_2 \cdot Cl_2$	—	356	—	980	—	—	13
30	$C_6H_5PF_2 \cdot Cl_2$	—	377	—	965	—	—	13
31	$C_6H_5PF_2 \cdot Br_2$	—	348	—	1000	—	—	13

* Values of δ_P given relative to H_3PO_4, and of δ_F relative to F_2.

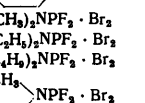
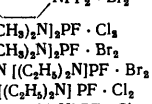
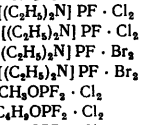
** Axial fluorines are magnetically non-equivalent (recorded at −50°C).

*** Values of δ_F and J_{P-F} arbitrarily attributed to axial fluorine atoms.

Likewise the equatorial fluorine atoms do not "sense" the non-equivalence of the axial fluorine atoms.

It was subsequently established[13,164] that magnetically non-equivalent axial fluorine atoms are present not only in trifluorophosphoranes containing an NHR group attached to the phosphorus atom but also in fluorophosphoranes containing NR^1R^2 and SR groups. There are grounds for assuming that the cause of this phenomenon is the relatively high energy barrier to internal rotation about the P−N and P−S bonds[13,163,164].

Table 4. Parameters of ^{31}P and ^{19}F n.m.r. spectra of fluorophosphoranes containing alkoxy- and alkylthio-groups attached to the phosphorus atom.

No.	Compound	δ_P^*, ppm	$\delta_{F_{ax}}^*$, ppm	$\delta_{F_{eq}}^*$, ppm	$J_{P-F_{ax}}$, c/s	$J_{P-F_{eq}}$, c/s	$J_{F-F'}$, c/s	Refs.
1	CH_3OPF_4	+65	498	—	—	870	—	166
2	$CH_3PF_3(OC_2H_5)$	—	456	502	840	990	64	131
3	$C_2H_5PF_3(OC_2H_5)$	—	460	500	855	1010	62	131
4	$CH_3PF_3(OC_6H_5)$	—	448	—	825	—	—	132
5	$C_6H_5PF_3(OC_6H_5)_2$	—	465	—	829	—	—	132
6	$(C_6H_5)_2PF_3(OC_6H_5)_2$	—	463	—	797	—	—	132
7	$(CH_3O)_3PF_2$	—	503	—	706	—	—	112
8	$(C_6H_5O)_3PF_2$	—	503	—	721	—	—	112
9	$CH_3PF_2(SC_2H_5)_2$	+15	—	—	690	—	—	131
10	$C_6H_5PF_2(SCH_3)$	—	445	502	942	1042	60	132
11**	$C_6H_5PF_3(SC_2H_5)$	+21	446	501	938	1049	59	132,164
12	$C_6H_5PF_3(SC_6H_5)$	—	444	501	970	1060	60	132
13	$(C_6H_5)_2PF_2(SCH_3)$	—	455	—	760	—	—	132
14	$(C_6H_5)_2PF_2(SC_2H_5)$	—	455	—	752	—	—	132
15	$(C_6H_5)_2PF_2(SC_6H_5)$	—	456	—	796	—	—	132
16	$(C_6H_5S)_2PF_2$	—	502	—	713	—	—	112
17	$(C_2H_5)_2NPF_2(SC_2H_5)_2$	+31	437	—	845	—	—	13
18		+28	471	—	785	—	—	47
19		+50	489	—	810	—	—	19
20		+81	—	—	915	—	—	19
21		+83	—	—	930	—	—	19

* Chemical shifts δ_P given relative to H_3PO_4, and δ_F relative to F_2.

** At −50°C the axial fluorine atoms exhibit magnetic non-equivalence: $\delta'_{F_{ax}} = 450$ ppm and $\delta''_{F_{ax}} = 442$ ppm; $J'_{P-F_{ax}} = 940$ c/s and $J''_{P-F_{ax}} = 1030$ c/s [13,164]. A similar phenomenon cannot be observed in compounds containing RO-groups[13].

