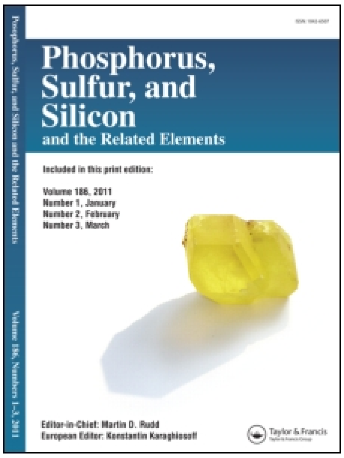

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SPECTROSCOPY AND STRUCTURE OF PENTACOORDINATED MOLECULES

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SPECTROSCOPY AND STRUCTURE OF PENTACOORDINATED MOLECULES

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Many proposed reaction mechanisms involve a transitory pentacoordinate intermediate. For example, the change in optical activity accompanying bimolecular displacement at tetrahedral carbon has reasonably been explained as resulting from the formation of a trigonal-bipyramidal transient with the entering and leaving groups occupying apical positions.[1] Also reasonable are mechanisms advanced to account for relative rates and products formed in the hydrolysis of phosphate esters[2] or displacements in phosphonium[3] systems. Certain hypotheses[4] governing the stability of the transitory trigonal-bipyramidal species are applied, and a specific intramolecular exchange process is stipulated to occur in order to account for some of the experimental information.[2] Mechanisms proposed to proceed *via* pentacoordinate species involving transition metal compounds[5,6] are more speculative, whether they be dissociative (involving octahedral structures) or bimolecular (involving four-coordinate geometries).

In view of the prominence of pentacoordination in mechanistic studies, it seems appropriate to focus attention on pentacoordinate species themselves. In this Account, evidence, largely obtained from spectroscopic techniques, will be discussed which provides information relating to structural stability and ease of isomeric conversion in these species.

UNIQUE FEATURES OF PENTACOORDINATION

The two common pentacoordinate structures, namely the trigonal bipyramid and the square pyramid, are unique among structures associated with simple coordination numbers in that an inequivalence of positions exists, giving rise to two sets of bonds with considerably different properties.

The differences between the two positions of a trigonal bipyramid show up in a variety of ways. For example, in nmr measurements of PCl_2F_3 conducted at low temperatures[4a,7] different ^{19}F resonances are observed, consistent with the presence of fluorine atoms in axial and equatorial positions of a trigonal bipyramid. Nuclear quadrupole resonance (nqr) measurements[7] on PCl_4F show different ^{35}Cl resonances assignable to the presence of chlorine atoms in equatorial and axial positions of a trigonal bipyramid. Vibrational stretching frequencies have been observed to

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be greater for equatorial compared to axial positions ranging from 100 to 200 cm^{-1} higher for many of the molecules of nontransition elements that we have studied.[8] Correspondingly, stretching force constants[9–11] are lower for axial compared to equatorial bonds. Consistent with the latter, diffraction studies show that, in molecules like PF_5[12] and $SbCl_5$,[13] equatorial bonds are shorter than axial bonds, while the reverse is found in the trigonal-bipyramidal $CuCl_5^{3-}$ and $CuBr_5^{3-}$ anions.[14] Less is known about the square-pyramidal structure containing simple ligands, although X-ray studies on both $InCl_5^{2-}$[15] and $Nb(NMe_2)_5$[16] have shown the presence of shorter axial bonds for this conformation.

Theoretical calculations on trigonal bipyramids are in agreement with the experimental evidence for nonequivalence of axial and equatorial positions. In general, MO calculations[17] have shown that little d orbital bonding is present in trigonal bipyramids involving second-row elements and that the central atom s orbital concentrates among the equatorial bonds. In this sense the axial bonding is related to an orbital-deficient model akin to Rundle's interpretation.[18] As a consequence weaker axial bonds compared to equatorial bonds are predicted and, in the case of PF_5, higher negative charges are calculated[17,a,c,d] to reside on the axial fluorine atoms.

