out using a sample of similar purity to that used above. *Anal.* Calcd. for Si_2H_5F: F, 23.70. Found: F, 23.7.

Vapor Pressure and Thermal Stability of H_3SiSiH_2F.—The vapor pressure of freshly distilled H_3SiSiH_2F was measured in an all-glass tensimeter connected to a mercury manometer which previously had been pretreated with H_3SiSiH_2F for 15 hr. Vapor pressures are given in Table V. Vapor pressures in the range -95.1 to $-45.9°$ are represented by the equation

$$\log P_{\text{mm}} = -\frac{1376.015}{t + 273.16} + 8.110310$$

Additional values to those given in Table V were used to derive the above relationship. The extrapolated boiling point is $-10.0°$, the heat of vaporization is 6.30 kcal. mole.$^{-1}$, and Trouton's constant is 23.9 cal. deg.$^{-1}$ mole^{-1}. The fact that the vapor pressure curve is reversible on decreasing the temperature indicates that little, if any, thermal decomposition of the compound had occurred during the experiment.

In order to test the thermal stability further, a sample of freshly distilled H_3SiSiH_2F (vapor pressure at $-63.7°$, found 35.25 mm., calcd. 34.75 mm.) was held at 0° for 25 hr. in a 10-ml. all-glass break-seal tube which previously had been pretreated with a sample of H_3SiSiH_2F at room temperature for 15 hr. All the compound was in the vapor phase. At the conclusion of the experiment, no non-condensable gas had been formed and the vapor pressure was unchanged (vapor pressure at $-63.7°$, found 35.30 mm., calcd. 34.75 mm.). The infrared spectrum of the sample at the conclusion of the experiment was identical with that of the pure material.

Infrared Spectra of $H_3SiSiH_2N(CH_3)_2$, $H_3SiSiH[N(CH_3)_2]_2$, and H_3SiSiH_2F.—All measurements were made with a Perkin-Elmer 137B Infracord spectrophotometer on the gaseous phase at 25° with the sample confined in a 10-cm. cell fitted with 6-mm. potassium bromide windows cemented with glyptal resin. The spectrum of $H_3SiSiH_2N(CH_3)_2$ was observed at pressures of 33.5 mm. (A), 15.0 mm. (B), and 3.5 mm. (C), while that of $H_3SiSiH[N(CH_3)_2]_2$ was observed at 12.0 mm. The spectrum of H_3SiSiH_2F was recorded at pressures of 10.5 and 3.0 mm. The absorption maxima are listed in Table VI and the spectra are given in Fig. 1.

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Stereochemistry of Phosphorus(V) Fluorides

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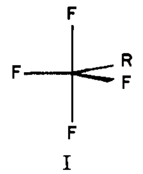
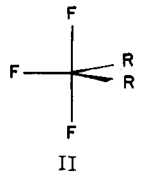
F^{19} n.m.r. spectral data for a number of mono-, di-, and trisubstituted phosphorus(V) fluorides are presented and discussed in terms of stereochemistry, configurational exchange, and general correlation of spin–spin coupling and chemical shift data. All dialkyl, diaryl, and alkyl–aryl derivatives have the R groups in equatorial positions of a trigonal bipyramid. In the cyclic compound $(CH_2)_4PF_3$, a rapid intramolecular, positional exchange of equatorial and apical fluorine atoms occurs; the barrier to this exchange is about 7 kcal.

Recent synthetic advances have made available a number of substituted phosphorus(V) fluorides,[1] and since little is known about stereochemistry in the trigonal bipyramidal or the tetragonal pyramidal structures, we were prompted to undertake a structural analysis of this class of compounds. Our major stereochemical probe has been nuclear magnetic resonance.

Sterically, the most stable isomers in a trigonal bipyramid for the three classes of alkyl or aryl derivatives of PF_5 would appear to be I, II, and III. These assignments are based on the assumptions that the only significant steric interactions are those between groups at 90° angles and that the magnitude of the ligand repulsions increases in the order F–F < F–R < R–R.



I



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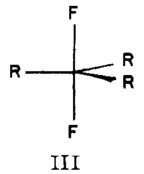
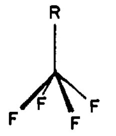
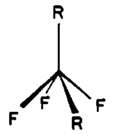


III

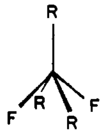
Similar considerations for the tetragonal pyramid yield the following favored structures.



