Ligand exchange and reaction mechanisms of fluorinated compounds

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CONTENTS

ABSTRACT

The topic of ligand exchange and reaction mechanisms of fluorinated compounds is reviewed, with emphasis on the main group fluorides. Mechanisms are divided into a series of elementary steps of bond formation and bond dissociation, using the coordination model of reaction mechanisms as an organizing principle. Included in this review is an analysis of the stereochemical behavior of pentacoordinated molecules, as well as

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a discussion of the role of impurities, anionic, cationic, free radical and fluorine-bridged intermediates, and fluoride-induced reactions.

NOTATION

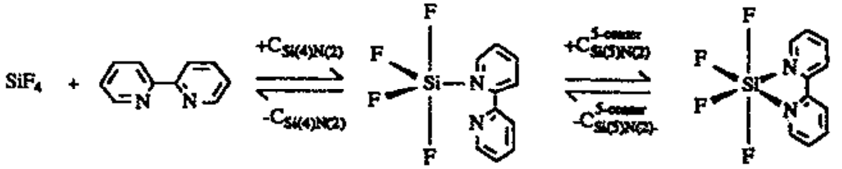
TBP	trigonal bipyramid
RP	rectangular pyramid
PFP	perfluoropinacolyl ligand
ax	axial substituents
eq	equatorial substituents
E–D	stable bond at ~25°C between main group element E and atom D
E--D	weak bond between element E and D which is cleaved rapidly at ~25°C
$+C_{M(m)N(n)}$	abbreviated as +C; increases the coordination number of elements M and N by 1, from m to $m+1$ and n to $n+1$.
$-C_{M(m)N(n)}$	abbreviated as –C; decreases the coordination numbers by 1, from $m+1$ to m and $n+1$ to n
$+C^{n\text{-center}}_{M(m)N(n)}$	abbreviated as $+C^c$; increases the coordination numbers by 1, via a cyclic n-center step
$-C^{n\text{-center}}_{M(m)N(n)}$	abbreviated as $-C^c$; decreases the coordination numbers by 1, via a cyclic n-center step
N-E-L	valence electron count and coordination number of element E; for example, silicon in SiF_4 can be designated as 8-Si-4 [6] or, alternatively, as $\lambda^4\sigma^4$-Si [7], $Si^{IV}(4)$ or $Si^8(4)$, and the reaction of SiF_4 with bipyridine changes silicon from 8-Si-4 to 10-Si-5 and to 12-Si-6.

A. INTRODUCTION

A reaction mechanism attempts to identify, with greater or lesser success, those intermediates and pathways that transform a reactant into a product. Mechanisms can be divided into a series of elementary steps, and these steps can be further subdivided, conceptually at least, into discrete changes in coordination number and electron count of individual atoms.

Studies of fluorinated compounds of the main group elements have provided very detailed information about the identity of highly reactive species that are involved in these elementary steps, and ^{19}F NMR has been particularly useful in monitoring the connectivity of chemical bonds in static and dynamic situations. Recent applications of NMR to dynamic systems are described in review articles and texts [1].

This review is organized around the elementary steps of bond formation and bond dissociation, and a multistep reaction path then consists, presumably, of a thermodynamically allowed sequence of these elementary steps. The notation of the coordination model of reaction mechanisms [2] is used as an organizing principle in headings and equations. In this model, elementary steps are described in terms of four coordination number operators, $+C$, $-C$, $+C^c$, $-C^c$, where $+C$ and $-C$ refer to intermolecular steps, and $+C^c$ and $-C^c$ refer to cyclic intramolecular steps, with the positive and negative signs indicating an increase or decrease in coordination number as bonds are made or broken. The connectivity of atoms in multistep pathways is represented in graphical form as pathway P(*X*,*C*), where the vertex set *X* consists of reactants, intermediates and products, and the edge set *C* consists of the coordination number operators, $+C$, $-C$, $+C^c$, $-C^c$, as illustrated by the reaction of silicon tetrafluoride with bipyridine to give a hexacoordinate adduct, SiF_4(bpy).

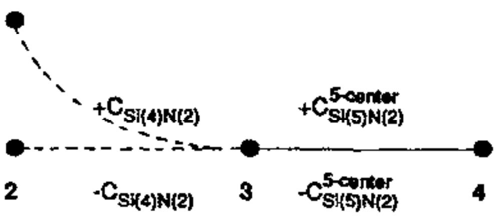


(1)

1 2 3 4

Since the formation of SiF_4(bpy) involves four species and two steps, a graph of 4 vertices and 2 edges is drawn, namely, pathway P(4,2). The first step in the forward direction is an intermolecular (bimolecular) step in which the coordination numbers of both Si and N are increased by 1, from Si(4) to Si(5), and N(2) to N(3), i.e. $+C_{Si(4)N(2)}$, and the second step is a cyclic intramolecular step, $+C^{5\text{-center}}_{Si(5)N(2)}$. Reverse steps are drawn below the edges of the graph, and dashed and solid lines refer to intermolecular and intramolecular steps, respectively.

Pathway P(4,2)



The coordination model has recently been tested mathematically [3] by carrying out kinetic simulations of pathways P(*X*,*C*) and comparing the results with extensive experimental data that are available for the reactions of boron trifluoride with Lewis bases [4]. The model accounts satisfactorily for the following experimental details, at least in a semi-quantitative manner: the formation of base:BF_3 is a bimolecular process with rate constants in the range 10^8 to 10^{10} M^{-1} s^{-1}; rates of reaction of base:BF_3 are inversely proportional to the gas phase enthalpies of dissociation; equilibrium data for BF_3-base systems; two modes of exchange in BX_3-base systems involving both halogen and base exchange; the boron cation $(amine)_2BF_2^+$ is an elusive species although, once formed, it is stable even in water; the formation of mixed base adducts such as $(Me_3N)(pyridine)BF_2^+$ depends on the order of addition of base; and the formation of chelated boron cations,

$(N–N)BF_2^+$, occurs in some cases, but not in others where only acyclic products, $F_3B{:}N–N{:}BF_3$, are formed.

This model allows chemical reactions to be analyzed in a systematic manner by, firstly, constructing a pathway $P(X,C)$ which defines each elementary step and specifies the connectivity of all atoms along that pathway, secondly, applying molecular orbital calculations to the postulated intermediates of the pathway and, thirdly, carrying out kinetic simulations of all proposed pathways $P(X,C)$ [3].

As an illustration of this approach, the reaction of pyridine and boron trifluoride can be described by the sequence of steps outlined in eqns. (2)–(5). Simple adduct formation of $py{:}BF_3$ is described by eqn. (2), while exchange of fluorine ligands and formation of ionic intermediates is described by eqns. (3),(4). If another base is added to this system, then rapid exchange of base is described by eqns. (3)–(5), and slower exchange of base by eqn. (2).

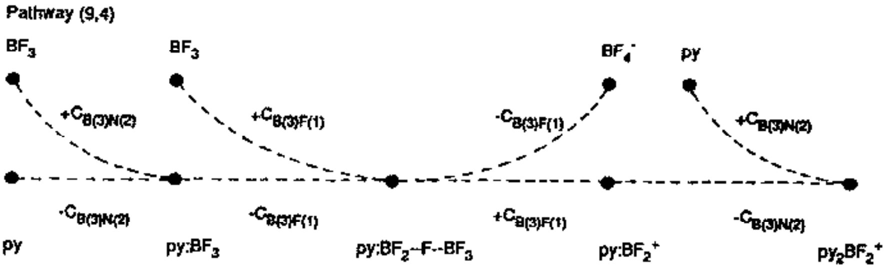
$$py + BF_3 \rightleftharpoons py{:}BF_3 \quad (2)$$

$$py{:}BF_3 + BF_3 \rightleftharpoons py{:}BF_2\text{--}F\text{--}BF_3 \quad (3)$$

$$py{:}BF_2\text{--}F\text{--}BF_3 \rightleftharpoons py{:}BF_2^+ + BF_4^- \quad (4)$$

$$py + py{:}BF_2^+ \rightleftharpoons py_2BF_2^+ \quad (5)$$

The mechanism of eqns. (2)–(5) consists of nine species and four steps and its graphical representation is pathway P(9,4).



For the kinetic simulation of pathway P(9,4), elementary rate constants must be associated with the four coordination number operators. Intermolecular steps, +C, are assigned rate constants equal to the diffusion-controlled value of about $10^9\ M^{-1}\ s^{-1}$, while rate constants associated with bond cleavage, –C, are estimated from bond enthalpy data; however, experimental bond enthalpies are not available for the fluorine-bridged intermediate, $py{:}BF_2\text{--}F\text{--}BF_3$, and ab initio molecular orbital calculations are therefore helpful in estimating the relative bond length/strength of the two bridging bonds. Once rate constants have been assigned to all Cs, then the kinetic simulation of pathway P(9,4) is a straightforward task and gives the concentration versus time curves on which further analysis and prediction is based.

The assumption that intermolecular (bimolecular) steps, +C, are diffusion controlled with rate constants of about $10^9\ M^{-1}\ s^{-1}$ places severe restrictions on any mechanism; however, the dilemma of slow reactions is resolved by taking into account the presence or absence of reactive intermediates. If these intermediates are present in exceedingly small amounts, then the importance of impurities and catalysts is greatly magnified. If all essential intermediates are readily available in multistep equilibria, as in catalytic or enzymatic systems, then chemical reactions are expected to display their intrinsically rapid rates.

All atoms of reactants and solvent can interact to form numerous bonds of varying strength, but a minimum set of coordination numbers formally limits the selection of coordination numbers for each system. For the pyridine–BF_3 system, this minimum set is B(3) B(4) N(2) N(3) F(1) F(2), and for the bipyridine–SiF_4 system, the minimum set is Si(4) Si(5) Si(6) N(2) N(3). Some interactions can be neglected because their influence on the formation of products is of minor consequence, but in other systems, even the weakest interaction is important, as in the low temperature (–258°C) formation of adducts CH_4–FF or CH_3F–HF [5]; for the latter systems, the minimum set of coordination numbers is F(1) F(2) H(1) H(2).

In this article, slow, fast, rigid, non-rigid or fluxional refer exclusively to the NMR time-scale, as judged by line-broadening effects. The other units of time that are relevant here are those of diffusion and cyclic n-center steps, but these are often too rapid for direct NMR study. In the majority of examples discussed in this review, bond cleavage occurs under mild thermal conditions, at either ambient or lower temperature, and an attempt is made to highlight those bonds, E--D, that are sufficiently weak to be cleaved spontaneously at 25°C or less, and we assign, somewhat arbitrarily, a bond strength of E--D < 100 kJ mol^{-1} and E–D > 100 kJ mol^{-1}.

Short-lived complexes may be designated in various ways: van't Hoff, van der Waals, collision, encounter, charge transfer, or donor-acceptor, but all will collectively be referred to as intermediates, with increased coordination number between two atoms being their defining property, and with a lifetime exceeding that of several vibrations, i.e. $>10^{-13}$ *s*. In some cases, lowering the temperature or trapping the reactive intermediate in a rigid medium permits identification, but in other situations, such as a diffusion-controlled step followed by a rapid intramolecular n-center step, the lifetime of the intermediate may be exceedingly short and identification by conventional techniques would not be feasible. In such cases, the designation of intermediate is used in a formal sense to assist in the classification of elementary steps of a reaction pathway.

B. IMPURITIES AND CATALYSTS

A century ago, Baker emphasized the influence of moisture on chemical change, thereby initiating the controversy about "intensively dried" liquids [8], and Euler launched the view that catalytic effect is always due to an increase in the concentration of reacting ions [9]. The classical experiments of Bodenstein on the decomposition of hydrogen iodide were, according to Taylor, influenced by the glass surface and slight traces of oxygen [10], and Lowry defined arrests in reactions as the period of time during which a pure material is taking up the impurities that are needed to promote the change [11]. In 1926, Moureu and Dufraisse wrote that the discovery of traces of impurities and the study of their influences will give us a true understanding of a multitude of chemical phenomena, if not to chemical reaction itself, but on the topic of catalysis they also passed along some advice: On such a delicate subject one always risks saying too much, however little one says [12].

(i) Water, alcohols, hydrogen fluoride and borosilicate glass

Most main group fluorides are susceptible to the effects of water, alcohols, hydrogen halides and glass surfaces, as emphasized continually in the literature of fluorine chemistry, e.g. [13], and early studies of fluorine exchange found that impurities grossly perturb the ^{19}F NMR spectra. Painstaking purification was often needed to obtain compounds of sufficient purity for NMR investigation, e.g. [14,15], but, conversely, NMR spectra are therefore among the most sensitive indicators of the presence or absence of impurities that may catalyze or inhibit chemical reactions.