While for nontransition elements the main conformation of pentacoordinated substances is a trigonal bipyramid, there is a preponderance of square pyramids for transition metal elements. Simple repulsion calculations[19,20] show that the two structures are quite close in energy, in agreement with inferences from experimental data.[4] The latter data are based largely on the ease with which some trigonal-bipyramidal molecules equilibrate equatorial and axial ligands intramolecularly on an nmr time scale. In these presumably nonrigid structures, the trigonal bipyramid is imagined to deform readily to a low-lying transition state represented by a square pyramid,[21] allowing loss of ligand identity. Recently nonempirical MO calculations[22a] on the hypothetical PH_5 molecule have yielded a 3.9 kcal/mole energy difference between the ground-state trigonal bipyramid and the square-pyramidal transition state.[22b] Alternatively, a "turnstile" mechanism has been invoked to explain intramolecular exchange.[23]

Pentacoordinate substances are, in general, remarkably free of isomeric conformations, although the crystalline structure[24] of $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5] \cdot 1.5H_2O$ reveals both a distorted trigonal-bipyramidal and a regular square-pyramidal environment for the $[Ni(CN)_5]^{3-}$ ion, each differently hydrogen bonded to the water molecules that are present. In the anhydrous substance, the $[Ni(CN)_5]^{3-}$ anion is present in the square-pyramidal form.[25]

STRUCTURAL CONSIDERATIONS

Let us now direct our attention to some specific structural features and in a later section outline the relationship between structure and the process of intramolecular exchange in pentacoordinated species. Since observations of the phenomenon of intramolecular exchange have been most numerous with five-coordinate structures of group V elements, the discussion will center primarily on these substances, with particular application to mixed phosphorus fluorides.

TABLE I

Bond Parameters for Some Pentacoordinate Molecules

	r_{eq}, Å	r_{ax}, Å	Bond angles,[a] deg e_2–e_3	Bond angles,[a] deg e_1–a	Method[e]	Ref
		Trigonal Bipyramid				
PF_5	1.534	1.577			E	12
CH_3PF_4	1.543 P–F 1.780 P–C	1.612	115.6	91.8	E	26
$(CH_3)_2PF_3$	1.553 P–F 1.798 P–C	1.643	124.0	88.9	E	26
HPF_4	1.55 P–F 1.36 P–H (assumed)	1.594	112	~90	M	27
$SnCl_5^-$ [b]	2.36 av	2.38 av			X	28
		Square Pyramid				
$InCl_5^{2-}$ [c]	2.456	2.415	86.7	103.9	X	15
$Sb(C_6H_5)_5$[d]	2.14 av	2.14 av	88 av	102 av	X	29

[a] Where it matters, the subscripts 2 and 3 on the equatorial atoms refer to the pair of identical atoms while the subscript 1 refers to the unique atom. [b] The anion is 3-chloro-1,2,3,4-tetraphenylcyclobutenium. [c] The cation is tetraethylammonium. [d] There is no evidence that the axial and equatorial bond lengths differ. Considerable distortions are present. The cis equatorial angles range from 84 to 91° and the axial–equatorial angles from 95 to 109°. [e] E, electron diffraction; M, microwave spectroscopy; X, X-ray diffraction.

Many of these members are highly volatile, reactive substances. Hence it is doubtful that diffraction techniques will be used at an accelerated rate to characterize their structures. However, sufficient structural determinations have been carried out to gain an appreciation for the main features encountered and for the deviations from idealized symmetries to be expected in going to more highly substituted members (Table I[12,15,26–29]).

While unable to give bond distance information, vibrational spectroscopy has proven invaluable in ascertaining the molecular symmetries of a variety of pentacoordinated species[30–50] (Table II). Definite information about the ground-state geometry is so obtained, uncomplicated by intramolecular exchange phenomena. Exchange, if it occurs for a particular member, invariably takes place at a rate coincident with the nmr time scale. With reference to faster techniques most pentacoordinated species may be regarded as rigid in the usual sense.[30] In this regard we have fully characterized the structures of the members of the phosphorus chlorofluoride series PCl_nF_{5-n} by means of vibrational spectroscopy[8,31] supplemented by studies involving nmr,[7,32,33] nqr,[7,31a] and vapor phase dipole moment[31a,34,35] measurements. Recently, we have extended such studies to include derivatives containing highly electronegative as well as bulky substituents.[36,37]

Much of the vibrational work has been conducted in the vapor state. The latter has proven important not only for the study of the structures free of environmental influences but also to understand more completely structural changes encountered on going to other states. For example, PCl_5, as is well known, is a trigonal bipyramid[40,41,51] in the vapor but exists as an ionic solid.[52] Several other compounds