IV



V



VI

As one possible approximation of the bonding in a trigonal bipyramid, phosphorus hybrid orbitals in the equatorial plane may be constructed from a combination of the 3s and two 3p orbitals and those on the apical axis from a 3p3d combination. The difference in energy levels between these two should reflect the s electron promotion energy. It is assumed that the energy difference will be smallest where the ligands are strongly electronegative, *e.g.*, PF_5, and will increase with increasing substitution with electropositive groups. On this basis, it is not unreasonable to presume that hydrogen or an alkyl group would achieve best overlap with a phosphorus sp^2 hybrid orbital in the equatorial plane.[2] Alternatively it may be assumed that better

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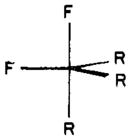
[1] (a) L. M. Yagupolskii and Zh. M. Ivanova, *Zh. Obshch. Khim.*, **29**, 3766 (1959); (b) W. C. Smith, *J. Am. Chem. Soc.*, **82**, 6176 (1960); (c) I. P. Komkov, S. Z. Ivin, K. W. Karawanov, and L. Je. Smirnov, *Zh. Obshch. Khim.*, **32**, 301 (1962); (d) R. Schmutzler, *Chem. Ind.* (London), 1868 (1962); (e) R. Schmutzler, to be published.

[2] It is perhaps significant that in $:SF_4$ and $:\ddot{C}lF_3$ the non-bonding electron pairs which should favor orbitals of maximum s character go to equatorial sites. However, since a non-bonding electron pair is a sterically large entity, the same stereochemical conclusions for $:SF_4$ and $:\ddot{C}lF_3$ should be drawn.

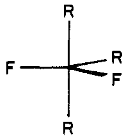
overlap for chlorine or bromine relative to fluorine may be achieved with an axial dp hybrid orbital. There are many alternative approaches to the complex and incompletely understood subject of bonding in a trigonal bipyramid. The foregoing is not intended to be limiting; detailed consideration of this subject is properly the exercise of the theoretician.

Results

R_3PF_2.—All the R_3PF_2 compounds examined by n.m.r. have spectroscopically equivalent sets of fluorine atoms and equivalent sets of R groups. In the case of the alkyl and trifluoromethyl derivatives, hyperfine structure due to spin–spin coupling of P–F fluorine atoms and the hydrogen or fluorine atoms attached to carbon was evident; therefore, spectroscopic equivalence is not due to some intermolecular exchange process. The possibility that spectroscopic equivalence of like ligands could arise in structures VII and VIII from some *intramolecular* process is considered rather unlikely because of the large size of the R groups.



VII



VIII

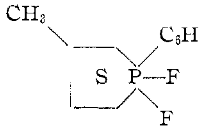
Thus, the n.m.r. data suggest structure III, the one favored on the basis of steric and overlap considerations.[3] Furthermore, chemical shift data discussed in a later section give internal consistency only if structure III for R_3PF_2 is accepted. Infrared data also support structure III in that only a single, very low frequency PF absorption is present in all these derivatives.

The spin–spin coupling data for the R_3PF_2 compounds are summarized in Table I. The very large variation of A_{PF} is unique for substituted PF molecules (*vide infra*) and, in fact, for any set of similar compounds in which geometry is fixed.[4] This variation in coupling constants may reflect variations in P–F bond distances and in hybridization. The Fermi contact term[5] describing the nuclear spin interactions contains a function which goes to zero unless the bonding electron has a finite existence at the nucleus. Thus large couplings may reflect more s character in the bond.[4c,6]

According to the observed progression of P–F coupling constants, the P–F bond distance or the s character of the axial phosphorus orbital or both would appear to decrease in the order $(CH_3)_3PF_2 \sim (C_2H_5)_3PF_2 \sim (C_4H_9)_3PF_2 > (C_6H_5)_3PF_2 > (CF_3)_3PF_2$. The order is rational in that as the R group becomes more electronegative the effective nuclear charge on the phosphorus atom increases and the P–F separation may reasonably be expected to decrease.[7]

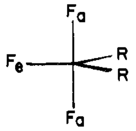
Table I

F^{19} N.M.R. Data for R_3PF_2

Compound	A_{PF}, c.p.s.	A_{PF-CF}, c.p.s.	A_{PF-CH}, c.p.s.
$(CH_3)_3PF_2$	545	...	11
$(C_2H_5)_3PF_2$	575	...	11
$(n\text{-}C_4H_9)_3PF_2$	585	...	16
$(C_6H_5)_3PF_2$	695	...	...
$(CF_3)_3PF_2$	988	16	...
	630		

Consistent with the interpretation of long apical P–F distances in the trialkyl and triaryl phosphorus difluorides, we find that the infrared P–F stretching frequencies of these derivatives occur at very low frequencies compared to those of the mono- and disubstituted derivatives (Table II). Furthermore, consistent with the large A_{PF} value for $(CF_3)_3PF_2$, the PF stretching frequency for this derivative is significantly higher than that for the alkyl and aryl derivatives.