A large number of fluorophosphoranes containing alkoxy- and alkylthio-groups attached to the phosphorus atom have recently been investigated by means of the ^{19}F n.m.r. spectra (Table 4). Compounds of this type are in most cases unstable, and their spectral characteristics are therefore especially important for identifying newly prepared products. Table 4 makes it clear that these compounds are characterised by positive chemical shifts δ_P, spin−spin interaction constants $J_{P-F_{eq}}$ exceeding 1000 c/s, and large fluctuations in the values of $J_{P-F_{ax}}$ (from 690 to 970 c/s). An appreciable increase in screening of the

axial fluorine atoms is noteworthy on passing from fluorophosphoranes containing a carbon–phosphorus bond (Table 4, compounds 2–6 and 9–15) to compounds containing more electronegative substituents (e.g. compounds 7, 8, and 16). The trigonal–bipyramidal configuration of compounds of this type is confirmed by the n.m.r. spectra of the trifluorophosphoranes (compounds 2, 3, and 10–12) containing signals from two (axial and equatorial) groups of fluorine atoms. In several cases, e.g. with the cyclic monofluorophosphoranes 20 and 21, whether the fluorine is located at the equator or in an axial position of the bipyramid remains an open question, since the values of δ_F remain unknown, while those of the constants J_{P-F} are nevertheless large for an axial position, usually occupied by the more electronegative substituents, to be assigned to the fluorine atoms solely on the basis of these data[165]. The spectral characteristics of the recently reported[166] compound CH_3OPF_4 demand special notice (Table 4, compound 1): the ^{31}P nuclei are considerably better screened than in CH_3PF_4 and PF_5, almost to the same extent as in $BrPF_4$ [98]; the quantity δ_F occupies an intermediate position between its values for CH_3PF_4 and PF_5 (but is closer to the latter); while the constant J_{P-F} is considerably smaller than in the above compounds.

The parameters of the n.m.r. spectra for all the phosphorus(V) hydrides other than the monohydride phenyltrifluorophosphorane[167] have been given in papers published since 1964. During this time n.m.r. spectroscopy has been used to examine about fifteen compounds having various types of structure, beginning from HPF_4 and H_2PF_3 and ending with the hydrides $XYPHF_2$ (where X and Y are substituents other than fluorine). The parameters (Table 5) and the character of the ^{31}P and ^{19}F n.m.r. spectra of the phosphorus hydrides investigated indicate that they have a five-coordinated structure, and are well interpreted on the basis of a trigonal–bipyramidal model. The compounds are characterised by positive values of the chemical shifts δ_P, reaching ±70 ppm for the hydrides $ROPHF_2NHR'$ (Table 5, compound 13) and extremely large numerical values of the constants J_{P-H}, exceeding by more than 100 c/s the constants $J_{P-F_{ax}}$. There is also a tendency for the constants J_{P-H} to increase with increase in the sum of the electronegativities of the substituents attached to the phosphorus atom.

2. Electron Diffraction

An examination of phosphorus pentafluoride, methylphosphorus tetrafluoride, and dimethyphosphorous trifluoride, made in 1965 by Bartell and Hansen[165], confirmed the trigonal–bipyramidal structure of the molecules and led to the following important conclusions: (1) the more electronegative substituents occupy the vertices of the bipyramid; (2) axial bonds are more polar and longer than equatorial bonds; and (3) the replacement of fluorine atoms by alkyl and other less electronegative substituents results in an increase in the difference $r_{ax} - r_{eq}$. The results can be satisfactorily explained both on the basis of Rundle's model[168–170], which postulates that axial bonds are three-centred and have a bond order of ~ 0.5, and by means of Gillespie's model[171–174], in which the stereochemistry of the molecule is determined by the repulsion of electron pairs. It is difficult to give preference to either model, for, as Bartell remarked[175], they both require additional postulates to explain all the details found for the five-coordinated structure.

3. Vibrational Spectra

Vibrational spectroscopy has also been fairly widely used for analysing the structure of the fluorides of phosphorus. The most significant results have been obtained when the vibrational spectra have been used to solve structural problems in the fluorides of five-coordinated phosphorus. The infrared and Raman spectra of HPF_4 [67,137], H_2PF_3 [67,137,138], and the fluorophosphoranes $(CH_3)_nPF_{5-n}$ ($n = 1-3$) [176] have been interpreted in terms of a trigonal–bipyramidal molecular model in which the less electronegative substituents occupy equatorial positions. In the vapours all the compounds are found to be monomeric,

Table 5. Parameters of ^{31}P and ^{19}F n.m.r. spectra of hydrides of five-coordinated phosphorus*.