TABLE II

Point Group Symmetries from Vibrational Spectroscopy

Trigonal bipyramid[a]						Square pyramid	
D_{3h}	Ref	C_{2v}	Ref	C_{2v}	Ref	C_{4v}	Ref
PF_5	8, 31b, 38, 39	$PClF_4$	31a	PCl_2F_3	8	SbF_5[b]	49
PCl_5	40, 41						
PCl_3F_2	8	PHF_4	45	PH_2F_3	45	$[(C_2H_5)_4N]_2$-$[InCl_5]$	50
$PCl_3(CF_3)_2$	42	CF_3PF_4	46	$(CH_3)_2PF_3$	43	$[(C_2H_5)_4N]_2$-$[TlCl_5]$	50a
$(CH_3)_3PF_2$	43	CCl_3PF_4	36				
AsF_5	38	CH_3PF_4	47	C_{3v}			
$SbCl_5$	40	t-$(CH_3)_3CPF_4$	37	PCl_4F	8		
$Sb(CH_3)_5$	44			CF_3PCl_4	48		

[a] All vapor state studies. [b] Matrix isolated at low temperatures with argon and neon host lattices.

are associated in the solid. $NbCl_5$ is a dimer[52a] containing chlorine atom bridges, NbF_5 is a tetramer,[53b] while SbF_5 may be more highly associated[53c] in the solid state. Using matrix isolation techniques, infrared spectra of both SbF_5[49] and $NbCl_5$[53d] in monomeric form have been obtained.

The geometrical shape of pentacoordinate molecules in a trigonal-bipyramidal framework (Tables I and II) generally agrees with expectations from the simple electron pair repulsion scheme extensively discussed by Gillespie.[54] Progressive methyl substitution in PF_5 from CH_3PF_4 to $(CH_3)_2PF_3$ leads to increased P—F bond distances, particularly in the axial positions.[26] Further, the axial bonds containing the fluorine atom ligands are bent away from the equatorially positioned methyl groups. In terms of electron pair repulsion,[54] the less electronegative methyl group allows the P—C bonding electron pair to come closer to the phosphorus atom compared to the situation in the P—F bond it replaced. Enhanced repulsion results, particularly with the electron pairs in the P—F axial bonds located near 90° relative to the P—C bond.

BONDING IN PHOSPHORUS CHLOROFLUORIDES, PCl_nF_{5-n}

As with the methyl derivatives, substitution of chlorine atoms for fluorine atoms in PF_5 is expected, because of enhanced repulsions, to lead to a general increase of bond lengths, more so in the axial than in the equatorial positions. The remaining axial P—F bond in the least fluorinated member, PCl_4F, should be the longest in the phosphorus chlorofluoride series. The implication is that it should be the weakest as well. Data from both nmr[7] and vapor phase dipole moment[34] measurements may be interpreted in support of this view. In agreement, Hückel-type molecular orbital calculations[17a] show a decrease in orbital overlap population in axial bonds with increased chlorine atom substitution. The decrease is attributable to increasing mismatch in orbital energies along the series as the phosphorus atom becomes more electropositive.

Both $PClF_4$[31a] and PCl_2F_3[34] have similar dipole moments, about that expected, while PCl_4F[35] has a very low value (Table III). Assuming 90 and 120° for the two sets of ligand angles, all structures may be reduced vectorially to a P—F opposing a P—Cl bond dipole. The small angular distortions from idealized symmetries

TABLE III

Gas-Phase Dipole Moments for the PY_nF_{5-n} Series

	μ, D	Ref		μ, D	Ref
$PClF_4$	0.78	31a	PHF_4	1.32	27
PCl_2F_3	0.68	34	CH_3PF_4	2.55	37
PCl_3F_2	0.0	34	$C_2H_5PF_4$	2.77	37
PCl_4F	0.21	35	$(CH_3)_3CPF_4$	2.82	37
			$(CH_3)_2PF_3$	2.22	37