R_2PF_3.—The R_2PF_3 derivatives have two distinct fluorine atom environments, as evidenced by the F^{19} n.m.r. spectra. In the case of the alkyl derivatives, hyperfine structure in the n.m.r. spectra provides the critical information that favors structure II over structure IX. The F^{19} spectrum of $(CH_3)_2PF_3$ consists of two (PF coupling) high field triplets of relative intensity one, representing the F_e environment, and two low field multiplets of relative intensity two representing the F_a environment. The low field multiplet is a basic doublet in which each component is further split into septuplets because of equal coupling of each F_a atom with the hydrogen atoms of both CH_3 groups. Thus, only structure II of all possible trigonal bipyramidal models is consistent with the data. It should be noted, however, that a tetragonal pyramid,



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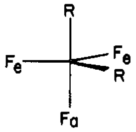

IX

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(3) An X-ray crystal structure determination of $(CH_3)_3SbCl_2$ has shown the three methyl groups to be at equatorial positions of a trigonal bipyramid: A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

(4) In octahedral molecules of the type MF_5X and MF_4X_2, it has been found that A_{MF} and also $A_{F_aF_b}$ are insensitive to gross variations in the nature of ligand X: (a) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1080 (1960); (b) E. L. Muetterties, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961; (c) E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 245 (1962); (d) C. Merrill, S. Williamson, G. Cady, and D. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 185.

(6) Reference 5, p. 184.

(7) The data in Table V show that the chemical shifts for apical fluorine atoms in R_3PF_2 increase with increase in electronegativity of the R group, *i.e.*, $(CH_3)_3PF_2 < (C_6H_5)_3PF_2 < (CF_3)_3PF_2$, which is the same relative ordering found for A_{PF} values. Application here of the Saika and Slichter treatment of fluorine chemical shifts (*J. Chem. Phys.*, **22**, 26 (1954)) suggests that the ionic character of the apical PF bond increases with increase in the electronegativity of the equatorial ligands. However, a disquieting note to such an oversimplified interpretation of chemical shift data is the rather large difference (29 p.p.m.) in δ_{PF} between $(CH_3)_3PF_2$ and $(n\text{-}C_4H_9)_3PF_2$ and between $(CH_3)_3PF_2$ and $(C_2H_5)_3PF_2$ where obviously the alkyl groups do not significantly differ in electronegativity.

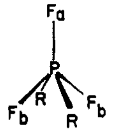
TABLE II

INFRARED PF STRETCHING FREQUENCIES

Compound	Apical PF, cm.$^{-1}$	Equatorial PF,[a] cm.$^{-1}$
R_3PF_2 Ar_3PF_2	620–640	
$(CF_3)_3PF_2$	855	
R_2PF_3 Ar_2PF_3	711–756	900–944 840–887
$(CF_3)_2PF_3$	...	952
Cl_2PF_3	1000	900, 930
RPF_4 $ArPF_4$	815–850	916–1015 857–935
CF_3PF_4	900, 915	990, 1018
PF_5[b]	938, 948, 957	1025

[a] No attempt is made to assign a particular frequency to a PF stretching mode for the equatorial PF sets. [b] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

structure X, also is fully consistent with these n.m.r. data.[8] However, as discussed in a later section, chemical shift data for R_2PF_3 and R_3PF_2 show internal consistency for trigonal bipyramid geometry. Furthermore, it would seem significant that an X-ray study[9] has shown that in $(C_6H_5)_2SbCl_3$ the phenyl groups are in equatorial positions of a trigonal bipyramid although this geometry may not necessarily be retained in the solution or molten state.



X

The F^{19} n.m.r. data for $(C_4H_9)_2PF_3$, $(C_2H_5)_2PF_3$, $CH_3(C_6H_5)PF_3$, and $(C_6H_5)_2PF_3$ are analogous to those for $(CH_3)_2PF_3$; the only difference is in the detail of the low field resonances. For the ethyl derivatives, the two low field multiplets are doublets with overlapping quintuplet fine structure. In the spectrum of the butyl derivative, the low field pair are doublets with superimposed fine structure due to $F–H_{CH_2}$ coupling; only eight of the expected ten lines are observed because of coincidence of lines. The low field pair for $CH_3(C_6H_5)PF_3$ consists of overlapping quadruplets. For the diphenyl derivative, the low field resonances are doublets. The n.m.r. data are summarized in Table III.