If a particular impurity is suspected, adding more of it while monitoring the system by NMR is a convenient way to proceed, as illustrated by a study of methyltetrafluorosilicate which showed progressively increasing rates of fluorine exchange as H_2O, HF and $MeSiF_3$ was added because rapid exchange occurred via a fluorine-bridged intermediate, and the role of H_2O, HF and $MeSiF_3$ was to increase the concentration of the bridged intermediate [16,17]; a roundabout way of detecting impurities, but once identified they are relatively easy to neutralize or eliminate.

$$H_2O \underset{MeSiF_3OH^-}{\overset{MeSiF_4^-}{\rightleftharpoons}} HF \underset{FHF^-}{\overset{MeSiF_4^-}{\rightleftharpoons}} MeSiF_3 \underset{-MeSiF_4^-}{\overset{MeSiF_4^-}{\rightleftharpoons}} MeF_3Si\text{--}F\text{--}SiF_3Me^- \tag{6}$$

The H_2O-HF-glass system introduces a variety of catalytic species, including boron- and silicon-containing Lewis acids which are essential for the cleavage of element-fluorine bonds via fluorine-bridged intermediates.

$$SiO_2 \underset{H_2O}{\overset{HF}{\rightleftharpoons}} SiF_4 \underset{-F^-}{\overset{F^-}{\rightleftharpoons}} SiF_5^- \underset{-F^-}{\overset{F^-}{\rightleftharpoons}} SiF_6^{2-} \underset{-SiF_5^-}{\overset{SiF_5^-}{\rightleftharpoons}} F_5Si\text{--}F\text{--}SiF_5^{3-} \rightleftharpoons SiF_6^{2-} + SiF_5^- \underset{-SiF_4}{\overset{SiF_4}{\rightleftharpoons}} \text{etc.} \tag{7}$$

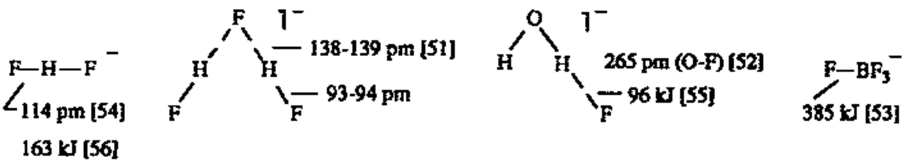
Some reactions, such as those of xenon difluoride with organotellurium(IV) compounds, do not proceed in Teflon apparatus unless a glass surface is exposed [18]. Other reactions of xenon difluoride are carried out with added Lewis acids or in the presence of HF, or BF_3:OEt_2 in glassware [19]. Fluorination of some compounds is accompanied by decomposition if carried out in glass, e.g. CH_3SF_3 to $CH_3S(O)F$ [20,21]. Methyldifluoroiodine reacts slowly with glass [22] and xenon difluoride is unstable when stored in acetonitrile in a glass container [23], but exceedingly rapid hydrolysis reactions can be moderated by using SiO_2, combined with a trace of HF, as a source of water [24]. Borates and silicates are invariably present in H_2O-HX-glass or ROH-HX-glass systems [25], and strong Lewis acid catalysts are therefore always potentially available in these systems. As a result, some reactions of organic and inorganic halides, although formally classified as S_N1 processes, may be catalyzed by H_2O-HX-glass or ROH-HX-glass systems [26]. On occasion, compounds can be prepared with glass as the only source of boron or silicon, as illustrated by the reaction of Pyrex glass with nitrosyl fluoride to give $NOBF_4$ and $(NO)_2SiF_6$ [27], or the reaction of catechol with silica or quartz under basic conditions to give the silicate $Si(O_2C_6H_4)_3^-$ [28]. The photochemical synthesis of xenon difluoride from xenon and fluorine in a Pyrex reactor is accelerated by the addition of small amounts of hydrogen fluoride [29], and a discussion of the effect of glass and metal apparatus is included in a historical account of the discovery of xenon fluorides [30].

Ligand exchange processes complicate the detection of small amounts of glass-produced boron and silicon fluorides, but identification of BF_4^- by ^{19}F NMR is aided by the characteristic $^{11}BF_4^-/^{10}BF_4^-$ pattern. The A_2B_2 and A_2BC ^{19}F NMR spectra of rigid adducts of SiF_4 and bipyridine, phenanthroline or 4-fluorobipyridine allow identification of small amounts of SiF_4 [26]. For the analytical detection of trace amounts of fluoride, ion chromatography and the Alizarin Fluorine Blue-lanthanum procedure have been recommended, the latter technique yielding a detection limit of 40 ng l^{-1} (0.025 ppb) [31]. From conductivity measurements of hydrogen fluoride, water concentrations down to 1.85×10^{-6} mol dm^{-3} (0.033 ppm) have been measured, and the effect of acid and SiO_2 impurities on the conductivity of HF has been studied [32].

Purified tetrapropylammonium fluoride can be made by the HF-neutralization of $^nPr_4NOH$, as monitored with a pH meter, and its purity checked indirectly by the ^{19}F NMR spectrum of $MeSiF_4^-$, which is a sensitive indicator of the presence of traces of HF or H_2O [16]. Purified tetramethylammonium fluoride has been used in the preparation of fluoroanions such as XeF_5^- [33], ClF_6^- [34], TeF_8^{2-} and IF_8^- [35]; slow reactions of Me_4NF with organic solvents do occur, including proton abstraction from acetonitrile and halogen exchange with chloroform and, to a lesser extent, dichloromethane [36]. Convenient sources of fluoride ion also include anhydrous spray-dried KF [37] and KF solubilized by 18-crown-6 [38].

Besides rigorous purification, other strategies can be used to slow down impurity-catalyzed fluorine exchange. Trace amounts of water or hydrogen fluoride can be converted in situ to less detrimental species by adding small amounts of silicon-nitrogen compounds [39] or triphenylphosphine imines [40,41]; hydrogen fluoride and hydrogen chloride may also be complexed with base, e.g. DMSO:HCl [42], Ph_3PO–HF [43], FHF^- or $Et_3N(HF)_n$. Slight changes in experimental procedure can sometimes moderate the effect of impurities, as illustrated by the addition of a small quantity of $PhPF_2$ to the $PhPF_3H$–$PhPF_4H^-$ system, which ensures that any water and HF is converted to PhP(O)HF and $PhPF_3H$ [44]. Adding a slight excess of fluoride ion slows down exchange in $PhSiF_5^{2-}$ by ensuring the absence of $PhSiF_4^-$ and $PhSiF_3$ [45], similarly, excess fluoride ion stops exchange in XeF_5^- [33] and $(CF_3)_2GeF_4^{2-}$ [46], and exchange in the SiF_5^-–SiF_6^{2-} system is stopped by adding a large excess of ammonia because all SiF_5^- is thereby converted to the hexacoordinate adduct $SiF_5(NH_3)^-$ [17]. Careful adjustment of stoichiometry can also stop fluorine exchange by preventing the formation of fluorine-bridged intermediates. In a study of impurity-catalyzed silyl exchange in *N*-trialkylsilylimidazole, it was found that several procedures can slow down silyl exchange, namely, purification of reactants and solvent, addition of excess triethylamine to hinder the coordination of water or imidazole at silicon, or introduction of a bulky t-butyl substituent at silicon to prevent the attainment of higher coordinate silicon intermediates [47,48]. Although the H_2O-HF-glass system complicates mechanistic and synthetic studies, numerous ways of eliminating impurities and avoiding or chemically treating glassware are described in the individual papers listed in the reference section and experimental details may be found there.

Fluoride ion binds strongly to HF, and the NMR spectrum of FHF^- shows retention of hydrogen–fluorine coupling in purified samples but rapid exchange and bond cleavage as HF is added [49,50], and this behavior is in agreement with bond length data which show significant lengthening (21%) of the hydrogen–fluorine bond as $F–H–F^-$ is converted to F–H--F--H-F.



Fluoride ion binds to alcohols, and the gas-phase cleavage of alcohol adducts, ROH--$F^-$and RO--HF^-, has been studied by ICR techniques [57]. Fluoride ion binds relatively weakly to water (96 kJ), as compared to hydrogen fluoride (163 kJ), and this difference can explain the fact that aqueous solutions of alkali fluorides are suitable for the preparation of organofluorosilicates,

$$CH_3SiF_3 + 2\,KF \xrightarrow{H_2O} K_2[CH_3SiF_5] \tag{8}$$

whereas decomposition into fluorosilane and bifluoride occurs in the presence of hydrogen fluoride [58].

$$(NH_4)_2[CH_3SiF_5] + 2HF \rightarrow CH_3SiF_3 + 2NH_4HF_2 \tag{9}$$

Aqueous potassium fluoride has been used for the preparation of $K_2[CF_3GeF_5]$ [59] and it appears that water is less detrimental than hydrogen fluoride towards fluoride ion. Numerous other fluorinated compounds, however, hydrolyze rapidly in the presence of $(H_2O)_nF^-$, and hydrolysis is favored by the high bond strength of E–O and E=O bonds.

(ii) Mechanistic uncertainty

The continual problem of identifying and eliminating trace amounts of impurities, combined with the elusive nature of reactive ions and radicals and the lack of information about interconversions among these species guarantees that mechanistic uncertainty will remain. We have therefore adopted an empirical approach in this review and selected many examples from the recent literature so that even if the interpretations vary with time, the work discussed will be useful in further study of chemical reactivity.

Coordination number and electron count may be used as discrete variables for mechanistic analysis [2], but these terms are not without their subjective character, for instance, the fluoride ion has a coordination number of 1, 2, 3 or 4 in BF_3, $Sb_2F_{11}^-$, $(XeOF_4)_3F^-$ [60] and (macrocyclic ether)F^- [61], respectively, and higher in the solid state [62], but it cannot always be decided which distant atom remains within a coordination sphere or which coordination numbers are relevant in solution. Comparable reservations apply, of course, to the use of electron count in mechanistic analysis.

Despite these uncertainties and the difficulty of identifying intermediates in solution, valuable mechanistic insight may be obtained from several sources: from a systematic study of closely related crystal structures [63–65], or from empirical bond length/bond strength relationships [66,67], and from analogous reactions carried out in the gas phase [68].

Molecular orbital calculations show good to excellent agreement between experimental and calculated geometries of stable main group fluorides [69], as illustrated in Table 1. These calculations accurately predict the site preference of fluorine versus other substituents in trigonal bipyramidal phosphoranes, arsoranes or silicates, e.g. [81,92–94]. Experimental trends are reproduced, such as a decrease in Si–F and Si–H bond lengths with increasing fluorine substitution in silanes [73], or a small *cis* influence on the equatorial fluorines in SF_5Br [95]. The calculation of the structure and bond energies of fluorinated intermediates, taking into account their coordination number and electron count, is important for the analysis of reaction mechanisms [3].

C. BOND FORMATION, +C AND +C^c

(i) Five- to six-coordination, +C

(a) Trigonal bipyramidal pentafluorides, EF_5

Trigonal bipyramidal molecules are among the most sensitive indicators of bond formation because of the change in symmetry and NMR spin pattern that accompanies the formation of six-coordinate adducts or intermediates. Numerous six-coordinate ad-

TABLE 1

Comparison of calculated and experimental E–F bond lengths of element fluorides (pm)

	Experimental	Ref.	Calculated	Ref.
SiF_4	155.98	[70]	155.93	[71]
SiH_2F_2	157.7	[72]	158.3	[73]
NF_4^+	130	[74]	132, 134	[74,75]
PF_5 (gas)	157.7 ax	[76]	157.50	[71]
	153.4 eq		153.74	
PF_5 (solid)	158.0 ax	[77]		
	152.2 eq			
PH_2F_3	161.8 ax	[78]	161.1	[79]
	153.9 eq		155.3	
PF_4Cl	158.1 ax	[80]	157.6	[81]
	153.5 eq		153.9	
CF_3SF_3	167.9 ax	[82]	168.4	[82]
	159.6 eq		160.0	
SF_6	156.1, 156.39, 155.61	[83]	156.09	[71]
IF_7	178.6 ax	[84]	177.05	[85]
	185.8 eq		183.33	
$C_6F_5I–F–IC_6F_5^-$	245.5–250.9 bridge	[86]		
$CF_3I–F–ICF_3^-$			234.7 bridge	[86]
XeF_2	197.7	[87]	198.4	[88]
XeF^+	187.3	[89]	188.6	[88]
$F(H_2O)_4^-$	~265 (O–F)	[90]	262 (O–F)	[91]

ducts are stable indefinitely at ambient or higher temperature, e.g. $F_5P–PMe_3$, $F_5P–NMe_3$, $AsF_5–NCCH_3$, $AlF_5–OH_2^{2-}$, etc. [96], and adducts with somewhat weaker E--D bonds can be identified by NMR at lower temperature, e.g. F_5P--OEt_2 at −65°C, F_5Si--NH_3^- at −80°C [97], and F_5As--PF_3 at −130°C [98]. For exceedingly weak E--D bonds, however, the temperature range normally available in NMR spectrometers may not be sufficient to slow down exchange; in that case, bond formation is detected only indirectly by the appearance of averaged peaks resulting from rapid exchange of axial and equatorial ligands, as demonstrated for TBP pentafluorides such as PF_5 and SiF_5^-, as well as TBP $Fe(CO)_5$.