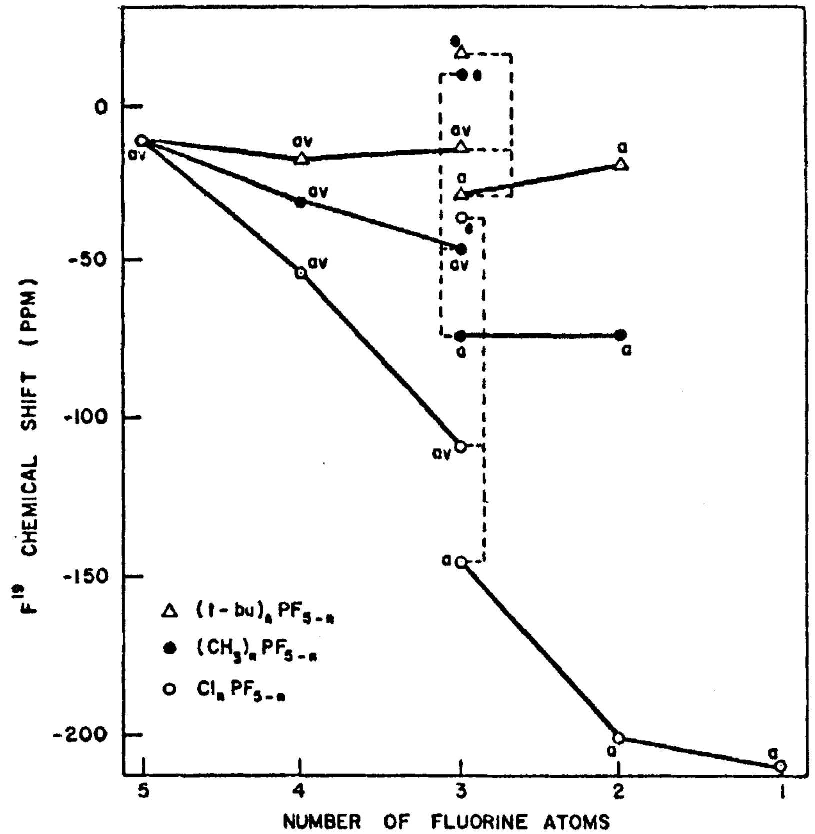


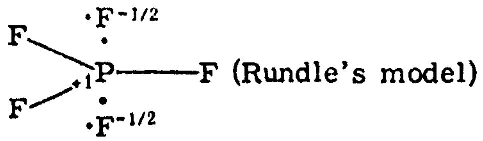
FIGURE 1 ^{19}F chemical shifts relative to CF_2CO_2H.

expected have been shown to be inadequate in explaining the low moment value for PCl_4F even if the distortions were in favorable directions.[34] The low value for PCl_4F then indicates a low charge separation in the axial P—F linkage since a very narrow range of pure ^{35}Cl nqr frequencies is observed[7,31a] in the PCl_nF_{5-n} series, while ^{19}F nmr data[7] show a very large deshielding occurring as fluorine atoms are replaced by chlorine atoms and a substantial deshielding of the fluorine nucleus for axial compared to equatorial fluorine atoms (Figure 1). If we associate this deshielding trend observed for the axial positions with a reduced charge distribution about the fluorine atom, the observation of the low dipole moment for PCl_4F is understandable.

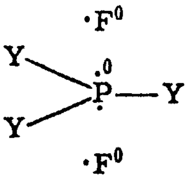
The mechanism by which a reduction in charge should occur, however, is not so readily understood. The trend in ^{19}F resonance values for the series PCl_nF_{5-n} is in a direction opposite from that expected based on electronegativity considerations. Enhancement of d—p π bonding in axial P—F bonds proceeding toward the least fluorinated member had been suggested[7,34] to account for the relative deshielding of axial fluorine atoms with the understanding that the total axial bond energy was less than that for the equatorial bonds. However the latter suggestion left unexplained the general downfield shift observed in the series, particularly with regard to the large difference between equatorial and axial positions. Furthermore, recent molecular orbital calculations on PF_5 and related structures[17,22a] are in accord in discounting any significant importance of phosphorus d orbital participation in bonding in PF_5. In addition, the weaker axial bonds in PF_5 result, having a slightly more negative fluorine atom compared to their equatorial counterpart in terms of charge density calculations.

Based on the above, it seems more likely that the pronounced deshielding observed in the series PCl_nF_{5-n} is associated with the lack of transmission of electron density to axial fluorine atoms as chlorine substitution increases. As a consequence, a reduction in the positive charge at phosphorus occurs. The accompanying progressive bond weakening effects, more so in axial than in equatorial positions (inferred from force constants,[9–11] bond distances (Table I), and overlap populations[17a]), take precedence as the dominant factor in leading to a small charge difference in the P—F bond in PCl_4F.