No.	Compound	δ_P, ppm	$\delta_{F_{ax}}$, ppm	$\delta_{F_{eq}}$, ppm	$J_{P-F_{ax}}$, c/s	$J_{P-F_{eq}}$, c/s	J_{P-H}, c/s	J_{F-F}, c/s	$\frac{J_{H-Feq}}{J_{H-Fax}}$	Refs.
1**	HPF_4	+53.6	~480***		~980***		1100	—	91	67,137
2**	H_2PF_3	+24	401	484	770	824	841	—	80	67,137
3	CH_3PHF_3	+10	446	530	795	965	850	19	120/30	42,139,140
4	$C_2H_5PHF_3$	—			810	976	862	22.7	121/30	139
5	CH_3PHF_2Cl	—	446	—	785	—	—	—	121	42
6	$CH_3PHF_2[N(C_2H_5)_2]$	—	469	—	832	—	—	—	132	42
7	$CH_3PHF_2(HNC_4H_9\text{-}i)$	+44.5	—	—	622	—	760	—	—	37,38
8	$CH_3PHF_2(HNCH_2{-}CH{=}CH_2)$	+42	—	—	609	—	739	—	—	37,38
9	$CH_3PHF_2(OC_2H_5)$	+20	—	—	757	—	850	—	—	34,35
10	$CH_3PHF_2(OC_3H_7\text{-}i)$	—	452	—	725	—	—	—	120	34,35
11	$\begin{matrix}\text{NH—PHF}_2(CH_3)\\ \text{NH—PHF}_2(CH_3)\end{matrix}$	+44	—	—	610	—	780	—	120	143
12	$CH_3C_6H_4PHF_3$	+30	$\Delta\delta_F = 53$ ppm		815	950	—	34	118/34	13,40
13	$CH_3O(C_2H_5NH)PHF_2$	+70	490	—	670	—	818	—	122	14
14	$(CH_3)_2N(C_2H_5NH)PHF_2$	—	488	—	712	—	—	—	127	14
15	$(CH_3)_2PHF_2$	+31.7	458	—	535	—	733	—	98	140

* Chemical shifts δ_P given relative to H_3PO_4, and δ_F relative to F_2.
** The n.m.r. spectra of the deuteriated derivatives are given in Ref. 67.
*** Axial and equatorial fluorine atoms indistinguishable.

whereas in the liquid state the phosphorane PH_2F_3 is associated by means of hydrogen bonds. It is interesting that in the liquid state the hydride HPF_4 is either considerably less or not at all associated.

Investigation by means of the vibrational spectra of phosphorus hydrides of different degrees of coordination has shown that the P–H stretching frequencies appear over a wide range from 2233 cm^{-1} (in HPF_2)[23] to 2545 cm^{-1} (in H_2PF_3). The most significant are the frequencies ν_{P-H} and the constants J_{P-H}, which vary in parallel with the former on passing from the phosphorus(III) fluorides to the four- and five-coordinated compounds (for HPF_2 [23], $HPOF_2$ [64], and HPF_4 [67] we have 2233, 2500, and 2485 cm^{-1} for ν_{P-H}, and 182, 844, and > 1000 c/s for J_{P-H}). Within groups of four- and five-coordinated compounds there is a tendency for ν_{P-H} and J_{P-H} to increase with the electronegativity of the substituents attached to the phosphorus atom (e.g. on passing from $HPSF_2$ [20] to $HPOF_2$ [20] the frequencies ν_{P-H} and the constants J_{P-H} increase by 42 cm^{-1} and 119 c/s respectively, and on passing from HPF_4 [67] to $RPHF_3$ [40,139] by ~40 cm^{-1} and ~150 c/s).

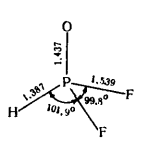
Table 6. Spin–spin interaction constants $J_{P-F_{ax}}$ and P–F stretching frequencies compared with lengths of $P-F_{ax}$ bond for the fluorophosphoranes X_nPF_{5-n}.

No.	Compound	ν_s^{P-F}, cm^{-1}	ν_{as}^{P-F}, cm^{-1}	Mean	$J_{P-F_{ax}}$, c/s	$P-F_{ax}$ bond length, Å
1	PF_5	640	945	793	—	1.577
2	CH_3PF_4	596	843	720	—	1.612
3	$(CH_3)_2PF_3$	540	755	648	772	1.643
4	$(CH_3)_3PF_2$	500	670	585	541	—

* Data taken from Ref. 176.

Increase in the sum of the electronegativities of the substituents in the series of fluorophosphoranes X_nPF_{5-n} ($n = 0-3$) has been shown[176] to be accompanied by contraction of the $P-F_{ax}$ bonds together with an increase in the frequencies of the symmetric and antisymmetric vibrations $\nu_{P-F_{ax}}$ (see Table 6). A similar relation between the sum of the electronegativities of the substituents and the frequencies ν_{P-F} is observed also for several series of compounds of four-coordinated phosphorus[148,149] [for the main results on the vibrational spectra of phosphorus(IV) fluorides see Refs. 148, 149, and 177–184].