Stereochemical non-rigidity is a common feature of pentacoordination [99,100–102] and energy barriers for axial-equatorial ligand exchange, as measured by NMR, extend over a wide range, ca. 15–125 kJ mol^{-1}. The energy barriers for some typical phosphorus and sulfur compounds are listed in Table 2, and more extensive compilations are available [101,102].

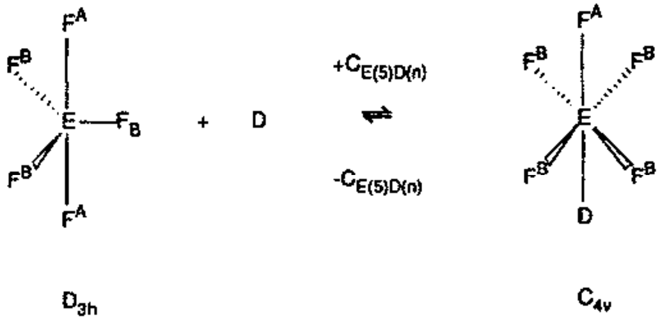
Among the mechanistic features that appear to be responsible for axial-equatorial ligand exchange are the following: (a) bond formation and a rapid equilibrium between five- and six-coordinate geometries; (b) formation of fluorine-bridged intermediates; (c) stereochemistry and symmetry properties of six-coordinate intermediates; (d) site preference of ligands and flexibility of five-coordinate species; (e) effect of four-, five- and six-membered rings; (f) rapid and reversible intramolecular coordination (chelation); (g) rotation about single or double bonds; and (h) inversion at nitrogen or sulfur atoms. While it is not expected that these dynamic effects can be easily separated, some effects will not be observable in certain systems, because of symmetry or energy considerations, while other systems may have only one or another dominant pathway of axial-equatorial ligand exchange.

Phosphorus pentafluoride has a trigonal bipyramidal structure of D_{3h} symmetry in the gas phase [76] and as a solid at −164°C [77]. According to VSEPR arguments, a square pyramidal C_{4v} structure is of higher energy because of the greater repulsions among the bonded electron pairs [115]. A model is available for estimating the relative stability of TBP and RP isomers of phosphoranes [116], and the energy difference between D_{3h} and C_{4v} structures of PF_5 is calculated to be 16 ± 2 kJ mol^{-1} [117], compared to experimental values of 11.9–16.4 kJ mol^{-1} [118] and an estimate of <21 kJ mol^{-1} from NMR [103]. If it is assumed that PF_5 exchanges its axial and equatorial fluorines by specific bond formation according to eqn. (10), then the P--D bond strength must exceed a value of about 12–21 kJ mol^{-1}. The symbol D represents any donor atom of reactant or solvent or intermediate that participates in adduct formation.

TABLE 2

Barriers for axial-equatorial fluorine exchange in TBP phosphorus and sulfur compounds

Compound	Energy barrier $\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})	Ref.
PF_5	<21	[103]
$ClPF_4$	18 (96 K)	[104]
Cl_2PF_3	30	[105]
Me_2PF_3	74.5	[106]
Ph_2PF_3	78.2	[106]
$CF_3(Me)PF_3$	36.8	[107]
H_2PF_3	42.7 (218 K)	[108]
$CF_3(H)PF_3$	26.4 (133 K)	[108]
$Ph(H)PF_3$	55.6	[44]
o-$CF_3C_6H_4(H)PF_3$	52.9	[109]
m-$CF_3C_6H_4(H)PF_3$	53.6	[109]
m-$CH_3C_6H_4(H)PF_3$	56.0	[109]
Me_2NPF_4	37–39	[104,110,111]
i-Pr_2NPF_4	31	[112]
$(Me_2N)_2PF_3$	82.0 (343 K)	[106]
$(Me_2N)_2P(CF_3)_3$	63 2	[111]
$CF_3(MeS)PF_3$	53.6	[113]
$CH_2{=}SF_4$	>105	[114]

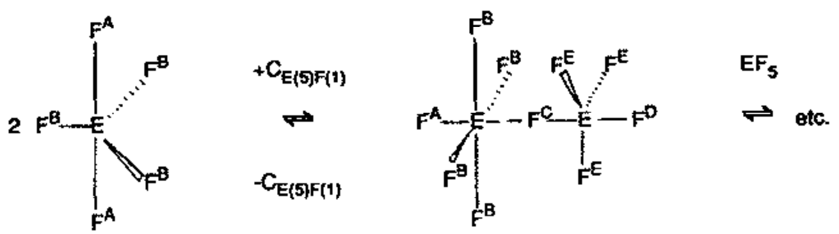


(10)

Temperatures as low as −197°C have failed to slow down exchange in PF_5 [99] and, in the absence of further experimental evidence, the permutation of axial and equatorial ligands can be viewed from two perspectives depending on whether interactions with the environment are omitted or specifically considered. Both views have been discussed in the literature, the former as Berry pseudorotation [101,119], or turnstile rotation [120], and the latter as collisional processes [121,122], donor-acceptor or solvent adducts [97,123,124] or fluorine-bridged species [17,125,126]. Definitive evidence for donor-acceptor adducts and rapid equilibration of five- and six-coordinate geometries, and of accompanying axial-equatorial fluorine exchange in PF_5 and SiF_5^-, is based on variable temperature ^{19}F NMR studies [97]. Fluorine-bridged adducts can be identified by NMR at low temperature, e.g. F_5As–FCH_3 at −165°C or F_5Sb–FCH_3 at −60°C [127], however, adducts of PF_5 or BF_3 with CH_3F cannot be detected, but that is in keeping with the order of acid strength of the main group fluorides: $PF_5 < BF_3 < AsF_5 < SbF_5$ [128,129].

For some purposes, a mechanistic distinction may not be significant, as long as the permutational character and symmetry properties of the exchange process are identical, but this distinction is important in synthesis and reaction mechanisms because the formation of a specific bond, even an exceedingly weak bond, may be a critical step of a multistep transformation. Furthermore, each step must be evaluated if the connectivity of atoms along a reaction pathway is of interest [2].

The formation of a fluorine-bridged intermediate necessarily permutes axial and equatorial fluorines. Strong Lewis acids form stable fluorine-bridged compounds, e.g. tetrameric Sb_4F_{20} [130] or chain-like BiF_5 [131],



(11)

however, there is no direct evidence of fluorine bridging in the case of weaker Lewis acids, and the solid state structures of PF_5 at −164°C [77] and of AsF_5 at −89°C show TBP geometry [132].

There is considerable variation in the properties of donor-acceptor adducts of phosphorus pentafluoride. From vapor pressure measurements, the heat of dissociation of the dimethyl ether adduct $Me_2O–PF_5$ is 106 kJ mol^{-1}, and this adduct is 94% dissociated into its gaseous components at 20°C [133], but the propyl ether adduct F_5P--OPr_2 has a significantly reduced enthalpy of formation of 45.2 kJ mol^{-1} [134]. A variable-temperature NMR study of the interaction of PF_5 with diethyl ether gives a reaction enthalpy of about 51 kJ mol^{-1} [97],

$$PF_5 \quad + \quad OEt_2 \quad \underset{-C_{P(5)O(2)}}{\overset{+C_{P(5)O(2)}}{\rightleftharpoons}} \quad F_5P\text{--}OEt_2 \tag{12}$$

but NMR studies are complicated by decomposition, which can be observed above −65°C in the F_5P--OEt_2 adduct. This decomposition is presumably caused by abstraction of fluoride ion by PF_5 to generate PF_6^-, as well as the reactive cation $Et_2O–PF_4^+$; in the case of the $Me_2O–PF_5$ adduct, decomposition eventually leads to $Me_3O^+PF_6^-$ and F_3PO [135]. Adduct formation is known to weaken the P–F bond, as illustrated by an average 2.2% bond lengthening as PF_5 (153.4–157.7 pm) [76] is converted to $F_5P–NH_3$ (158.1–160.0 pm) [136].

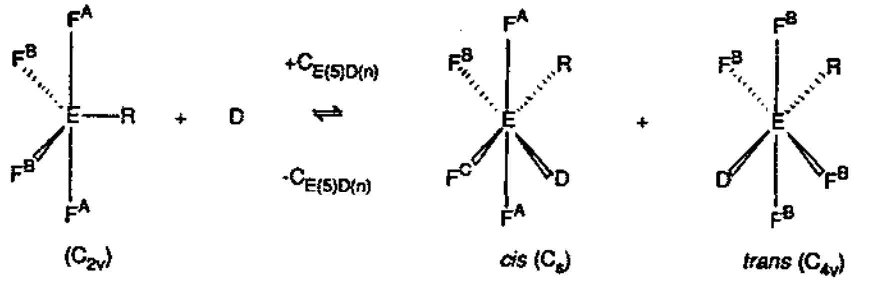
If the permutation of axial and equatorial ligands in D_{3h} molecules is related to adduct formation and molecular association, it cannot be restricted to main group fluorides but should appear as a general property of five-coordinate molecules and, indeed, fluxional behavior has been demonstrated in many other TBP molecules, e.g. $(p\text{-}MeC_6H_4)_5P$ is fluxional at −60°C [137], Ph_5Sn^- and Me_5Sn^- at −80°C [138], Me_5As at −95°C [139], Me_5Sb at −100°C [140] and $(p\text{-}MeC_6H_4)_5Sb$ at −135°C [141].

For the related TBP molecule $Fe(CO)_5$, where axial-equatorial exchange is still rapid in solution at −170°C [142], intermolecular effects have been greatly reduced by recording the ^{13}C NMR spectrum in the solid state, in that way separating axial and equatorial carbonyl signals at −38°C [143]. The difference in rates of exchange in solution, as compared to the solid state, has been estimated as 1.1×10^{10} s^{-1} at −20°C in solution [144] and 100 s^{-1} at −38°C [143] in the solid state.

(b) Mono-substituted trigonal bipyramidal fluorides, REF_4

Compounds of the formula REF_4 can interact with donor atoms to give *cis* and *trans* intermediates, but only the *trans* isomer (C_{4v}), with its four equivalent E–F bonds, necessarily leads to axial-equatorial fluorine exchange. The *cis* isomer, although favored statistically (4:1), is not expected to permute F^A and F^B fluorines in REF_4 because the simplest mode of formation of the *cis* isomer, involving attack of D on an adjacent face or edge of REF_4, followed by loss of D by the same route, does not permute the F^A and F^B

substituents. Any other trajectory would, presumably, require more extensive structural displacement of ligands during the formation of *cis*-D:REF_4 and have a higher energy barrier.



(13)

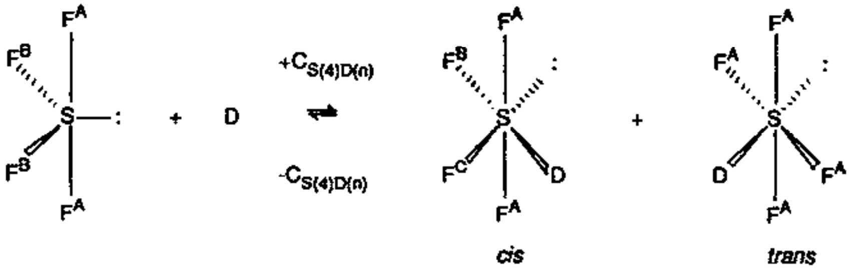
One of the reasons that equatorial sites may be favored as sites of entry and departure of D is the decreased resistance to equatorial bending in TBP molecules, compared to axial bending, as calculated for PF_5 [117]. Such behavior is expected on the basis of VSEPR considerations [145].

Axial-equatorial exchange in REF_4 is expected to resemble closely that of EF_5, with comparable rates and energies and, consistent with this view, exchange is rapid and has not been slowed down in molecules such as $MePF_4$ at −177°C [104], CF_3PF_4 at −150°C [146], or SOF_4 at −150°C [147], and $ClPF_4$ is fluxional at −185°C [104].