As one extreme, the orbital deficient model simply gives the resultant charges as



As the covalent contribution to the total bonding energy decreases with substitution along the series, the other extreme representation becomes

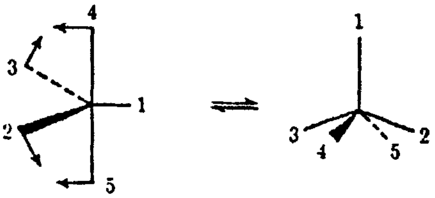


Using groups of greater electron-releasing ability such as methyl and *tert*-butyl, successive replacement of fluorine atoms may be anticipated to result in reduced covalent bonding for similar reasons given for the PCl_nF_{5-n} series. However, transmission of the greater electron density supplied to the phosphorus atom should be facilitated, yielding more ionic fluorine atoms and, consequently, an enhanced importance to ionic contributions to the total bonding energy. In accord, the trend in ^{19}F shifts in Figure 1 in the series $(t\text{-Bu})_nPF_{5-n}$[55] is more in line with electronegativity considerations and the equatorial and axial ^{19}F shifts for $(t\text{-Bu})_2PF_3$ tend to converge relative to that for Cl_2PF_3.

MODEL FOR EXCHANGE IN PF_5 AND PYF_4

Vibrational spectroscopy indicates[31a] that $PClF_4$ exists as a trigonal-bipyramidal molecule with two types of fluorine atom environments, an axial pair and an equatorial pair. In contrast, ^{19}F nmr measurements[33] show only one fluorine atom environment spin coupled to the phosphorus atom similar to that observed[4,56] for PF_5 and many other members of the PYF_4 class. The apparent discrepancy is resolved by considering $PClF_4$ to be undergoing rapid intramolecular exchange on an nmr time scale but slow relative to vibrational motions.

The pathway for exchange for $PClF_4$, as first suggested by Berry[21] for PF_5, may be imagined to result from a vibrational bending motion, involving both axial and equatorial fluorine ligands, leading to a square-pyramidal transitory conformation. The ligand labeled 1 in the model executes little movement in the exchange process



and does not interfere in allowing equivalence of fluorine atom positions to take place. Consequently, this model for exchange for trigonal bipyramids of the class MF_5 is the same as that for the class MYF_4 for all practical purposes.

In view of the above concerning the ease of intramolecular exchange of some trigonal bipyramids on the one hand and the lack of formation of isomers on the other, one might infer as a guiding principle in constructing exchange mechanisms that energy differences between isomeric trigonal bipyramids for a particular molecular formulation are appreciable while energy differences between a nonrigid trigonal bipyramid and its associated square-pyramidal conformation are relatively small assuming, of course, that the square pyramid is an adequate representation of the transitory exchange state.

VIBRATIONAL POTENTIAL FIELDS AND INTRAMOLECULAR EXCHANGE

Considerable insight may be gained into mechanisms of intramolecular exchange by carrying out normal coordinate calculations based on assignments of fundamental frequencies for various members.[11,57] The calculations lead to a definition of a vibrational force field which associates an internal vibrational motion of a specified amplitude with each fundamental frequency. Examination of the bending motions and their respective amplitudes may suggest a suitable low-energy pathway for exchange, especially in cases where the exchange process does not appear obvious.

The lowest frequency fundamental will contribute importantly to the exchange coordinate. In PF_5, for example, the bending frequency thought to be largely responsible[57] for intramolecular exchange has been assigned to a Raman vibrational band appearing in the gas phase[58] at 174 cm^{-1}. The magnitude of the exchange energy calculated[11,59] in this process using at first a harmonic approximation is related to the amount of angular change in reaching the square-pyramidal structure. In this respect the process is analogous to the treatment used by Costain and Southerland[60] to estimate the barrier to inversion for the NH_3 molecule.

The Berry mechanism[21] referral to earlier had its initial basis in its intuitive appeal. However, by the latter type of calculation we were able to confirm[11,57,59] that the bending motion depicted above traverses a pathway of low energy. Consequently, the Berry motion defines an acceptable exchange coordinate based on vibrational analysis. Whether the detailed mechanism involves activation over or tunneling through the barrier from excited vibrational states is a question unanswered as yet.[38,57]

Actually, two acceptable fields result,[11] differing in the assignment of equatorial and axial bending modes. Fortunately, a decision as to the appropriate function to use was aided by vibrational amplitude data from electron diffraction work,[51,61] at least for some of the most symmetrical trigonal-pyramidal molecules, PF_5, VF_5, AsF_5, and PCl_5. This field is one which associates the lowest vibrational frequency with a greater degree of in-plane equatorial bending motion in the lower vibrational states compared to an axial bend[59] and results in larger vibrational amplitudes for equatorial liquid atoms compared to amplitudes for the same kind of ligand in the axial positions.