Quite recently[185] the microwave spectrum has yielded for $HPOF_2$ the parameters



∠OPF = 116.5°
∠OPH = 117.9°
Dipole moment 2.65 ± 0.03 D

Vibrational and especially microwave spectroscopy has been used very rarely to solve structural problems in the phosphorus(III) fluorides, the number and significance of papers published during the period in which we are interested being fairly limited[186–188].

REFERENCES

1. R. Schmutzler, Adv. Fluorine Chem., 5, 31 (1965).
2. F. Olstowski, US P. 3 248172 (1962); C.A., 64, 19 040f (1966).
3. R. G. Cavell, J. Chem. Soc., 1992 (1964).
4. R. Rudolph, J. Morse, and R. Parry, Inorg. Chem., 5, 1464 (1966).
5. J. Morse and R. Parry, Inorg. Synth., 10, 147 (1967).
6. R. Rudolph, R. Taylor, and R. Parry, J. Amer. Chem. Soc., 88, 3729 (1966).
7. A. Finch, Canad. J. Chem., 37, 1793 (1959); G. Harris and D. Payne, Quart. Rev., 15, 173 (1961).
8. M. Lustig, J. Ruff, and O. Colburn, J. Amer. Chem. Soc., 88, 3875 (1966).
9. H. Roesky, Chem. Ber., 100, 2142 (1967).
10. H. Anderson, J. Amer. Chem. Soc., 69, 2495 (1947).
11. M. Lustig and Will, Inorg. Chem., 6, 1448 (1967).
12. M. Lustig, Inorg. Chem., 7, 2054 (1968).
13. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, M. A. Sokal'skii, M. A. Landau, and S. S. Dubov, "IV Konferentsiya po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Fourth Conference on the Chemistry and Application of Organophosphorus Compounds), Kazan, 1969.
14. G. I. Drozd, M. A. Sokal'skii, V. V. Sheluchenko, M. A. Landau, and S. Z. Ivin, Zhur. Vses. Khim. Obshch. Mendeleeva, 14, 592 (1969).
15. Zh. M. Ivanova, Zhur. Obshch. Khim., 35, 164 (1965).
16. K. Kohn and R. Parry, Inorg. Chem., 7, 46 (1968).
17. G. I. Drozd, M. A. Sokal'skii, V. V. Sheluchenko, M. A. Landau, and S. Z. Ivin, Zhur. Obshch. Khim., 39, 936 (1969).
18. J. Clune and K. Cohn, Inorg. Chem., 7, 2067 (1968).
19. G. I. Drozd and S. Z. Ivin, Zhur. Obshch. Khim., 39, 1179 (1969).
20. A. A. Petrov, N. A. Razumov, and Zh. L. Evtikov, Zhur. Obshch. Khim., 37, 1410 (1967).
21. G. I. Drozd and S. Z. Ivin, Zhur. Obshch. Khim., 38, 1907 (1968); 40, 502 (1970).
22. J. Nixon, Chem. Comm., 669 (1967).
23. R. Rudolph and R. Parry, Inorg. Chem., 4, 1339 (1965).
24. R. Rudolph and R. Parry, J. Amer. Chem. Soc., 89, 1621 (1967).
25. V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, Zhur. Obshch. Khim., 29, 3957 (1959).
26. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, B. I. Tetel'baum, G. M. Luganskii, and A. D. Varshavskii, Zhur Obshch. Khim., 37, 1343 (1967).
27. G. I. Drozd, S. Z. Ivin, and V. V. Sheluchenko, Zhur. Vses. Khim. Obshch. Mendeleeva, 12, 472 (1967).
28. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and B. I. Tetel'baum, Zhur. Obshch. Khim., 37, 958 (1967).
29. F. Seel, K. Rudolph, and R. Budenz, Z. anorg. Chem., 341, 196 (1965).
30. F. Seel, K. Rudolph, and W. Gombler, Angew. Chem., 79, 686 (1967).
31. R. Schmutzler, Chem. Ber., 98, 552 (1965).
32. G. I. Drozd and S. Z. Ivin, USSR P. 181 111 (1965); Byull. Izobr., No. 9 (1966).
33. V. V. Sheluchenko, S. S. Dubov, G. I. Drozd, and S. Z. Ivin, Zhur. Strukt. Khim., 9, 909 (1968).
34. G. I. Drozd, S. Z. Ivin, and V. V. Sheluchenko, Zhur. Vses. Khim. Obshch. Mendeleeva, 12, 474 (1967).
35. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and V. N. Kulakova, Zhur. Obshch. Khim., 38, 576 (1968).