Mono-substituted silicates $RSiF_4^-$ are also fluxional at ambient and lower temperature. There is no evidence of significant slowing of fluorine exchange in (mesityl)SiF_4^- at −100°C, although exchange can be slowed down with more sterically crowded ligands, as in 2,4,6-tri-tert-butylphenyltetrafluorosilicate at −68°C [148], however, free rotation about the Si–C bond in the latter species cannot be assumed at lower temperature. The sterically crowded phosphorus analogue, 2,4,6-tri-tert-butylphenyltetrafluorophosphorane, is rigid at −60°C [149].

The formation of a *trans*-D:REF_4 intermediate in eqn. (13) satisfies the criterion of Whitesides and Mitchell that both axial and equatorial fluorines must undergo simultaneous interchange [104,150]. Attack of D on a TBP face or edge opposite to the ligand R places the axial and equatorial ligands in mutually *trans* positions in the octahedral *trans*-D:REF_4 adduct. For any reversal along the same trajectory, there is an equal probability that two fluorines will revert to two axial or two equatorial sites in trigonal bipyramidal REF_4. A ^{31}P NMR study of Me_2NPF_4 established that solvents such as tetrahydrofuran or dimethyl ether accelerate the exchange of axial and equatorial fluorines; moreover, the permutational character of the exchange process is the same as in the absence of ether solvents [104].

TBP molecules with a lone pair of electrons may also interact with a donor molecule to give *cis* and *trans* pseudo-octahedral intermediates, but only the *trans* isomer necessarily leads to axial-equatorial exchange. A higher energy barrier for axial-equatorial exchange in SF_4, ~47–68 kJ mol^{-1} [97,151,152], as compared to PF_5, may be attributed to a combination of statistical factors, related to the probability of forming a *trans* isomer, and to the greater repulsion of the non-bonded electron pair in the *trans* intermediate. In agreement with this view, the barrier to axial-equatorial exchange in PF_4^-, which is isoelectronic with SF_4, is also significantly higher than in PF_5 [153].

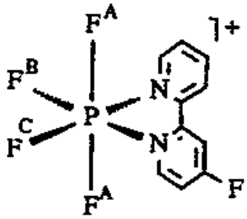


(14)

A pseudo-octahedral intermediate, with an ether solvent molecule and a pair of electrons in *trans* positions, can account for the single peak, down to −120°C, in the fluorine NMR spectrum of the tellurium compound $Te(CF_3)_4$ [154].

Sulfur tetrafluoride and its organic derivatives are susceptible to the effects of trace impurities, as emphasized over the years, and this impurity-catalyzed exchange process is accompanied by the cleavage of S–F bonds [20,21,39,97,152,155–158]. Lewis acids such as PF_5, AsF_5 and SbF_5 are particularly effective as catalysts [159]. Since the H_2O-HF-glass system generates Lewis acids such as BF_3 and SiF_4 [26], it seems reasonable to propose that Lewis acids interact with SF_4 to furnish the cation SF_3^+, and that S–F bond cleavage in the impurity-catalyzed pathway involves the bridged intermediate F_3S--F--SF_3^+. In addition to S–F bond cleavage and axial-equatorial exchange in SF_4, a third dynamic process can be identified by NMR at low temperature, namely, molecular association of SF_4 via fluorine bridges [160].

The possibility that hexacoordinate D:REF_4 adducts undergo ligand scrambling by an intramolecular twist mechanism, without bond dissociation, is considered unlikely. Non-dissociative mechanisms have been proposed for octahedral complexes [161], but alternative bond cleavage processes are often compatible with the experimental results, especially for fluoro complexes where the effect of H_2O-HF-glass must be taken into account [2]. In many cases, the NMR spectra clearly demonstrate that hexacoordinate adducts do not undergo permutational exchange of ligands, unless there is bond dissociation, as illustrated by the ^{19}F NMR spectra of **5**, **6** and **7**, which show A_2BC, AA'BC and ABC spin patterns, respectively, characteristic of rigid complexes. Fluorinated ligands such as 4-fluoro-2,2'-bipyridine (fbpy) are helpful in probing the fluxional character of octahedral complexes, as illustrated by the ^{15}N NMR spectrum of *mer*-$Fe(fbpy)_3^{2+}$ (**7**) which shows six non-equivalent nitrogens in the inner coordination sphere of iron, thereby confirming the absence of intra- or intermolecular ligand exchange processes.



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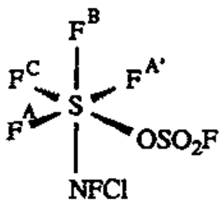

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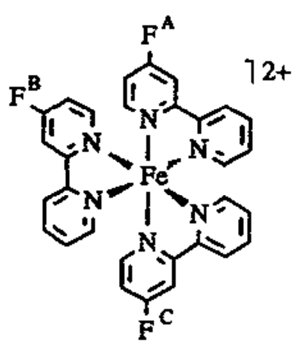
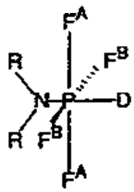


7 [163]

Although axial-equatorial exchange in REF_4 molecules can be attributed to a rapid equilibrium involving a *trans*-D:REF_4 intermediate, the nature of R determines the symmetry properties of such an intermediate and, as a result, some equilibria may not be observable processes. For instance, the formation of *trans*-D:REF_4 intermediates **8–11**, in which the R substituent lacks cylindrical symmetry, is not expected to permute fluorine ligands unless accompanied by rotation about single or double bonds and inversion at nitrogen and sulfur atoms. If an equilibrium between five- and six-coordinate species is not observable for symmetry reasons, and if rotation and inversion processes are rate-determining, then the rate of the latter dynamic processes can be measured by the rate of axial-equatorial exchange, and ^{19}F NMR provides a sensitive method of studying such behavior because of the large chemical shift difference of fluorine substituents in REF_4 and the large dynamic range that is available.



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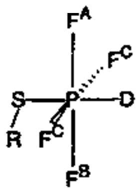

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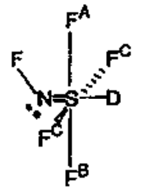

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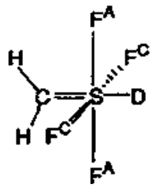
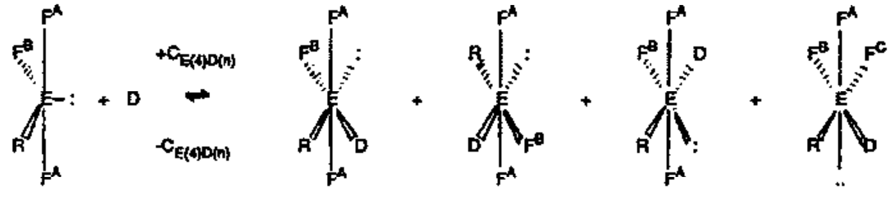


11

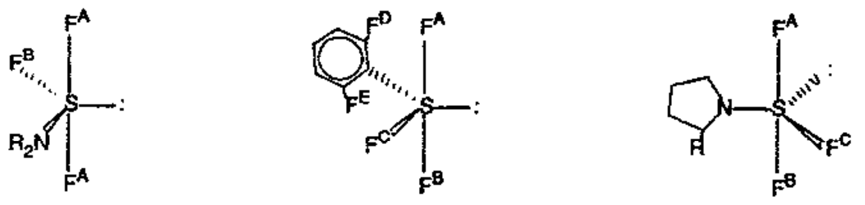
Rotation about P–N and P–S single bonds, accompanied by inversion at nitrogen and sulfur atoms, occurs rapidly in aminofluorophosphoranes, e.g. $\Delta G^{\ddagger}$ is 37 kJ mol^{-1} at –85°C for Me_2NPF_4, with more rapid rates observed on addition of ether solvents [104]. Similar dynamic processes are also found in alkylthiofluorophosphoranes, for example, the A_2BC ^{19}F NMR spectrum of $MeSPF_4$ can be observed at –90°C [164], and the slowing of rotation and inversion at lower temperature makes all four fluorines non-equivalent in methyl-substituted piperidyltetrafluorophosphorane, $MeC_5H_9NPF_4$ [165]. On the other hand, there is no fluorine site exchange in $FN{=}SF_4$ or $CH_2{=}SF_4$ up to +100°C, reflecting barriers to rotation of N=S and C=S double bonds in excess of 105 kJ mol^{-1} [114,166].

Mono-substituted compounds REF_3 with a lone pair of electrons can interact with a donor molecule to give five stereoisomers **12–15** (**15** is chiral). If the formation of intermediates **12–14** involves attack of D at an equatorial site, then a permutation of fluorines is not expected. A change in spin pattern from AB_2 to ABC accompanies the formation of isomer **15** but, depending on the potential surface of adduct formation, fluorine exchange may or may not occur via intermediate **15**. Based on these considerations, it is problematical whether axial-equatorial exchange is observable in these molecules and, experimentally, the ^{19}F NMR spectrum of sulfurane CF_3SF_3 in the gas phase or in solution shows no signs of fluxionality [82]. Related aryl and perfluoroalkyl fluorosulfuranes also have high barriers to axial and equatorial exchange [167].



(15)

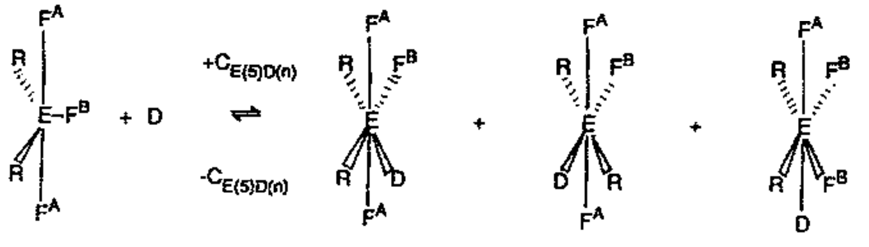
Purified samples of dialkylaminosulfur fluorides R_2NSF_3 (**16**) do not exchange axial and equatorial fluorines [157]. Restricted rotation about a S–N bond in Me_2NSF_3 makes the axial fluorines non-equivalent because the Me_2N substituent, although planar, is not coincident with the axial plane [168]. Rotation about a C–S bond in sulfurane **17** equilibrates the non-equivalent axial, as well as the non-equivalent *ortho* fluorines, with reaction parameters of $\Delta H^{\ddagger} = 43.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -32$ J mol^{-1} deg^{-1}. Axial-equatorial fluorine exchange in **17**, however, was not detected up to +50°C, where decomposition by glass set in, and the exchange barrier must exceed ~63 kJ mol^{-1} [169].



Impurity-catalyzed exchange in organosulfur trifluorides is most likely due to the H_2O-HF-glass system, and rapid S–F bond cleavage may be attributed to the bridged intermediate RF_2S--F--SF_2R^+. Impurity-catalyzed bond cleavage in aminofluorosulphurane (**18**) is stopped by the addition of silicon-nitrogen compounds, and all three fluorines are non-equivalent because of the asymmetry of the cyclic substituent. Sulfurane **18** has been suggested as a potential enantioselective fluorinating agent [170].

(c) Di-substituted trigonal bipyramidal fluorides, R_2EF_3

Interaction of a di-substituted TBP fluoride, R_2EF_3, with a donor molecule may give rise to three isomeric six-coordinate intermediates **19–21**. Attack of D at an equatorial site of R_2EF_3 is viewed as a favorable process, but the resulting *mer*-isomers **19–20** do not necessarily exchange axial and equatorial fluorines; such exchange is expected, however, if a *fac*-isomer **21** is formed.



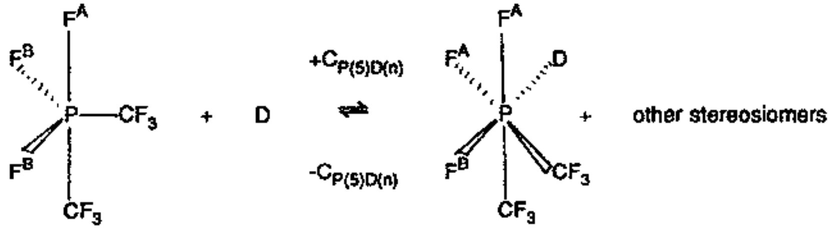
(16)

mer **19** *mer* **20** *fac* **21**

Axial-equatorial exchange is predicted to be slower in R_2EF_3, as compared to REF_4 or EF_5, partly because of statistical factors, since only the *fac* **21** isomer permutes fluorine ligands, but also because of the "stiffness" of a TBP, i.e. an energy barrier is associated with the displacement of ligands that must accompany the formation of a *fac* **21** intermediate. These arguments are supported by NMR experiments which invariably show that di-substituted phosphoranes R_2PF_3 are rigid at higher temperatures than the corresponding mono-substituted phosphoranes RPF_4, e.g. Me_2PF_3 (+30°C) [106] versus $MePF_4$ (<–177°C) [104], $(^tBu)_2PF_3$ (–40°C) [171] versus $^tBuPF_4$ (<–150°C) [172], Cl_2PF_3 (–120°C) [105] versus $ClPF_4$ (<–185°C) [104], and H_2PF_3 (–90°C) [108] versus HPF_4 (<–90°C) [173].