Nuclear spin coupling data (Table III) and PF infrared stretching frequencies suggest that apical bond lengths are greater than equatorial in R_2PF_3. Apical PF coupling constants average about 170 c.p.s. less than the equatorial. Apical PF stretching frequencies are significantly lower (~730 cm.$^{-1}$) than the equatorial frequencies (840–900 cm.$^{-1}$). Apical PF bond distances appear to be greater in R_3PF_2 than in R_2PF_3 (Tables I, II, and III) since PF stretching frequencies and coupling constants are significantly lower in R_3PF_2.

TABLE III

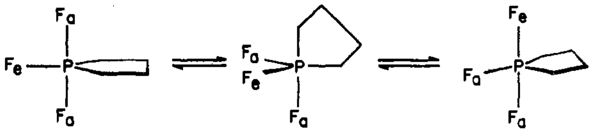
F^{19} N.M.R. DATA FOR R_2PF_3

Compound	A_{PF_a}, c.p.s.	A_{PF_e}, c.p.s.	$\lvert \delta_{F_e} - \delta_{F_a} \rvert$, p.p.m.	$A_{F_eF_a}$, c.p.s.	A_{HF_e}, c.p.s.	A_{HF_a} c.p.s.
$(CH_3)_2PF_3$	772	960	61	26	~2	
$(C_2H_5)_2PF_3$	815	980	68	29	...	12
$(n\text{-}C_4H_9)_2PF_3$	810	985	70	28	~2	14
$CH_3(C_6H_5)PF_3$	785	935	60	33	...	14
$(C_6H_5)_2PF_3$	838	970	45	37	...	13.5
$(CH_2)_4PF_3$ (−100°)	865	990	...	50	...	...
$(CH_2)_4PF_3$ (25°)	915[a]		...	...	...	8.6
$(CH_2)_5PF_3$	800	1005	64	42	...	...
$(CF_3)_2PF_3$		1260	...	...	175_{P-CF}	16_{CF-PF}
Cl_2PF_3	1050 (av.)					
Br_2PF_3	1140 (av.?)		...	...	...	...

[a] This compares well with the value of 907 c.p.s. calculated by averaging the two A_{PF} obtained for $(CH_2)_4PF_3$ at −100°.

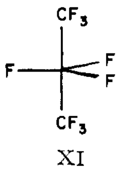
$(CH_2)_4PF_3$.—The F^{19} spectrum of this cyclic phosphorane at 25° consists of two peaks of equal intensity, each with quintuplet hyperfine structure reflecting FH coupling. The spectrum is temperature dependent. Spectra of toluene solutions begin to broaden on cooling and at ~−70° there is complete collapse of the basic doublets. Below −70°, the typical R_2PF_3 spectrum for structure II, a pair of triplets and a pair of multiplets (~8–10 lines), appear. The exchange process occurring in this cyclic phosphorane must be intramolecular since FP and FH coupling is preserved to well above 25°.

Bond angles are not known for a PC_4 ring system; however, the C–P–C angle probably is about 108–110°, which would be intermediate between the idealized 120° equatorial–equatorial angle and the 90° apical–equatorial bond angles of the trigonal bipyramid. Thus, it would seem reasonable that effective positional exchange occurs through isomeric structures like XII and that ring strain in the PC_4 system lowers the activation for exchange. A crude approximation of the exchange barrier by analysis of n.m.r. line broadening is ~7 kcal./mole. A six-membered ring system should be less likely to exhibit this exchange process, and, in fact, $(CH_2)_5PF_3$ shows no evidence of an intramolecular exchange process up to ~100°.



II XII II

X_2PF_3.—In $(CF_3)_2PF_3$, there is n.m.r. spectroscopic equivalence of PF and CF fluorine atoms. These data are consistent with but do not establish structure XI



XI

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(8) Structures II and X are only two possibilities from an infinite array that have C_{2v} symmetry. Thus, a distinction cannot be made from the n.m.r. symmetry arguments. Certainly, repulsion of the large organic groups in structure II will lead to a decrease in the $F_a–P–F_a$ angle and the $C–P–F_e$ angle but there should remain a qualitative distinction in bond angle criterion between the two extremes in this symmetry group.