36. S. Z. Ivin, Yu. M. Zinov'ev, V. N. Kulakova, and G. I. Drozd, USSR P. 182158 (1965); Byull. Izobr., No. 9 (1966).
37. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and B. I. Tetel'baum, Zhur. Obshch. Khim., 37, 957 (1967).
38. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, B. I. Tetel'baum, G. M. Luganskii, and A. D. Varshavskii, Zhur. Obshch. Khim., 37, 1631 (1967).
39. S. Z. Ivin and G. I. Drozd, USSR P. 181109 (1965); Byull. Izobr., No. 9 (1966).
40. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and A. D. Varshavskii, Zhur. Obshch. Khim., 38, 567 (1968).
41. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and B. I. Tetel'baum, Collected Papers, "Radiospektroskopicheskie i Kvantovokhimicheskie Metody v Strukturnykh Issledovaniyakh" (Radiospectroscopic and Quantum-chemical Methods in Structural Investigations), Nauka, Moscow, 1967, p. 204.
42. V. V. Sheluchenko, G. I. Drozd, M. A. Landau, and S. S. Dubov, Zhur. Strukt. Khim., 11, 450 (1970).
43. M. Green, R. Haszeldine, B. Iles, and D. Rowsell, J. Chem. Soc., 6879 (1965).
44. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and M. A. Landau, Zhur. Obshch. Khim., 38, 1653 (1968).
45. G. I. Drozd, M. A. Sokal'skii, V. V. Sheluchenko, M. A. Landau, and S. Z. Ivin, Zhur. Obshch. Khim., 39, 935 (1969).
46. J. F. Nixon and R. G. Cavell, J. Chem. Soc., Suppl. 2, 5983 (1964).
47. G. I. Drozd, S. Z. Ivin, and V. V. Sheluchenko, Zhur. Obshch. Khim., 38, 1906 (1968).
48. V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, Zhur. Obshch. Khim., 39, 579 (1969).
49. V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, Zhur. Obshch. Khim., 39, 838 (1969).
50. G. I. Drozd, O. G. Strukov, and S. Z. Ivin, Zhur. Obshch. Khim., 39, 1418 (1969).
51. V. N. Kulakova, Yu. M. Zinov'ev, S. P. Makarov, V. A. Shpanskii, and L. Z. Soborovskii, Zhur. Obshch. Khim., 39, 385 (1969).
52. G. I. Drozd and S. Z. Ivin, Zhur. Obshch. Khim., 39, 1417 (1969).
53. T. Kruck, Angew. Chem., 79, 27 (1967).
54. K. Morse and R. Parry, J. Amer. Chem. Soc., 89, 172 (1967).
55. W. Deewer and D. Ritter, J. Amer. Chem. Soc., 89, 5073 (1967).
56. A. Burg and J. Street, Inorg. Chem., 5, 1532 (1966).
57. J. Nixon, J. Chem. Soc., 1136 (1967).
58. T. Kruck, K. Bauer, and W. Lang, Chem. Ber., 101, 138 (1968).
59. O. Glemser, E. Niecke, and A. Muller, Angew. Chem., 78, 593 (1966).
60. G. Reddy and R. Schmutzler, Inorg. Chem., 6, 823 (1967).
61. R. Clark, J. Harganden, H. Haas, and R. Shelim, Inorg. Chem., 7, 673 (1968).
62. O. Glemser and U. Biermann, Chem. Ber., 100, 1184 (1967).
63. H. Roesky, Chem. Ber., 101, 636 (1968).
64. T. Charlton and R. Cavell, Inorg. Chem., 6, 2204 (1967).
65. T. Charlton and R. Cavell, Chem. Comm., 763 (1966).
66. T. Charlton and R. Cavell, Inorg. Chem., 7, 2195 (1968).