If axial-equatorial exchange is an unobservable process, then other dynamic processes such as internal rotation may be rate-limiting, as discussed for mono-substituted derivatives. Restricted rotation about the P–N bond has been observed in amino phosphoranes $(Me_2N)_3PF_2$ [174] or $H_2(NH_2)PF_2$ [175], and the barrier to rotation is 46.7 kJ mol^{-1} in $PF_3(NH_2)_2$ [110] and 43.9 kJ mol^{-1} in $Me_2NPF(CF_3)_3$ [111]. Rotation about the P–N bond in a chiral phenylpiperidyltrifluorophosphorane was found to have a barrier height of ~50 kJ mol^{-1} [176], and the barrier to P–S bond rotation in $MeSPF_3CF_3$ is 42.6 kJ mol^{-1} [113].

An interesting situation arises if the substituents in a TBP are of equal, or nearly equal, apicophilicity because an isomeric TBP then allows the formation of *fac* intermediates by equatorial attack of a donor molecule, as illustrated in eqn. (17) where a trifluoromethyl substituent occupies an axial site.



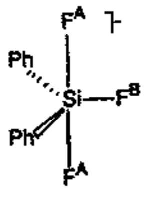
(17)

22 *fac*-**23**

A small energy difference between TBP stereoisomers containing F and CF_3 substituents has been established for CF_3PF_4, which consists of two conformers with equatorial ($60 \pm 10\%$) and axial CF_3 groups in the gas phase [177]. The striking difference between the molecule $(CF_3)_2PF_3$, which is fluxional down to −160°C [146], and Me_2PF_3 which is rigid at +30°C [106], may be attributed to a smaller difference in apicophilicity between F and CF_3, as compared to the difference between F and CH_3. According to this argument, stereoisomer **22** provides a lower energy path for axial-equatorial ligand exchange because the formation of intermediate *fac*-**23** can occur by a favorable attack of D at an equatorial site.

The apicophilicity series, which indicates the relative tendency of ligands to occupy axial positions, i.e. the site preference of ligands in a TBP, is based on NMR and structural studies [178,179] and further supported by calculations, including ab initio methods [81,116,180,181].

More flexible molecules are expected to undergo axial-equatorial exchange at a more rapid rate. A comparison of exchange barriers for silicates with the isoelectronic phosphoranes shows lower energy barriers for the silicon derivatives, e.g. $Ph_2SiF_3^-$ (**24**) (49.0 kJ mol^{-1}) [182] versus Ph_2PF_3 (**25**) (78.2 kJ mol^{-1}) [15], and this difference is associated with the greater flexible character of anionic silicates, i.e. a "looser" structure with greater charge dispersal as a result of lower nuclear charge on silicon. Ab initio calculations performed on the D_{3h}-C_{4v} energy difference between PF_5 and SiF_5^- support this conclusion, showing a smaller energy difference for the anionic pentafluorosilicate compared to that for phosphorus pentafluoride [180].



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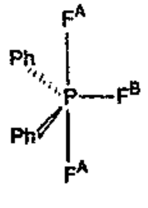

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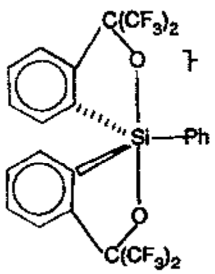

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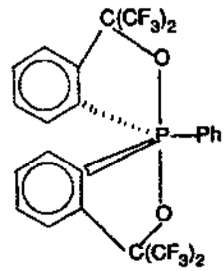


27

A lower exchange barrier is also found for the cyclic phenylsilicate (**26**) (109 kJ mol^{-1}) than for the isoelectronic phosphorane **27** (118 kJ mol^{-1}) [183]. Typical barriers for axial-equatorial fluorine exchange in trigonal bipyramidal silicates are found in Table 3.

(d) Tri-substituted trigonal bipyramidal fluorides, R_3EF_2

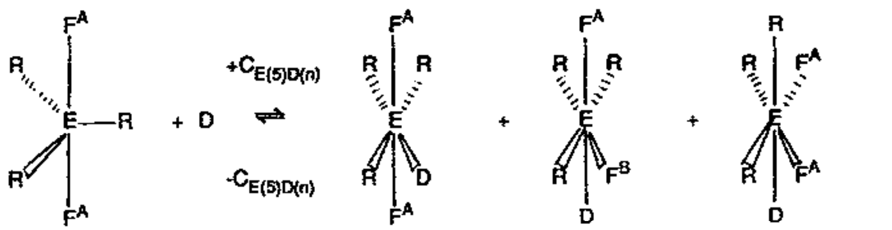
Interaction of tri-substituted compounds R_3EF_2 with donor atoms in the equatorial plane generates isomer **28**. The formation of stereoisomers **29**–**30** is also possible but that would require more extensive displacement of R and F substituents; in any case, the

TABLE 3

Barriers for axial-equatorial exchange in TBP silicates

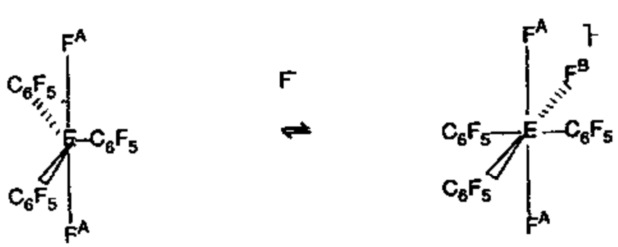
Compound	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})	Ref.
$Ph_2SiF_3^-$	44.4	[182]
$PhMeSiF_3^-$	44.8	[182]
$Ph(^tBu)SiF_3^-$	43.5	[38]
$(o\text{-tol})_2SiF_3^-$	41, 44.8 (E_a)	[38,184]
$(p\text{-tol})_2SiF_3^-$	44.8	[38]
$(1\text{-Nap})_2SiF_3^-$	39	[38]
$2,4,6\text{-}^tBu_3C_6H_2SiF_4^-$	53.6 (E_a)	[148]
$(CH_2)_5SiF_3^-$	38 (E_a)	[184]
$(C_6H_4C(CF_3)_2O)_2SiF^-$	73.2 (424 K)	[183]
$(C_6H_4C(CF_3)_2O)_2SiC_6F_5^-$	91.6 (424 K)	[183]

equivalence of axial fluorines in TBP R_3EF_2 prevents direct observation of rapid equilibria involving six-coordinate intermediates.



mer-R_3E **28** *mer*-R_3E **29** *fac*-R_3E **30** (18)

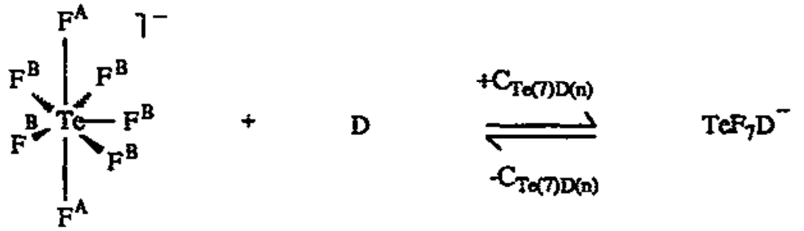
Some evidence for the assumption that bond formation occurs preferentially in the equatorial plane of a TBP is based on the reactions of tri-substituted fluorides R_3EF_2. For instance, fluoride ion adds to arsenic and antimony fluorides $(C_6F_5)_3EF_2$ at an equatorial site to give the *mer*-**31** isomer [185].



mer-**31** E = As, Sb (19)

Furthermore, an NMR study of the *mer*-Ph_3TeF_2X–Ph_3TeFX^+ system (X = F, Cl, OH) shows that addition and departure of a fluorine ligand occurs exclusively at an equatorial site, thus implying that any fluorine-bridged intermediate retains its *mer* arrangement of phenyl substituents [2,186,187].

Rapid permutational isomerization of ligands is also a feature of higher coordinate fluorides, such as heptacoordinate (D_{5h}) IF_7 and TeF_7^- [35,188] and, just as for the five-coordinate TBP molecules, rapid intermolecular association is expected to lead to observable scrambling of non-equivalent axial and equatorial fluorines. The ^{19}F NMR spectra of IF_7 and TeF_7^- show a single averaged peak, while the ^{125}Te NMR spectrum of TeF_7^- in acetonitrile solution shows retention of tellurium–fluorine coupling to seven equivalent fluorines. That IF_7 and TeF_7^- can interact with Lewis bases to give eight-coordinate species is confirmed by their reaction with fluoride ion to give octafluoro anions IF_8^- and TeF_8^{2-} of D_{4d} symmetry [35].



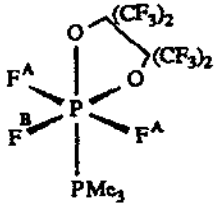
(20)

A recent study of the fluxionality of IF_7 has concluded that axial-equatorial exchange is slower than a dynamic puckering of the pentagonal equatorial plane [85].

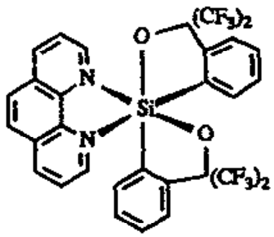
(ii) Five-membered rings and axial-equatorial exchange

The effect of a five-membered ring on the rate of axial-equatorial exchange in TBP molecules may be traced to several factors: (a) increased Lewis acidity of the central element; (b) symmetry properties of the hexacoordinate adducts or intermediates; (c) preference of the ring to span axial and equatorial sites; (d) structural distortions between trigonal bipyramidal (TBP) and rectangular pyramidal (RP) geometries; and (e) bond cleavage of a five-membered ring.

Among fluorinated five-membered ring derivatives, those with the perfluoropinacol (PFP) [189] and $C_6H_4C(CF_3)_2O$ or $C_6H_3[C(CF_3)_2O]_2$ [190] ligands have been studied in detail, and stable hexacoordinate adducts are known which contain these five-membered rings and typical Lewis bases such as Me_3P and phenanthroline, e.g. **32**–**33**.



32 [191]

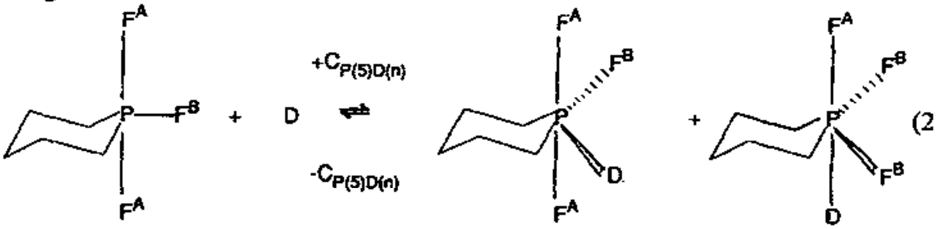


33 [192]

The phenanthroline adduct of spirosilane $Si[OC(CF_3)_2C_6H_4]_2$ (**33**) undergoes reversible enantiomerization and diastereomerization in solution by dissociation of the phenanthroline ligand [192]. Non-fluorinated cyclic and bicyclic phosphoranes also form stable adducts with Lewis bases or fluoride ion, e.g. $HP(O_2C_6H_4)_2F^-$ [193], $HP(O_2C_6H_4)_2 \cdot NC_5H_5$ [194] or $Si(catecholyl)_2 \cdot 2MeOH$ [195].

The tendency of four- and five-membered rings to span the axial and equatorial sites in a TBP, and the continuous structural changes between the ideal TBP and ideal RP can be treated quantitatively [101,180]. Trigonal bipyramidal structures include $FSi[C_6H_4C(CF_3)_2O]_2^-$ [196] and $FGe(MeC_6H_3S_2)_2^-$ [197], and rectangular pyramidal geometries are found for $FSi(C_6H_4O_2)_2^-$ [198], $FGe(C_6H_4O_2)_2^-$ [197] and $FP(C_6H_4O_2)_2$ [199].

A comparison of cyclic phosphoranes, $(CH_2)_4PF_3$ and $(CH_2)_5PF_3$, illustrates the dramatic effect that ring size has on rates of axial-equatorial exchange. Exchange in $(CH_2)_4PF_3$, which has a five-membered ring, is rapid and can only be stopped below –70°C [200]. On the other hand, $(CH_2)_5PF_3$, with a six-membered ring, is rigid and shows no evidence of axial-equatorial fluorine exchange, even at +100°C [200]. The lack of exchange in $(CH_2)_5PF_3$ may depend on the occupancy of only equatorial sites by the six-membered ring, consequently, any attack by a donor molecule at an equatorial site will generate a *mer*-**34** isomer, but such an isomer does not permute fluorine ligands. A *fac*-**35** isomer allows exchange, but its formation is presumably associated with greater distortion energies.