While the preferred force field[11,59,61] for symmetrical trigonal bipyramids shows a greater amplitude in the ground and lower excited states for in-plane equatorial bond bending relative to axial atom bending, most likely the relative motion of the axial atoms increases due to decreased repulsion as the exchange coordinate is traversed. In this manner one may reach the square pyramid formulated by Berry yet be consistent with the use of the potential function suggested by vibrational[11,59] and electron diffraction[61] data.

Barrier energies calculated[11] in the manner described above and based on the preferred force field[62] are presented in column 2 of Table IV. These values include an empirical correction for anharmonicity.[57] Values listed in column 3 are consid-

TABLE IV

Calculated Energy Barriers for Intramolecular Exchange

	ΔE, kcal/mole[a]	ΔE, kcal/mole
PF_5	15.3	3.8
AsF_5	11.8	3.0
VF_5	7.2	1.8
PCl_5	14.9	3.7
$SbCl_5$	8.9	2.2
$Sb(CH_3)_5$	12.7	3.2
$NbCl_5$	14.9	3.7
PH_5	6.3	1.6
$InCl_5^{2-}$	36.7	9.2[b]

[a] Values taken from ref 11 (field B) except VF_5 and $InCl_5^{2-}$. The value here for VF_5 is calculated based on the recently observed[63] ν_7 frequency of 109 cm^{-1}. [b] Reference 64.

ered more realistic. They are scaled relative to VF_5. The value for the latter substance was calculated based on observed[65] anharmonicity effects for its low-frequency band (109 cm^{-1}) concluded to be largely responsible for the exchange motion. Unfortunately, at present, anharmonicity effects have not been revealed for the other molecules listed. Included in the table is a value calculated by the same method[64] for positional exchange in square-pyramidal $InCl_5^{2-}$ proceeding through a trigonal-bipyramidal transition state. The normal coordinate appropriate to the latter calculation is of b_1 symmetry and has an associated frequency of 165 cm^{-1}.[66]

The value of 1.6 kcal/mole in Table IV for the hypothetical PH_5 molecule compares favorably with a value of 3.9 kcal/mole resulting from molecular orbital calculations.[22a] The results of the barrier calculations suggest the order of nonrigidity $VF_5 > AsF_5 > PF_5$. Experimental verification of this order, at least, regarding the extent of nonrigidity of VF_5 compared to the other two has been supplied by molecular beam studies.[67]

EXCHANGE IN THE PY_2F_3 SPECIES

For the most part, pentacoordinated molecules of the type PY_2F_3 show[4,56,] ^{19}F nmr spectra consistent with a trigonal-bipyramidal structure containing two axial and one equatorial fluorine atoms. For many of these molecules intramolecular exchange takes place at a sufficiently rapid rate that the latter nmr spectrum is observed only at low temperatures.[68] Taken by itself, the nmr patterns corresponding to the nonexchanging systems are also consistent with square-pyramidal structures. However, vibrational spectroscopy, on many of these systems (Table II) and electron diffraction[26] on one, $(CH_3)_2PF_3$, have established that the ground state is the trigonal-bipyramidal structure.

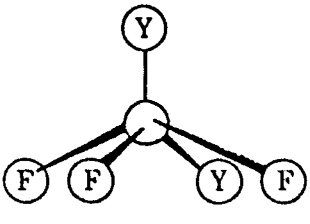
As with PF_5 and PYF_4 systems, low-frequency fundamental vibrations are assignable to bending motions. However, unlike the latter systems, intramolecular exchange *via* a simple equatorial-axial angle bending process (single-stage Berry process) does not correspond to an exchange coordinate unless the bending motion is allowed to proceed further to yield the more symmetrical trigonal bipyramid containing all three fluorine atoms in equatorial positions or if the process is made more complex by allowing successive positional exchanges to occur. In both of these processes the presumed structure would be considered relatively unstable since it places less electronegative groups in axial positions. As mentioned, isomers like that represented have not been prepared.[4,56]

Less is known about the exchange process for PY_2F_3 than for PYF_4 systems. For $(CH_3)_2NPF_4$ Whitesides and Mitchell[69] observed the temperature dependence of the ^{31}P nmr spectrum and concluded that both sets of fluorine ligands exchange simultaneously. The latter information provides additional support for a Berry mechanism for nonrigid members of the MX_5 and MYX_4 series. This type of experimental information is unavailable for any PY_2F_3 system.