(9) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **2**, 445 (1961).

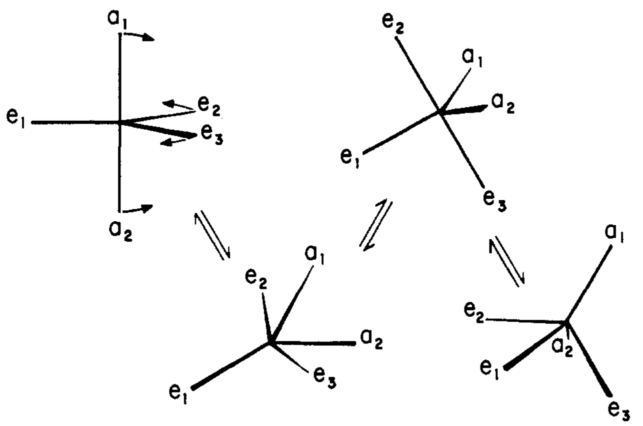
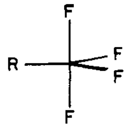


Fig. 1.—Possible mechanism for intramolecular exchange of ligands in a five-coördinate structure.

for this fluoride. Similarly, in Cl_2PF_3 and Br_2PF_3 there is spectroscopic equivalence of fluorine atoms at 25°; however, below −80°, the Cl_2PF_3 spectrum breaks into the typical R_2PF_3 spectrum. Thus, Cl_2PF_3 (and possibly Br_2PF_3) has the stereochemistry of II.[10] Repulsions between chlorine atoms may provide the activation for this intramolecular exchange process.

RPF_4.—All of the monosubstituted phosphorus(V) fluorides examined (Table IV) were found to have spectroscopically (n.m.r.) equivalent fluorine atoms.[11] Variations in the apparent PF coupling constants are not particularly significant, and there is no obvious correlation of A_{PF} with the substituent.

The n.m.r. data for these derivatives, although consistent with a tetragonal pyramid structure in which the alkyl or aryl substituent occupies an apical position, do not establish such a structure. Although neither of the two possible trigonal bipyramid structures for RPF_4 fits the n.m.r. data, spectroscopic equivalence of fluorine atoms in either structure could result from some exchange process. A similar situation obtains in PF_5 itself where the F^{19} resonance shows spectroscopic equivalence of fluorine atoms; here, however, independent structural data from electron diffraction studies have established trigonal bipyramidal geometry.[10b,12]



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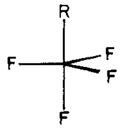
and



XIII

Table IV

F^{19} N.m.r. Data for RPF_4

Compound	A_{PF}, c.p.s.	A_{HF}, c.p.s.
PF_5	916	. . .
CH_3PF_4	967	6–7
$ClCH_2PF_4$	997	6–7
$C_2H_5PF_4$	987	6–7
n-$C_4H_9PF_4$	990	6
$C_8H_{15}PF_4$ isomer A	955	6.5
isomer B	955	6.5
$C_6H_5CH_2PF_4$	1002	6–7
cis-$(C_6H_5)HC{=}CH(PF_4)$	940	6–7
$C_6H_5PF_4$	963	<0.5
m-$CH_3C_6H_4PF_4$	960	<0.5
p-$CH_3C_6H_4PF_4$	960	<0.5
m-$C_3H_7C_6H_4PF_4$	963	<0.5
p-$C_3H_7C_6H_4PF_4$	958	<0.5
m-$ClC_6H_4PF_4$	960	<0.5
p-$ClC_6H_4PF_4$	960	<0.5
2,5-$(CH_3)_2C_6H_3PF_4$	981	<0.5
CF_3PF_4	1103	12 (FC–PF)

Although the tetragonal pyramid and the trigonal bipyramid appear at first glance to be grossly different, they are rather closely related, and in an ML_5 species, concerted ML vibrations may well be sufficient to carry the tetragonal pyramid over to the trigonal bipyramid and *vice versa*. This is, in essence, the positional exchange process which was postulated by Berry[13] for the PF_5 molecule and which is illustrated in Fig. 1. Also in Fig. 1 the intermediate position in Berry's scheme, the tetragonal pyramid, is drawn. In such dynamic systems, the molecule may either spend most of its time in one configuration or equally in the two geometric configurations. The electron diffraction data clearly indicate the former to be the case for PF_5. In PCl_5, the apical and equatorial bond distances are not equal[14] and tracer studies[15] have shown that only three chlorine atoms exchange rapidly in PCl_5, clearly ruling out any fast intramolecular exchange.