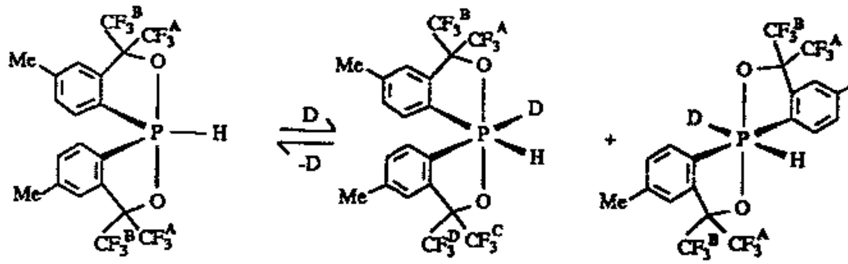
(21)

mer-F_3P **34** *fac*-F_3P **35**

The cyclic and isoelectronic fluorosilicates show a similar trend as the phosphoranes, except that rates of exchange are greater. Thus exchange in $(CH_2)_4SiF_4^-$ cannot be slowed down on lowering the temperature, while the limiting spectrum of $(CH_2)_5SiF_4^-$ can be observed at −117°C [184].

Five-membered rings show a preference for axial-equatorial occupancy in a TBP and this fact, combined with the tendency for distortion from TBP towards RP geometry and the greater Lewis acidity of five-membered ring phosphoranes, is expected to favor a *fac* isomer, thereby increasing the rate of axial-equatorial ligand exchange. In support of this argument, it is known that the enhanced apicophilicity of ring atoms can force a fluorine substituent into an equatorial site in some five-membered ring systems, e.g. $(OCHMeCH_2O)PF_2OMe$ [201]. That $(CH_2)_4PF_3$ is a stronger Lewis acid than $(CH_2)_5PF_3$, is demonstrated by the reaction with 8-trimethylsiloxyquinoline which gives a stable hexacoordinate adduct with the five-membered, but not with the six-membered, cyclic phosphorane [202].

Some phosphoranes are rigid despite the presence of a five-membered ring, but in these cases the ring may lack a plane of symmetry. For example, the trifluoromethyl groups are non-equivalent in spirophosphorane **36** [203], however, any equatorial attack by a donor molecule is expected to generate hexacoordinate intermediates **37** and **38**, neither of which equilibrates the trifluoromethyl groups.



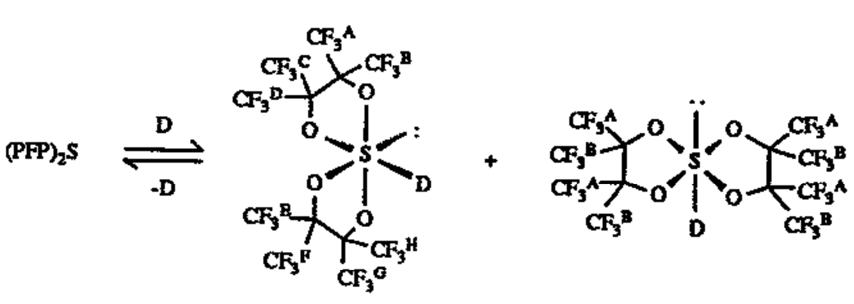
(22)

36 *cis*-HD **37** *trans*-HD **38**

A similar explanation can account for the rigid nature of phosphoranes $MeP(OSiMe_3)_2(PFP)$ and $PhP(OSiMe_3)_2(PFP)$ which, despite the presence of five-membered perfluoropinacolyl rings, show no exchange of trifluoromethyl groups up to their decomposition temperature of +160°C; an energy barrier in excess of 88 kJ mol^{-1} is estimated [204]. Exchange of trifluoromethyl groups cannot be observed at room temperature in the perfluoropinacol derivative $Me_2NP(PFP)[OCH(CF_3)_2]_2$ [205]. A comparison of energy barriers ($\Delta G^{\ddagger}_{424}$) for trifluoromethyl permutation in TBP silicates and phosphoranes shows lower barriers for silicates $[C_6H_4C(CF_3)_2O]_2SiF^-$ (73.2 kJ), $[C_6H_4C(CF_3)_2O]_2$-$SiC_6F_5^-$ (91.6 kJ), and $[C_6H_4C(CF_3)_2O]_2SiPh^-$ (109 kJ) than for phosphorane $[C_6H_4C$-$(CF_3)_2O]_2PPh$ (118 kJ), reflecting the more flexible structure of silicates. Bonds to 10-Si-5 silicates are typically 7–15 pm longer than those in isostructural phosphoranes, and geometric distortion is energetically less costly for silicates than for phosphoranes [183].

Rapid ligand permutation is, of course, expected in those cyclic phosphoranes which undergo ring cleavage and are in equilibrium with their acyclic isomers [206]. If an eight-membered ring occupies two equatorial sites, then the remaining three OCH_2CF_3 substituents are placed into two axial sites and one equatorial site of a rigid pentaoxyphosphorane [207].

In perfluoropinacolyl spirosulfurane $S(PFP)_2$ (**39**), a lone pair of electrons occupies an equatorial site, but neither a *cis*-**40** nor a *trans*-**41** intermediate is expected to lead to an observable permutation of all trifluoromethyl groups and, indeed, $S(PFP)_2$ **39** is known to be a rigid molecule with non-equivalent trifluoromethyl groups at –150°C [208], as well as at 25°C [189]. The *trans*-**41** intermediate, however, is compatible with the appearance of two sets of non-equivalent trifluoromethyl groups, as found experimentally for $S(PFP)_2$ (**39**).



(23)

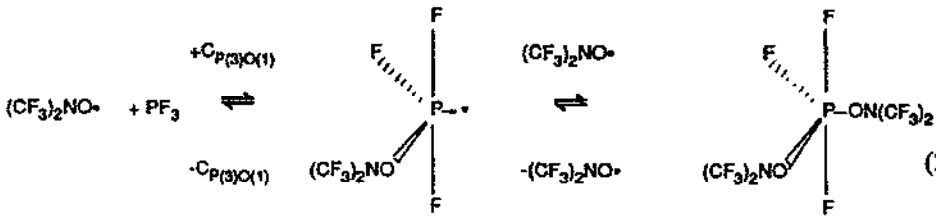
39 *cis*-**40** *trans*-**41**

Since the related phenylphosphorane $PhP(PFP)_2$ has the same symmetry properties as $S(PFP)_2$, an intermediate analogous to *trans*-**41** is also expected to lead to two sets of non-equivalent trifluoromethyl groups in the ^{19}F NMR spectrum, and such a spectrum has been observed at ambient temperature, and up to +160°C [209].

This analysis appears to be contradicted by the ^1H NMR spectrum of spiroselenurane $Se(OCH_2CH_2O)_2$, which shows only a single resonance at room temperature, however, the permutation of hydrogens can be traced to ring-opening reactions since addition of an acid and water scavenger, i.e. Et_2NSiMe_3, changes the ^1H NMR spectrum from a single line to a more complex AA'BB' spectrum, consistent with a rigid TBP geometry. When purified $Se(OCH_2CH_2O)_2$ was examined by ^{13}C NMR under conditions of proton-decoupling, only a single carbon peak was observed at room temperature or at –75°C [210]. Presumably, an intermediate analogous to *trans*-**41** is in equilibrium with the spiroselenurane, and proton-decoupling removes the symmetry constraints of the hydrogen substituents. If all ring substituents are in a plane of symmetry, then rapid equilibration of substituents is expected, and such is the case in bis-4,4'-dimethyl-2,2'-biphenylene-tellurium, which shows only a single ^1H NMR methyl signal at temperatures as low as –60°C [211].

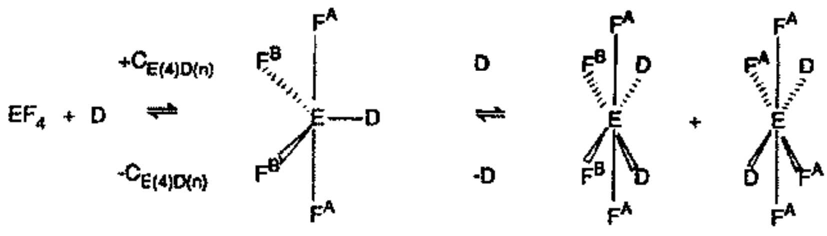
(iii) Three-to-five and four-to-six coordination, +C, +C

The preceding discussion has examined the stereochemical consequences of bond formation by means of a one-step reaction. Two-step reactions, in which the coordination number is increased from, say, three to five, may be illustrated by the low-temperature (−78°C) reaction of phosphorus trifluoride with $(CF_3)_2NO$ [212], in which phosphorus is converted from 8-P-3 to 9-P-4 in the first step, and to 10-P-5 in the second step as the product $[(CF_3)_2NO]_2PF_3$ is formed. Oxidation of phosphorus(III) compounds is common with oxygen-containing radicals [213].



(24)

Two-step reactions, in which a four-coordinate molecule is converted to a stable six-coordinate 1:2 adduct, are illustrated by the interaction of silicon or tin tetrafluoride with Lewis bases or donor solvents such as pyridine or DMSO [214]. Adducts with weaker bases can be identified by low temperature NMR studies. Thus, *cis* and *trans* adducts of tin tetrafluoride and ethanol, $SnF_4(EtOH)_2$, can be observed at −42°C [215], and *cis* and *trans* isomers of $GeF_4(SCN)_2^{2-}$ can be observed at −90°C [216]. More weakly bound adducts can be identified in various ways, including tensimetric titration at low temperature, e.g. 1:2 complexes of SiF_4 with dialkyl ethers at −78°C [217], or matrix-isolation techniques, e.g. 1:2 adducts of SiF_4 and amines [218]; in some cases, these adducts have been studied by ab initio methods, e.g. [219].



cis-**42** *trans*-**43**

(25)

Six-coordinate intermediates may be inferred from kinetic orders of reaction, as well as from increased rates of reaction at lower temperature, as illustrated by the base-catalyzed hydrolysis of trimethylfluorosilane [16,220]. Solvent-induced racemization of chlorosilanes [221] and nucleophile assisted substitution of organosilanes [222] provides evidence of six-coordinate silicon intermediates. Once formed, intermediates such as

$Me_3SiF(NHEt_2)(H_2O)$ often react further by either fluoride ion abstraction or by deprotonation of water, alcohol or amine ligands [47,220].

(iv) Formation of fluorine-bridged intermediates, +C

The first step in the transfer of a fluorine ion or atom is generally the diffusion-controlled formation of a fluorine-bridged intermediate. Fluorine bridging is a common feature of main group fluorides in the crystal state, in neutral or ionic compounds [223], as it is for transition metal fluorides [224], and various modes of bridging are possible, e.g. μ-F, $(\mu\text{-F})_2$, $(\mu\text{-F})_3$, $(\mu\text{-F})_4$, as illustrated by fluorides such as $In_2F_{10}(\mu\text{-F})_2^{6-}$ [225], $[(R_3P)_3H_2MO)_2(\mu\text{-F})_3]^+$ [226] and $Mo_4(\mu\text{-F})_4(O\text{-}^tBu)_8$ [227].

Strong fluorine bridges can be characterized in solution or in the solid state, e.g. $Sb_4F_{17}^-$ [228], $F_3PO\text{–}SbF_4\text{–}FSbF_5$ [229] or $H_3F_2^+Sb_2F_{11}^-$ [230], but more labile bridged intermediates are detected with greater difficulty, and the fluorine-bridged anion $As_2F_{11}^-$ can only be observed at $-140°C$ [231] and $B_2F_7^-$ at $-155°C$ [232].

$$BF_3 + BF_4^- \underset{-C_{B(3)F(1)}}{\overset{+C_{B(3)F(1)}}{\rightleftharpoons}} F_3B\text{--}F\text{--}BF_3^- \qquad (26)$$

Other intermediates such as $P_2F_{11}^-$ or $Si_2F_{11}^{3-}$ have not yet been directly observed, although their intermediacy is supported by NMR exchange studies [17,233]. Molecular orbital calculations have been carried out on fluorine-bridged species such as $H_3Si\text{–}F\text{–}SiH_3^+$ [234], $P_2F_{11}^-$ [235], $FI\text{–}F\text{–}IF^-$ and $CF_3I\text{–}F\text{-}ICF_3^-$ [86], and some fluorine-bridged species can be observed in the gas phase by ICR, e.g. $CH_3\text{–}F\text{–}CH_3^+$ [236], or by negative ion fast atom bombardment spectroscopy, e.g. $ArOH\text{–}F\text{–}HOAr^-$ [237].