By analogy with the exchange mechanism proposed for PF_5 and PYF_4 systems, it seems reasonable to expect exchange in PY_2F_3 systems to proceed through a low-lying square-pyramidal conformation. The relative rates[4,31a,56] of exchange in

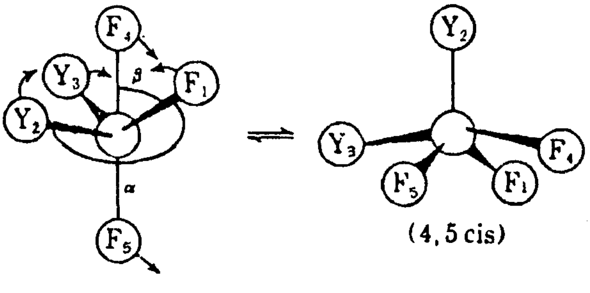
PY_2F_3 compared to PYF_4 systems are considerably slower. Thus any transitory state would differ more in structural makeup relative to the ground-state configuration than in the PYF_4 series.

For the purpose of discussion, an idealized square-pyramidal geometry is used. It is taken to be that one which has an axial-equatorial angle of approximately 104°. This geometry is predicted[19] to be the most stable square pyramid on the basis of simple repulsion arguments and is the one observed for $InCl_5^{2-}$ (Table I). It is also the geometry suggested by the Berry mechanism.[21] It is noted that the square-pyramidal transitory state suggested for exchanging PYF_4 compounds contains the least electronegative group in the lone axial position. Based on the assumed axial-basal angle of 104° in the square pyramid, minimization of electron-pair repulsions predicts a shorter axial bond relative to the bond lengths to the basal ligands oriented at 87° to one another. Proceeding with this approach, introduction of an additional ligand, forming the series PY_2F_3, leads to

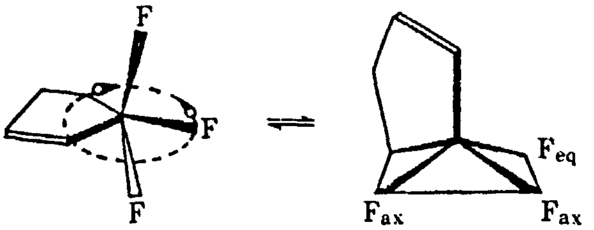


for the transitory structure.

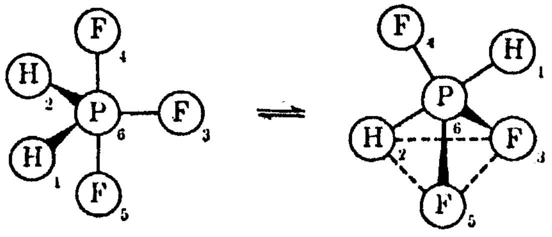
In order to test whether this hypothesis has any basis in fact, an analysis[70] of internal vibrations and their relative amplitudes was carried out for a number of examples. It was found, as with PF_5, that the preferred force field leads to the greatest ground-state amplitudes for equatorial ligands executing in-plane bending motions coupled with bending motions from axial atoms to a lesser but significant degree. Based on these amplitudes, a motion leading to exchange *via* the square-pyramid transitory state discussed above becomes reasonable. The mode postulated[70b] to largely govern the exchange combines an asymmetric in-plane bend simultaneous with an axial bend. As the angle α increases, space is provided for the axial atoms bending toward each other. During the course of this motion, a 90° rotation is assumed between atom sets 1, 3 and 4, 5, providing for minimum repulsion of ligands leading to the desired isomer. In this way equivalence of fluorine atom positions exhibited by ^{19}F nmr data for exchanging members[4,7,56,71] is achieved.



The pathway suggested offers a better rationalization[4a] of intramolecular exchange observed in the cyclic structure $(CH_2)_4PF_3$ in that it avoids placing an alkyl group in an axial position of a trigonal-bipyramidal transitory state.