67. P. Treichell, R. Goodrich, and S. Pierce, J. Amer. Chem. Soc., 89, 2017 (1967).
68. H. Roesky, Angew. Chem., 79, 85 (1967).
69. H. Roesky, Chem. Ber., 100, 2147 (1967).
70. H. Roesky, Angew. Chem. Internat. Edn., 6, 61 (1967).
71. G. I. Derkach and E. I. Slyusarenko, Zhur. Obshch. Khim., 37, 2069 (1967).
72. O. Glemser, U. Biermann, and H. Fild, Chem. Ber., 100, 1082 (1967).
73. Zh. M. Ivanova, E. A. Stukalo, and G. I. Derkach, Zhur. Obshch. Khim., 37, 1144 (1967).
74. D. Marteau and G. Cady, Inorg. Chem., 5, 1829 (1966).
75. G. I. Derkach and A. V. Norbut, Zhur. Obshch. Khim., 37, 1364 (1967).
76. M. Lustig and J. Ruff, Inorg. Chem., 6, 2115 (1967).
77. H. Roesky, Chem. Ber., 100, 950 (1967).
78. H. Falius, Chem. Ber., 100, 1179 (1967).
79. H. Roesky, F. Tebbe, and E. L. Muetterties, J. Amer. Chem. Soc., 89, 1272 (1967).
80. W. Mahler, J. Amer. Chem. Soc., 90, 523 (1968).
81. A. P. Kreshkov, V. A. Drozdov, and I. Yu. Orlova, Zhur. Obshch. Khim., 36, 307 (1966).
82. A. P. Kreshkov, V. A. Drozdov, and I. Yu. Petrov, Zhur. Obshch. Khim., 36, 2014 (1966).
83. R. Greenhalgh and I. Blanchfield, Canad. J. Chem., 44, 501 (1966).
84. V. G. Pesin and I. G. Vitenberg, Zhur. Obshch. Khim., 36, 1268 (1966).
85. S. Kongprich and W. Preusse, Inorg. Chem., 6, 1915 (1967).
86. M. Becke-Goehring, and K. Niedenzu, Chem. Ber., 89, 1771 (1956); 90, 151 (1957).
87. R. Clement and L. Benck, Z. anorg. Chem., 287, 12 (1956).
88. O. Glemser, H. Roesky, and P. Heinze, Angew. Chem., 79, 723 (1967).
89. G. I. Derkach and M. V. Kolotilo, Zhur. Obshch. Khim., 36, 1437 (1966).
90. Zh. M. Ivanova, E. S. Lechenko, and A. V. Kirsanov, Zhur. Obshch. Khim., 35, 1607 (1965).
91. J. Shreeve, J. Inorg. Nuclear Chem., 30, 3375 (1968).
92. Zh. M. Ivanova, S. K. Mikhailik, and G. I. Derkach, Zhur. Obshch. Khim., 38, 1334 (1968).
93. V. A. Shokol, V. F. Gamaleya, and G. I. Derkach, Zhur. Obshch. Khim., 37, 2528 (1966).
94. H. Boter and G. Berg, Rec. Trav. chim., 85, 919 (1966).
95. B. M. Gladshtein, I. P. Kulyulin, and L. Z. Soborovskii, Zhur. Obshch. Khim., 36, 488 (1966).
96. M. Lustig, Inorg. Chem., 4, 104 (1965).
97. R. Carter and R. Holmes, Inorg. Chem., 4, 738 (1965).
98. R. Rogowski and K. Cohn, Inorg. Chem., 7, 2193 (1968).
99. L. Kolditz, Z. anorg. Chem., 286, 307 (1956).
100. T. Kesavadas and D. S. Payne, J. Chem. Soc. (A), 1001 (1967).
101. D. Brown, G. Fraser, and D. Sharp, J. Chem. Soc. (A), 171 (1966).
102. D. Brown, G. Fraser, and D. Sharp, Chem. and Ind., 367 (1964).
103. F. Ramirez, C. Smith, and S. Megerson, Tetrahedron Letters, 3651 (1966).
104. F. Ramirez, A. Gulati, and C. Smith, J. Amer. Chem. Soc., 89, 6283 (1967).
105. L. Kolditz and W. Rehak, Z. anorg. Chem., 342, 32 (1966); Angew. Chem., 78, 452 (1966).
106. F. N. Tebbe and E. L. Muetterties, Inorg. Chem., 6, 129 (1967).
107. J. Jones, Inorg. Chem., 5, 1229 (1966).