Main group anions such as BF_4^-, PF_6^-, AsF_6^- and SbF_6^- can interact with transition metal complexes via fluorine bridges, but these weakly coordinated fluoroanions are good leaving groups and can be readily displaced in substitution reactions [238,239].

$$Me_3PL_4(solv)W^+ + SbF_6^- \underset{-C_{W(6)F(1)}}{\overset{+C_{W(6)F(1)}}{\rightleftharpoons}} Me_3PL_4(solv)W\text{--}F\text{-}SbF_5 \underset{+\text{solvent}}{\overset{-\text{solvent}}{\rightleftharpoons}} Me_3PL_4W\text{--}F\text{-}SbF_5 \rightleftharpoons \text{etc.} \qquad (27)$$

$$L_4 = (CO_3)NO$$

Trace amounts of moisture can generate new fluoroanions such as BF_3OH^- or $PO_2F_2^-$; occasionally, the only source of silicon and boron in fluoroanions such as SiF_5^-, BF_4^- or F_3BOH^- is the glass apparatus [240]. If moisture is present, there is the further possibility that fluoroanions are hydrogen bonded to the aqua ligand, as in $L_nMOH_2\text{–}FBF_3$ [241].

The consecutive formation of fluorine bridges in multistep pathways occurs in the oligomerization of antimony pentafluoride, or on addition of excess HF to F^-, which gives initially FHF^- and then, in turn $H_2F_3^-$, $H_3F_4^-$, $H_4F_5^-$ and $H_5F_6^-$ [51,242].

$$F^- + HF \underset{-C_{F(0)H(1)}}{\overset{+C_{F(0)H(1)}}{\rightleftharpoons}} F\text{-}H\text{-}F^- \underset{-HF}{\overset{HF}{\rightleftharpoons}} F\text{-}H\text{-}F\text{--}H\text{-}F^- \underset{-HF}{\overset{HF}{\rightleftharpoons}} (FH)_nF^- \qquad (28)$$

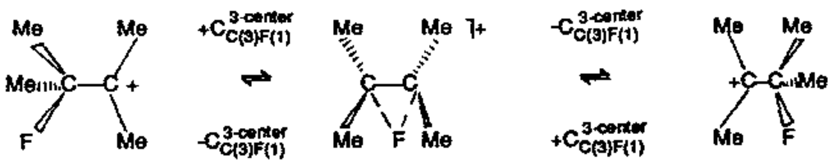
(v) Intramolecular n-center steps, $+C^c$

Cyclic n-center steps generally lead to enhanced rates of reaction because of entropy factors. The interacting atoms are in close proximity and rate enhancement is expected to be greatest for 3-, 4-, 5- and 6-center steps, but diminish as the value of n increases [2]. A maximum entropic advantage for intra- over intermolecular reactions of about 140 J K^{-1} mol^{-1} has been assessed, or a 10^8 enhancement factor [243]. Rate enhancements of the order of 10^6–10^8 are known for five-membered ring intermediates in the reactions of organophosphates [244] or sulfur radicals [6]. The formation of cyclic intermediates is a very common feature of numerous reaction pathways [245,246], including radical mediated cyclization [247].

The enhanced stability of metal complexes containing a five-membered ring (chelate effect) is attributed mainly to a favorable entropy term [248], and the stabilizing effect of five-membered rings can be used to advantage in preparing otherwise reactive or transient species [249,250]. In this way, pentacoordinate derivatives of phosphorus(III), arsenic(III), antimony(III) and bismuth(III) have been stabilized by using the 2,6-bis[(dialkylamino)methyl]phenyl ligand system for the introduction of five-membered rings [251].

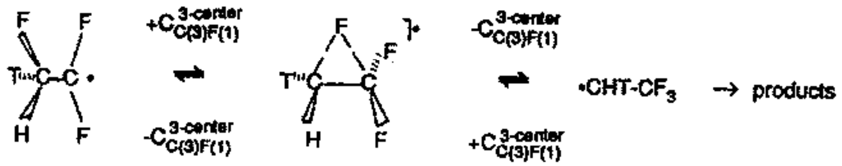
(a) Three-center steps, $+C^{3\text{-center}}$

The transfer of a fluorine substituent to an adjacent atom, i.e. a 1,2-shift, is a common feature of reaction mechanisms, and this transfer may occur exceedingly rapidly, as illustrated by the 2,3-difluoro-2,3-dimethylbutane–SbF_5–SO_2 system in which an equilibrium involving 3-center steps cannot be slowed down even at –90°C [252].



(29)

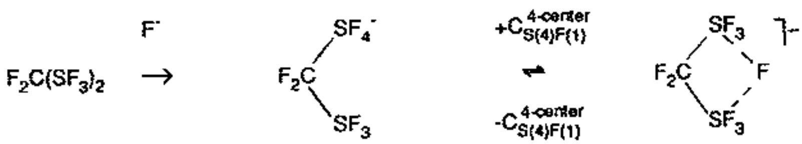
Analogous fluorine transfer processes also occur in radical species, as demonstrated with the aid of tritium labelling for the 1,1,2-trifluoroethyl radical [253].


(30)

The relative tendency of fluorine and hydrogen migration in radical, anionic or cationic species has been investigated by INDO molecular orbital calculations and highly selective behavior was found. For the 1,1,2,2-tetrafluoroethyl radical, $CF_2HCCF_2^{\cdot}$, the results suggest that fluorine atom migration through a fluorine-bridged intermediate will occur more readily than hydrogen atom migration though a hydrogen-bridged intermediate, but the corresponding cation $CF_2HCCF_2^+$ will undergo hydrogen migration more readily than fluorine migration, however, it will be difficult for the anion $CF_2HCCF_2^-$ to undergo migration of either a fluorine or a hydrogen atom [254].

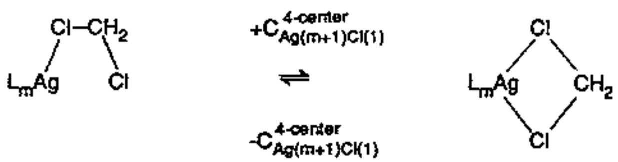
(b) Four-center steps, $+C^{4\text{-center}}$

A four-membered ring can be prepared by the addition of fluoride ion to $F_2C(SF_3)_2$, using either CsF or $Me_3SiF_2^-$ as a source of fluoride ion, and the structure of the symmetrically bridged anion has been determined by X-ray crystallography, with the bridging S--F bond (211.7 pm) being 12.7% longer than the terminal S–F bonds (160.7–172.9 pm). Ab initio calculations show a relatively small energy difference of 4.5–5.7 kJ mol^{-1} between a symmetrically and an asymmetrically bridged structure [255].


(31)

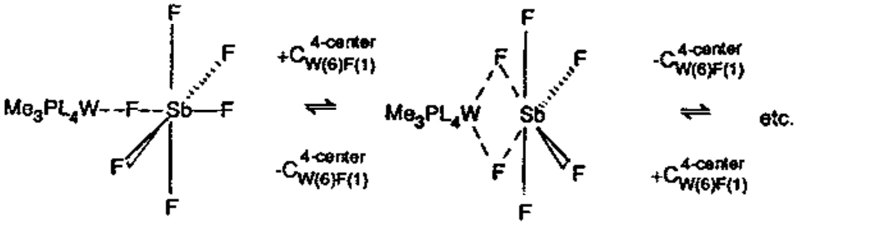
In the absence of fluoride ion, the molecule $F_2C(SF_3)_2$ retains its ability to form a fluorine-bridged four-membered ring, but the structure, as determined by electron diffraction, shows a substantially longer/weaker S--F bridging bond (266 pm) than in the anion (211.7 pm), although still shorter than the sum of the van der Waals radii (330 pm) [256].

The coordination of dichloromethane to silver ion in a bidentate fashion, confirmed by X-ray structure determination [257], must include a four-center step.


(32)

A rapid succession of four-center steps can equilibrate all fluorines of the bridged

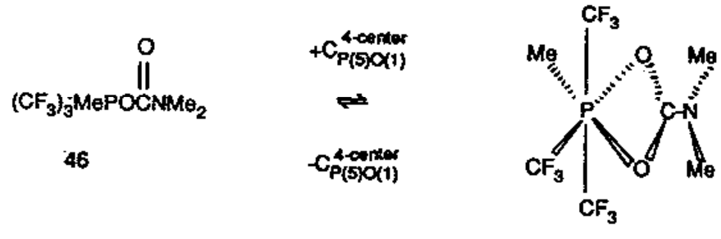
SbF_6^- ligand in the tungsten complex **44**, and the ^{31}P NMR spectrum shows retention of P–F coupling between the phosphine ligand and all six fluorines throughout the exchange process. The NMR spectra can separate this "anion spinning", for which $\Delta H^{\ddagger} = 41.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -1.5$ J mol^{-1} K^{-1}, from an accompanying intermolecular process that cleaves the weak tungsten-fluorine bond and for which $\Delta H^{\ddagger} = 27.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -128$ J mol^{-1} K^{-1} [258].



44 **45** $L_4 = (CO)_3(NO)$ (33)

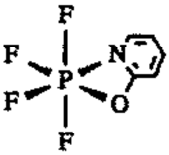
The rotation of fluoroanions such as BF_4^- and SbF_6^- may be rapid in the solid state and can lead to crystallographic disorder, with the magnitude of the atomic thermal parameters serving as an indicator of the fluxionality of the species [74]. Rotation of the F_5TeO^- anion in the solid state is also rapid above −70°C, and IR and solid state ^{19}F NMR studies show that the oxygen atom interchanges between protonated sites of 1,8-bis(dimethylamino)naphthalene [259].

A series of four-membered ring phosphoranes, containing the carbodiimide, carbamate and thiocarbamate ligand have been prepared recently, and a rapid equilibrium between 10-P-5 and 12-P-6 phosphorus compounds, involving a four-center step, is compatible with the experimental results [260], as illustrated by the equilibrium between **46** and **47**.



47 (34)

Fluorine exchange in the cyclic phosphoranes **48**–**50** was studied by means of saturation-transfer NMR techniques and it was found that exchange was too rapid in **48** to be stopped at lower temperature, but the limiting spectrum of **49** was obtained at −50°C, while **50** was rigid at room temperature, therefore, it may be concluded that the order of bond strength in **48**–**50** is P--O < P–N < P–S, if exchange is initiated by dissociation of the P–E bond in the hexacoordinate adducts [261].



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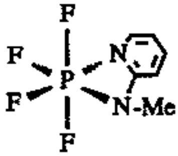

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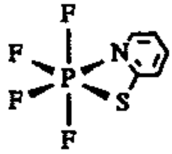
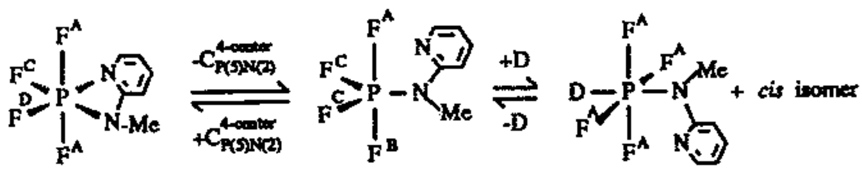


50

Cleavage of a four-membered ring in the hexacoordinate adduct **49** generates a five-coordinate phosphorane intermediate **51** in which the equatorial ligands are equivalent but the axial fluorines are non-equivalent, provided that the amino substituent lies along the axial plane. Only the axial fluorines are permuted by rotation about the P–N bond in **51**, but further interaction with a donor atom allows equilibration of all four fluorine substituents via the intermediate *trans*-**52**. In this NMR experiment, three competitive dynamic processes can be observed: firstly, cleavage of the P–N bond and ring opening of a four-membered ring in **49**, secondly, rotation about the P–N bond (56.1 kJ) in intermediate **51** and, thirdly, axial-equatorial ligand exchange (57.8 kJ) [261].



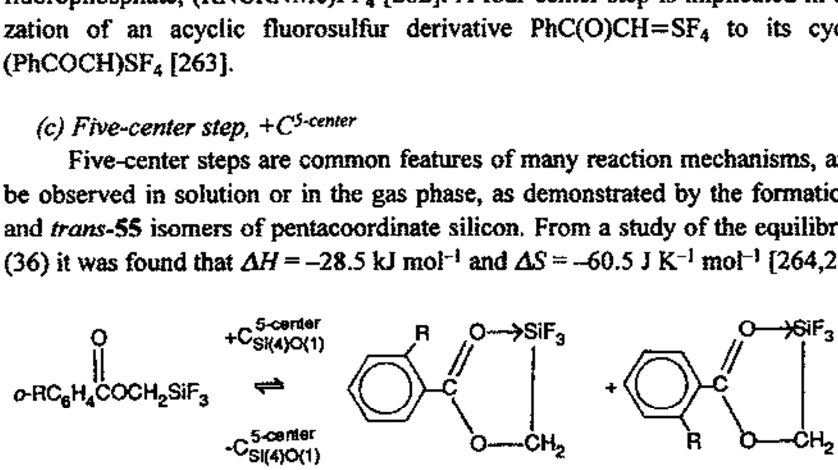
(35)

49 51 *trans*-52

Reversible ring-opening and -closing of a four-membered N–C–N–P ring also provides a mechanism of exchange of non-equivalent fluorines in a related hexacoordinated fluorophosphate, (RNCRNMe)PF_4 [262]. A four-center step is implicated in the isomerization of an acyclic fluorosulfur derivative PhC(O)CH=SF_4 to its cyclic isomer (PhCOCH)SF_4 [263].