The recently discussed[23] "turnstile" mechanism may be applied to PY_2F_3 molecules as an alternate possibility. The barrier height by this route corresponds to a structure having three ligands arranged at the corners of a triangle on one side of the central atom and the other two ligands residing on the opposite side of the central atom. Applied to PH_2F_3, atoms H_1 and F_4 rotate relative to the other three as the angle $H_2P_6F_3$ approaches 90°. In the barrier structure on the right atoms 1, 2, 4, and 6 are in one plane bisecting the F_3–P—F_5 angle and show the equivalence of equatorial fluorine atom 3 and axial fluorine atom 5. Actually the mechanism



is similar to the "twist" mechanism associated with rearrangements in octahedral compounds[72] but with the necessity of accompanying bond bending motions to achieve the desired state. Using the CNDO/2 approximation about 15 kcal/mole results[23] for the barrier for the above turnstile structure compared with 6 kcal/mole estimated[23] *via* the mechanism proceeding through the "favored" square-pyramidal transition state. Although the turnstile process appears less feasible when considering intramolecular exchange phenomena for the less substituted pentacoordinate systems containing simple ligands, it does appear that this process should become increasingly more important in certain chelated and more highly substituted members.[23] In the less fluorinated molecules PY_3F_2 and PY_4F no evidence[4,7,56] for intramolecular exchange is available.

Isomer Stabilization

The apparent lack of isolation of isomers for pentacoordinate substances is a consequence of the considerable difference in properties for the two sets of positions in each of the two basic conformations. However, if ligand properties are matched in an effort to reduce energy differences among isomeric structures, an enhanced rate of ligand exchange occurs. Representative data listed in Table V illustrating

TABLE V

Exchange Rates for PY_2F_3 Compounds

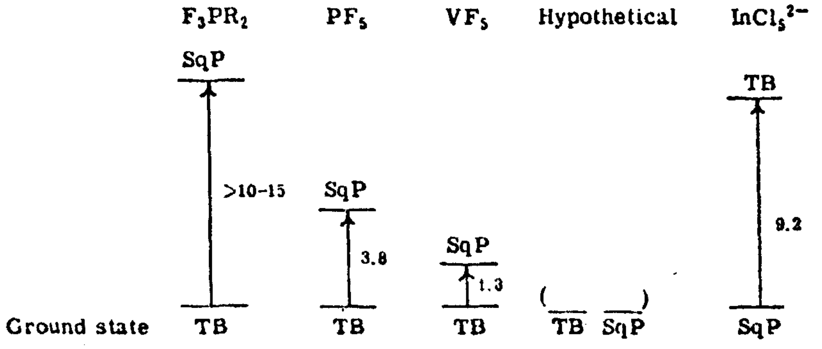
Y	^{19}F nmr exchange rate	Ref
CF_3[a]	Rapid at −120°	4
Cl	"Stopped" below ~ −120°	4, 7
H	"Stopped" below −45°	71
CH_3	No exchange at 25°	4
t-$(CH_3)_3C$[b]	No exchange at 25°	55

[a] Structure uncertain. See text. [b] Structure recently determined as C_s by vibrational spectroscopy in our laboratory (unpublished work).

this point show that, as the electronegativity difference of the ligands in the two positions decreases for PY_2F_3 compounds, the rate of ligand exchange increases.

The only indication that isomers may have been isolated for substances containing simple ligands is found with the use of the electronegative CF_3 group as a ligand in CF_3PF_4. Results of a microwave study[73] and a vibrational investigation[46] have led to different conclusions concerning its structure. An explanation of the preference for a square-pyramidal form for $InCl_5^{2-}$ is not known. In the isoelectronic sequence, $InCl_5^{2-}$, $SnCl_5^-$, and $Sb(CH_6H_5)_5$, X-ray studies (Table I) show $Sb(C_6H_5)_5$ to possess a distorted square-pyramidal structure and $SnCl_5^-$ to have a trigonal-bipyramidal structure. It may be that the reduced electronegativity found with these metal atoms provides for greater ionicity of attached ligands, possibly enhanced in the solid state, leading to stabilization of the square-pyramidal form. By going to larger less electronegative atoms, electron-pair repulsion effects are lessened. Alternatively, bond energy differences among the two sets of positions in the trigonal bipyramid and square pyramid may be minimized such that either structure is stabilized by smaller perturbing influences. As a consequence, packing factors or simple ion-ion interactions in the solid may provide the stabilization energy for either of the structures or some structure intermediate between them.

Future work focused on the stereochemistry and bonding differences in square pyramids of nontransition elements should be rewarding, particularly so if intramolecular exchange exists for some members of this class. Especially revealing would be the preparation of an exchanging member existing at the crossover "point" in stability between the square pyramid and trigonal bipyramid. Such a member



would be expected to have a most rapid exchange rate, perhaps high enough to allow quantum mechanical tunneling to become a significant process. Observance of the resultant spectroscopic splittings would then provide the necessary evidence to distinguish critically among exchange pathways.[74]

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