108. R. Goodrich and P. Treichel, J. Amer. Chem. Soc., 88, 3509 (1966).
109. J. J. Harris and B. Rudner, J. Org. Chem., 33, 1392 (1968).
110. G. Demitras and A. McDiarmid, Inorg. Chem., 6, 1903 (1967).
111. R. Schmutzler, Angew. Chem., 76, 893 (1964).
112. R. Mitch, J. Amer. Chem. Soc., 89, 6297 (1967).
113. H. J. Emeléus and T. Onak, J. Chem. Soc. (A), 1291 (1966).
114. R. Schmutzler, Angew. Chem., 77, 530 (1965).
115. P. Treichel and R. Goodrich, Inorg. Chem., 4, 4124 (1965).
116. K. V. Karavanov, S. Z. Ivin, and V. G. Gruzdev, Collected Papers, "Khimiya Organicheskikh Soedinenii Fosfora" (Chemistry of the Organic Compounds of Phosphorus), Nauka, Leningrad, 1967, p. 157.
117. W. Firth, S. Frank, M. Garber, and V. Wystrach, Inorg. Chem., 4, 365 (1965).
118. R. Banhs, R. N. Haszeldine, and Hatton, Tetrahedron Letters, 3994 (1967).
119. M. Garber and W. Firth, US P. 3 268 580 (1963); C. A., 65, 15 245 (1966).
120. J. Griffiths, Inorg. Chim. Acta, 127 (1967).
121. Zh. M. Ivanova and A. V. Kirsanov, Zhur. Obshch. Khim., 32, 2592 (1962).
122. R. Schmutzler, Angew. Chem., 76, 570 (1964).
123. R. Schmutzler and J. Reddy, Inorg. Chem., 4, 191 (1965).
124. S. Z. Ivin, K. V. Karavanov, V. V. Lysenko, and T. N. Sosina, Zhur. Obshch. Khim., 36, 1246 (1966).
125. M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, Zhur. Strukt. Khim., 8, 1097 (1967).
126. R. Schmutzler, US P. 3 300 503 (1965); C. A., 66, 65 631 (1967).
127. G. I. Drozd, S. Z. Ivin, M. A. Landau, and V. V. Sheluchenko, Zhur. Obshch. Khim., 38, 1654 (1968).
128. M. A. Landau, V. V. Sheluchenko, G. I. Drozd, L. E. Saltykova, and S. S. Dubov, Zhur. Strukt. Khim., 10, 736 (1969).
129. R. Schmutzler and J. Reddy, Inorg. Chem., 5, 164 (1966).
130. R. Schmutzler, J. Chem. Soc., 5630 (1965).
131. G. I. Drozd, M. A. Sokal'skii, V. V. Sheluchenko, and S. Z. Ivin, Zhur. Obshch. Khim., 39, 1177 (1969).
132. S. Peake and R. Schmutzler, Chem. Comm., 665 (1968).
133. S. Z. Ivin, K. V. Karavanov, I. D. Shelakov, and V. V. Lysenko, Zhur. Obshch. Khim., 37, 1341 (1967).
134. E. L. Muetterties and W. Mahler, Inorg. Chem., 4, 119 (1965).
135. Zh. M. Ivanova and A. B. Kirsanov, Zhur. Obshch. Khim., 31, 3991 (1961).
136. B. Blaser and K. Worms, Angew. Chem., 73, 76 (1961).
137. R. Holmes and R. Storey, Inorg. Chem., 5, 2146 (1966).
138. T. Gaubeau, R. Baumgartner, and H. Weiss, Z. anorg. Chem., 348, 286 (1966).
139. R. Goodrich and P. Treichel, Inorg. Chem., 7, 694 (1968).
140. F. Seel, W. Gombler, and K. Rudolph, Z. Naturforsch., 23b, 387 (1968).
141. S. Z. Ivin, K. V. Karavanov, V. G. Gruzdev, V. V. Lysenko, I. D. Shelakova, and G. I. Drozd, "3-ya Konferentsiya po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Third Conference on the Chemistry and Application of Organophosphorus Compounds), Moscow, 1965.
142. S. Z. Ivin and G. I. Drozd, USSR P. 181 110 (1965); Byull. Izobr., No. 9 (1966).
143. G. I. Drozd, S. Z. Ivin, and V. V. Sheluchenko, Zhur. Obshch. Khim., 38, 1655 (1968).
144. M. Van der Akker and F. Jellinek, Rec. Trav. chim., 86, 275 (1967).
145. J. Van Wazer, C. Callis, J. Shoolery, and R. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
146. R. Schmutzler, J. Chem. Soc., 4551 (1964).