In the exchange process depicted in Fig. 1 it should be noted that one position, e_1, remains "fixed" in the equilibration of ligands e_2, e_3, a_1, and a_2. That is to say, one equatorial position is unaffected in a single interconversion. Thus, for an equatorially substituted RPF_4 species, the same mechanism is available for positional exchange of fluorine atoms as for PF_5. In the following sections, arguments based on n.m.r. chemical shift and spin–spin coupling data are advanced for equatorial substitution (≡ apical substitution in a tetragonal pyramid) in the monoalkyl and aryl derivatives.

Discussion of A_{HF} and δ_F Data for RPF_4.—The FH coupling constants in the monoalkyl derivatives average 6.5 c.p.s. In the dialkyl and alkyl aryl derivatives, A_{FH} is 2 c.p.s. or less for the fluorine atoms that have FPC angles of 120° and ~13.5 c.p.s. for those that have FPC angles of 90° (assuming an idealized trigonal bipyramid). If the values obtained for the disubstituted derivatives are employed for calculation of the averaged values in an RPF_4 structure in

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[10] (a) J. Goubeau in a private communication reported that the Raman and infrared spectra of Cl_2PF_3 are consistent with structure II and definitely rule out structure XI. (b) L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 1836 (1938), from an electron diffraction study proposed structure XI for Cl_2PF_3 and Br_2PF_3.

[11] We have been unable to reproduce our originally reported F^{19} n.m.r. spectrum for CF_3PF_4 (W. Mahler and E. L. Muetterties, *J. Chem. Phys.*, **33**, 636 (1960)) and now find only spectroscopic equivalence of fluorine atoms.

[12] H. Braune and P. Pinnow, *Z. physik. Chem.*, **B35**, 239 (1937).

[13] S. Berry, *J. Chem. Phys.*, **32**, 936 (1960).

[14] M. Rouault, *Ann. Phys.* (Paris), [11] **14**, 78 (1940); M. Moureu, M. Magat, and G. Wetroff, *Compt. rend.*, **205**, 276 (1937).

[15] J. Downs and R. E. Johnson, *J. Chem. Phys.*, **22**, 143 (1954).

TABLE V

Compound	δ_{CF_3}, p.p.m.	$\delta_{F(mono)}$, p.p.m.	δ_{F_e}, p.p.m.	δ_{F_a}, p.p.m.
CF_3PF_4	−3.4	−10		
$(CF_3)_2PF_3$	−3.8		−7.5	
$(CF_3)_3PF_2$	−12			−16.8
CH_3PF_4		−31		
$(CH_3)_2PF_3$			+9.8	−74
$(CH_3)_3PF_2$				−73
$(CH_2)_5PF_3$			+6	−58
$C_2H_5PF_4$		−25		
$(C_2H_5)_2PF_3$			+16	−52
$(C_2H_5)_3PF_2$				−44
n-$C_4H_9PF_4$		−27		
$(n$-$C_4H_9)_2PF_3$			+13	−56
$(n$-$C_4H_9)_3PF_2$				−44
$C_6H_5PF_4$		−23		
$(C_6H_5)_2PF_3$			+1.2	−44
$(C_6H_5)_3PF_2$				−39
$C_6H_5(CH_3)PF_3$			+5.4	−60
$ClCH_2PF_4$		−24		
$C_8H_{15}PF_4$		−31		
$C_6H_5CH{=}CHPF_4$		−32		
2,5-$(CH_3)_2C_6H_3PF_4$		−25		

which positional exchange of fluorine atoms occurs, then for alkyl derivatives calculated A_{FH} values are 7.8 c.p.s. for equatorial and 10.6 c.p.s. for apical substitution compared with 6.5 c.p.s. observed. Similar considerations for CF_3PF_4 yield calculated values of 12 c.p.s. for apical and 9 c.p.s. for equatorial substitution *vs.* the observed value of 12 c.p.s. Thus, these data would tend to support equatorial substitution, *i.e.*, structure I (≡ tetragonal pyramid, structure IV, averaged basis) in monoalkyl derivatives and apical substitution for CF_3PF_4. The differences here in A_{FH} among observed and the two calculated values are, however, too small for the arguments to stand on these data alone. Further support is based on chemical shift data.