147. V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, Zhur. Vses. Khim. Obshch. Mendeleeva, 12, 351 (1967).
148. A. Müller, E. Niecke, and O. Glemser, Z. anorg. Chem., 350, 246 (1967); 347, 275 (1966).
149. A. Müller, H. Roesky, and B. Krebs, Z. Chem., 7, 159 (1967).
150. H. Horn and A. Müller, Z. anorg. Chem., 346, 266 (1966).
151. H. Roesky, Chem. Ber., 100, 1447 (1967).
152. H. Horn, Z. Naturforsch., 21b, 617 (1967).
153. O. Glemser, E. Niecke, and J. Stenzel, Angew. Chem., 79, 723 (1967).
154. G. I. Drozd, S. Z. Ivin, and A. D. Varshavskii, Zhur. Obshch. Khim., 39, 1178 (1969).
155. A. Müller, E. Niecke, and O. Glemser, Z. anorg. Chem., 350, 246 (1967).
156. V. V. Sheluchenko, M. A. Landau, S. S. Dubov, A. A. Neimysheva, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 177, 376 (1967).
157. V. F. Bystrov, A. A. Neimysheva, A. U. Stepanyants, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 156, 637 (1964).
158. J. Letcher and J. Van Wazer, J. Chem. Phys., 44, 815 (1966).
159. D. Purdela, Rev. Rom. Chem., 16, 949 (1965).
160. B. I. Ionin, Zhur. Obshch. Khim., 38, 1651 (1968).
161. N. M. Sergeev, "Spektry YaMR-^{19}F i Struktura Ftorvinil'nykh Soedinenii" (Fluorine-19 Nuclear Magnetic Resonance Spectra and the Structure of Fluorovinyl Compounds), Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1966.
162. W. Mahler and E. L. Muetterties, Inorg. Chem., 4, 1520 (1965).
163. G. I. Drozd, M. A. Sokal'skii, M. A. Landau, and S. S. Dubov, Zhur. Strukt. Khim., 10, 142 (1969).
164. M. A. Sokal'skii, G. I. Drozd, M. A. Landau, and S. S. Dubov, Zhur. Strukt. Khim., 10, 1113 (1969).
165. L. Bartell and K. Hansen, Inorg. Chem., 4, 1777 (1965).
166. K. Crosbie, G. Freser, and D. Sharp, Chem. and Ind., 423 (1968).
167. E. L. Muetterties, W. Mahler, K. Packer, and R. Schmutzler, Inorg. Chem., 3, 1298 (1964).
168. R. E. Rundle, Acta Cryst., 14, 585 (1961).
169. R. E. Rundle, Rec. Chem. Progr., 23, 195 (1962).
170. R. E. Rundle, J. Amer. Chem. Soc., 85, 112 (1963).
171. R. J. Gillespie and R. S. Nyholm, Quart. Rev., 11, 339 (1957).
172. R. J. Gillespie, J. Chem. Educ., 40, 295 (1963).
173. R. J. Gillespie, J. Amer. Chem. Soc., 85, 467 (1963).
174. R. J. Gillespie, Inorg. Chem., 5, 1634 (1966).
175. L. Bartell, Inorg. Chem., 5, 1635 (1966).
176. A. J. Downs and R. Schmutzler, Spectrochim. Acta, 21, 1927 (1965); 23a, 681 (1967).
177. A. Müller and H. Roesky, Z. Phys. Chem. (Frankfurt), 55, 218 (1967).
178. H. Horn and A. Müller, Z. Naturforsch, 21b, 729 (1966); 20a, 746 (1965); 23a, 2189 (1967).

179. J. Chockalackal and F. Stafford, J. Amer. Chem. Soc., 88, 9823 (1966).
180. J. Griffiths, Spectrochim. Acta, 24a, 115 (1968).
181. J. Darig, B. Mitchell, J. Yorio, and F. Block, J. Chem. Phys., 70, 3190 (1966).
182. R. Niquist, Spectrochim. Acta, 23a, 845 (1967).
183. E. Stenzel and M. Kuntze, Spectrochim. Acta, 23a, 2189 (1967).
184. R. Cavel, Spectrochim. Acta, 23a, 249 (1967).
185. L. Centofanti and R. Kuczkowski, Inorg. Chem., 7, 2582 (1968).
186. M. Fleming, R. Wyma, and R. Taylor, Spectrochim Acta, 21, 1189 (1965).
187. A. Müller, E. Niecke, and O. Glemser, Z. anorg. Chem., 350, 256 (1967).
188. A. Müller, E. Niecke, and O. Glemser, Z. Naturforsch., 21b, 732 (1966).