In Table V, fluorine chemical shifts for the pure liquids are presented for a number of the derivatives investigated. We found that the variation in chemical shift on dilution with chloroform or carbon tetrachloride was sufficiently small (from <1 to <2 p.p.m.) in relation to the large differences involved in the following arguments that refinement of data by extrapolation of δ to infinite dilution was unnecessary.

In the alkyl and aryl derivatives of PF_5, δ_F for the monoderivatives falls within a relatively narrow range of −23 to −31 p.p.m. In the dialkyl derivatives, the equatorial fluorine shifts are all positive and fall in the range of 1 to 16 p.p.m. The chemical shifts for the apical fluorine atoms in R_2PF_3 are large negative values (−39 to −74 p.p.m.) which are significantly different from those for the equatorial positions. The range here is large but in view of the probable greater sensitivity of apical bond distances this larger range of values is not unreasonable. In R_3PF_2, δ_F ranges from −44 to −73 p.p.m., well within the range found for apical fluorine atoms in R_2PF_3. Even more significantly, comparison of apical δ_F values for R_2PF_3 and $R_3'PF_2$ where R = R′ shows very close correlation; only in the butyl series is the difference significant, 12 p.p.m.

TABLE VI

Compound	Obsd. δ_F, p.p.m.	Calcd. δ_F for eq. R, p.p.m.	δ_F Calcd. for ap. R, p.p.m.
CH_3PF_4	−31	−32	−11
$C_2H_5PF_4$	−25	-18^a	-1^a
		-14^b	$+1^b$
		-16^c	0^c
n-$C_4H_9PF_4$	−27	-22^a	-4^a
		-16^b	-1^b
		-19^c	-3^c
$C_6H_5PF_4$	−23	-22^a	-10^a
		-19^b	-9^b
		-20^c	-9^c
CF_3PF_4	−10 (PF) − 3.4 (CF)	−12 (PF) −12 (CF)	−10 (PF) − 3.8 (CF)

[a] Value calculated using apical value found in R_2PF_3. [b] Value calculated using apical value found in R_3PF_2. [c] Value calculated using average of apical values in R_2PF_3 and R_3PF_2

The very large fluorine chemical shifts between apical and equatorial positions in R_2PF_3 and R_3PF_2 lend confidence to using the data to calculate average chemical shifts for apical and equatorial P–F in RPF_4 compounds in which fast positional exchange of fluorine atoms may occur. The results of these calculations are presented in Table VI. For the alkyl and aryl derivatives the agreement for equatorial substitution is excellent[16] and the differences between predicted apical and equatorial substitution are sufficiently large to be meaningful.

Data also are presented in Table V for the trifluoromethyl derivatives. For these, the difference between δ_F for apical and equatorial positions is rather small (~9 p.p.m.). The chemical shift for the CF_3 fluorine atoms between apical and equatorial positions is of the same order of magnitude. If both the δ_{CF} and δ_{PF} parameters are used, there is excellent fit (Table VI) for apical substitution; however, the difference in chemical shift between the two types of substitution is rather small and these considerations for just one series of perfluoroalkyl derivatives do not have the import or conviction of the alkyl and aryl cases.

General Comments on MX_5 Stereochemistry.—The infrared and n.m.r. data for the alkyl and aryl derivatives of PF_5 provide an internally consistent framework for the conclusions that: (1) in R_3PF_2 and R_2PF_3, the alkyl or aryl groups occupy equatorial sites in a trigonal bipyramid[17]; (2) in RPF_4, the R groups either occupy the apical position of a tetragonal pyramid or an equatorial position[16] of a trigonal bipyramid in which positional exchange of fluorine atoms occurs at a rate fast with respect to the observed n.m.r. parameters expressed in c.p.s. (*i.e.*, $k >> \sim 10^3$).

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(16) It should be emphasized that equatorial substitution in a trigonal bipyramid undergoing intramolecular exchange is *identical* with apical substitution in a tetragonal pyramid within the context of these arguments.

(17) As noted before, both steric and hybridization considerations favor alkyl ligands for equatorial positions. There appear to be no exceptions in the literature to this stereochemical arrangement. A recent example supporting this contention is an X-ray study of $(CH_3)_3SnCl \cdot NC_5H_5$ where it was shown that the three methyl groups are at equatorial positions of a trigonal bipyramid: I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962).

Of the possibilities presented in (2) for RPF_4 we prefer the dynamic model of an equatorially substituted trigonal bipyramid on the basis of analogy to PF_5. It has been shown recently[18] that $Sb(C_6H_5)_5$ is a tetragonal pyramid in the solid state. However, packing factors in the solid state could easily lead to distortion of a trigonal bipyramid.[19]

Our observations indicate that the more electropositive groups always are found at equatorial positions. Hydrogen atoms or alkyl groups may tend to be equatorial because the phosphorus bonding orbitals in this plane have maximum s character.[20] Alternatively, the stereochemical results may be generalized by stating that the more electronegative ligands tend to go to axial positions where the bonds are more ionic. There is, of course, the possibility that large steric repulsions may lead to stereochemistries that do not fit these generalizations; this would be most likely in an X_2PF_3 species.

It is further suggested that intramolecular exchange processes are quite common in trigonal bipyramid structures. It is significant that spectroscopic equivalence of ligands is found for $Fe(CO)_5$[21] in C^{13} n.m.r. and for PF_5,[22] RPF_4, AsF_5,[23] and SOF_4[24] in F^{19} n.m.r. We plan to test this hypothesis by a general n.m.r. study of MX_5 and MX_4Y structures. Ease of intramolecular exchange may well account for the indicated absence of isomers in the large number of substituted phosphorus fluorides that we have examined.

Experimental

The preparation of the phosphoranes has been described previously.[1] The volatile derivatives were purified by distillation. To minimize any intermolecular fluorine exchange process, the alkyl and aryl phosphoranes were distilled from sodium fluoride, and in many cases a small amount of sodium fluoride was added to the n.m.r. tubes to remove possible traces of hydrogen fluoride. Transfer of all volatile reagents was effected in a vacuum system.

Apparatus—The F^{19} n.m.r. spectra were obtained on a Varian high resolution spectrometer Model V4300 and associated magnet at 56.4 Mc. Calibration of spectra was effected by superposition of an audiofrequency on the sweep field to produce side band peaks. The external reference was trifluoroacetic acid.

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(18) P. J. Wheatley, *Proc. Chem. Soc.*, 251 (1962).

(19) The dipole moments of $P(C_6H_5)_5$, $As(C_6H_5)_5$, and $Sb(C_6H_5)_5$ in solution are about 1 D.[18] Non-zero values could be due to a field induced moment.

(20) In $[(CH_3)_3N]_2AlH_3$, the hydrogen atoms attached to the aluminum atom are at the equatorial positions of a trigonal bipyramid: R. W. Parry, personal communication.

(21) (a) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); (b) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(22) H. W. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

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

(24) F. B. Dudley, J. N. Shoolery, and G. H. Cady, *ibid.*, **78**, 568 (1956).

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Some High Pressure Studies on Ytterbium[1a]

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Pressure, temperature, volume, resistance, and X-ray diffraction measurements have made it possible to establish a partial P–T phase diagram for metallic ytterbium. An electronic transition, previously indicated as occurring at 60 kb., 25°, has been shown to occur at 39.5 kb., 25°. This transition pressure is lowered by increasing temperature, $\Delta P/\Delta T$ being -19.1 bars/deg., and is accompanied by a change in volume of -0.65 cm.^{3}/mole simultaneously with a change in crystal structure from FCC to BCC. This is the first time a pressure-induced transition from a close-packed to a non-close-packed structure has been observed. Heat absorption at the transition is 89 cal./mole. A number of second-order transitions were discovered. Of particular interest are transitions in bond type from P–T regions in which directional bonds predominate to P–T regions in which metallic bonding predominates.

Introduction

In 1954 Bridgman published data showing the change in electrical resistance of Yb as a function of pressure as measured in his opposed anvil apparatus.[2] He reported a discontinuity occurring at 60 kb. where the resistance, after having increased by a factor of about 12, suddenly decreased by a factor of about 15. Bridgman's resistance *vs.* pressure curve is reproduced as curve A in Fig. 1. Curve B, which shows the Yb resistance discontinuity occurring at 39.5 kb., represents results obtained in this study.

Bridgman also measured the compressibility of Yb which he reported in table form.[2] These data are given in graph form in Fig. 2 along with the compressibility data from this work.

Electrical Resistance Measurements

The Yb used was purchased from Nuclear Corporation of America, Research Chemicals Division, Burbank, California. Purity was indicated as being 99% nominal with tantalum and oxygen as the principal

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(1) (a) Research supported by the National Science Foundation and the Alfred P. Sloan Foundation; (b) Alfred P. Sloan Research Fellow.

(2) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **83**, 1 (1954).