(c) Five-center step, $+C^{5\text{-center}}$

Five-center steps are common features of many reaction mechanisms, and they can be observed in solution or in the gas phase, as demonstrated by the formation of *cis*-**54** and *trans*-**55** isomers of pentacoordinate silicon. From a study of the equilibrium of eqn. (36) it was found that $\Delta H = -28.5$ kJ mol^{-1} and $\Delta S = -60.5$ J K^{-1} mol^{-1} [264,265].

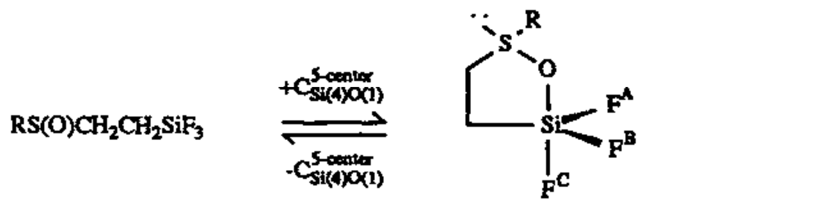


(36)

53 *cis*-54 *trans*-55

Related (aryloxymethyl)trifluorosilanes are pentacoordinate in both solid and condensed phases, with an intramolecular Si–O bond that is part of a five-membered ring, and axial-equatorial fluorine exchange has energy barriers between 29 and 38 kJ mol^{-1} [266]. For the related compound $PhC(O)OCH_2CH_2SiF_3$, where a Si–O bond is part of a six-membered ring, $\Delta H = -3.0$ kJ mol^{-1} and $\Delta S = -28$ J K^{-1} mol^{-1} [265].

A five-center step can play a crucial role in enhancing the selectivity of a chemical reaction or in determining its stereochemical outcome, as illustrated by the conversion of chiral silylsulfoxide **56** into pentacoordinate silylsulfoxide **57**. The latter species has three distinct silicon–fluorine bonds, as verified by ^{19}NMR below −100°C [267], and any subsequent reaction of intermediate **57** could, potentially, discriminate among the different silicon-fluorine bonds.

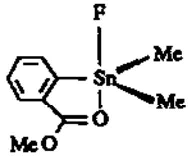


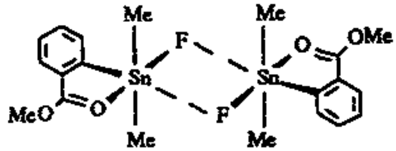
(37)

56 **57** R = Me, Et, $PhCH_2$

A transformation which involves successive *n*-center steps is illustrated by the conversion of fluorostannane **58** to **60**. Initially, a five-center step converts **58** to a cyclic pentacoordinate tin adduct **59**; the formation of a fluorine bridge between two molecules of **59** can then be followed by a four-center step to give a cyclic fluorine-bridged dimer **60**. The tin fluorine bridges in dimeric **60**, i.e. $Sn(\mu\text{-}F)_2Sn$, are of unequal length, 197.4 and 364.1 pm, with the weaker bond being similar in length to that of a van der Waals Sn–F contact of 363 pm [268], but the stronger bond is comparable to that of a single Sn–F bond in $(mesityl)_3SnF$ (196.1 pm) [269].

$o\text{-}MeOC(O)C_6H_4SnMe_2F$



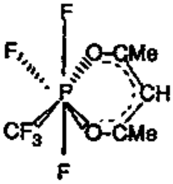


58 **59** **60**

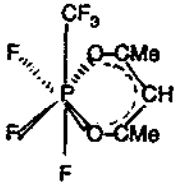
The coordination of dihalocarbons such as $ClCH_2CH_2Cl$ or $o\text{-}C_6H_4Cl_2$ to metal ions in a bidentate fashion must, necessarily, involve a five-center step [270,271]. A five-center step is also involved in the formation of an iridium complex of 8-fluoroquinoline, where chelation of C–F to iridium is observed [272]. Numerous other examples are known of the formation of chelated donor-acceptor complexes via five-center steps, e.g. [273–277].

(d) Six-center steps, $+C^{6\text{-center}}$

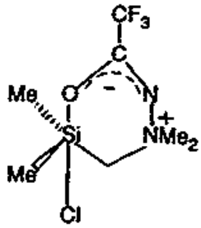
Six-membered chelate rings are formed by acetylacetone, 8-hydroxyquinoline and related ligands and they are well known for main group elements, including phosphorus, e.g. **61**–**62** [278–281] and silicon **63** [282]. Cyclic six-membered intermediates have been proposed for many reactions, e.g. the stereoselective alkylation of aldehydes with pentacoordinate fluorosilicates [283].



mer-**61** [278]



fac-**62** [278]

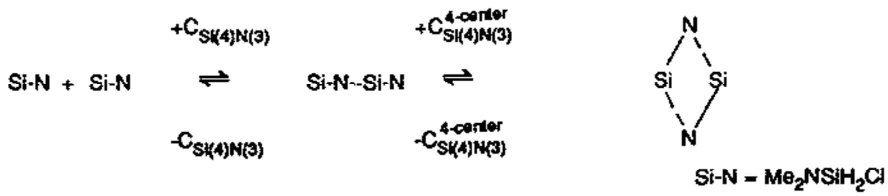


63 [282]

(vi) Intra- versus intermolecular steps: $+C^c/+C$

The ratio $+C^c/+C$ describes the formation of bonds by discrete *n*-center versus intermolecular steps [3]. Although this ratio applies to elementary steps, it is related to the experimentally determined rate constants for intra- and intermolecular reactions, and the magnitude of the ratio k_{intra}/k_{inter}, referred to as the "effective molarity", is useful for analyzing the relative importance of intra- and intermolecular reactions in organic, organometallic, and enzymatic reactions [284].

Multistep reaction pathways often contain both acyclic and cyclic steps, and the competition among the various steps is influenced by the size of the ring, stereochemical constraints, small changes in bond strength, and nature of substituents or reaction conditions. The silanes Me_2NSiH_2Cl and Me_2NSiH_3 may serve as an illustration, since Me_2NSiH_2Cl is dimeric at −157°C, with unequal Si–N bridging bonds of 181.4 and 205.4 pm in the four-membered ring, compared to 168.9 pm in the monomer [285],



(38)

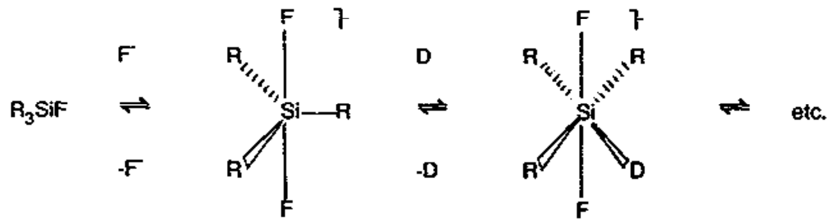
whereas Me_2NSiH_3 forms a cyclic pentamer, with all Si–N bonds involving pentacoordinate silicon being equal, 197.6 pm [286].

$$\text{Si-N} + \text{Si-N} \underset{-C_{Si(4)N(3)}}{\overset{+C_{Si(4)N(3)}}{\rightleftharpoons}} \text{Si-N--Si-N} \overset{\text{Si-N}}{\rightleftharpoons} \rightleftharpoons \text{Si-N-Si-N-Si-N-Si-N-Si-N} \underset{-C^{10\text{-center}}_{Si(4)N(3)}}{\overset{+C^{10\text{-center}}_{Si(4)N(3)}}{\rightleftharpoons}} (\text{Si-N})_5 \qquad (39)$$

$$\text{Si-N} = Me_2NSiH_3$$

(vii) Fluoride-induced reactions

Fluoride ion catalyzes the cleavage of numerous chemical bonds, for example, aryl–Si [58,183,287], alkenyl–Si [288], Ph_2PCH_2–Si [289], Si–H and Si–N [290], Si–O [290,291], and Si–Fe bonds [292], as well as ring-cleavage of Si–CCC bonds [148]. Common sources of fluoride ion include KF in 18-crown-6, KF and CsF in donor solvents, tetraalkylammonium fluoride, $Me_3SiF_2^-$, or FHF. Fluoride-induced reactions of silicon and phosphorus compounds probably involve the stereospecific formation of five- and six-coordinate intermediates [293,294].



(40)

The presence of relatively strong Si–F or P–F bonds in these reactants and intermediates may be expected to divert any bond-cleavage process towards weaker bonds. As discussed below, there is evidence that a carbon–element bond is cleaved only after an odd-electron intermediate is formed, however, the exact role of ionic or radical intermediates in many fluoride induced reactions has not yet been clarified.

Extensive applications of fluoride catalyzed reactions have been described [295,296], including a general method for carbon–carbon bond formation by way of the fluoride-induced reaction of enoxysilanes [297]. Silicon compounds, in combination with fluoride ion, have been used for the synthesis of highly fluorinated organic derivatives, with improvement in selectivity and yield [298]. The reactive anion F_5SNF^- is generated by the addition of fluoride ion to $F_4S{=}NF$ [162]. Fluoride addition to perfluoroalkenes gives useful intermediates in fluorocarbon chemistry [299], and $Me_3SiF_2^-$ is a convenient source of fluoride ion for the preparation of stable isolable perfluoroalkyl carbanion salts [300]. In the presence of fluoride ion, alkyl halides react rapidly with purines and pyrimidines [301].

Fluorinated alkoxides are also convenient fluoride donors, and the C–F bond is relatively long and weak in the anion CF_3O^- (139.0–139.7 pm) or the anion $(CF_3)_2CFO^-$ (144.6 pm, calcd.) [302]. The anion $(CF_3)_2CFO^-$ donates a fluoride ion to the phosphorane $(PFP)PF_3$ to give the corresponding fluorophosphate $(PFP)PF_4^-$, along with hexafluoroacetone, eqn. (41) [303].

$$(PFP)PF_3 + (CF_3)_2CFO^- \underset{-C_{P(5)F(1)}}{\overset{+C_{P(5)F(1)}}{\rightleftharpoons}} (PFP)PF_3\text{-}F\text{--}C(CF_3)_2O^- \underset{+C_{C(3)F(1)}}{\overset{-C_{C(3)F(1)}}{\rightleftharpoons}} (PFP)PF_4^- + (CF_3)_2CO \tag{41}$$

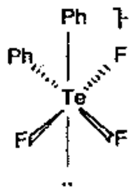
The reaction of (chloromethyl)trimethylsilane with KF or CsF in the presence of 18-crown-6 must initiate the transfer of a methyl substituent, perhaps by forming a pentacoordinate fluorosilicate followed by a 3-center step, because the final product is exclusively dimethylethylfluorosilane, as shown in eqn. (42) [304].

$$Me_3SiCH_2Cl + F^- \underset{-C_{Si(4)F(0)}}{\overset{+C_{Si(4)F(0)}}{\rightleftharpoons}} Me_3Si(F)CH_2Cl^- \longrightarrow Me_2EtSiF + Cl^- \tag{42}$$

Isomerization and racemization of alkylsilanes occurs in the presence of CsF in dimethylformamide [305], and isomerization is observed in fluorinated heteroaromatics using CsF or KF in sulpholan or acetonitrile [306].

Fluoroanionic intermediates have often been postulated in oxidative-addition reactions. The oxidation of sulfur tetrafluoride with Cl_2 in the presence of CsF is assumed to involve the anion SF_5^- [307] and $C_2F_5SeF_4^-$ is a postulated intermediate in the reaction of $C_2F_5SeF_3$ with ClF in the presence of CsF [308]. These anionic 10-E-5 intermediates presumably have a square pyramidal structure (C_{4v}) with a lone pair of electrons in an octahedral site, as established for the anions SF_5^- [309] and TeF_5^- [310]. In the related anions $C_2F_5SeF_4^-$ [308], $CF_3SF_4^-$, $(CF_3)_2CFSF_4^-$ [311], TeF_4OR^- or $F_3Te(OCH_2CH_2NH)^-$ [312], perfluoroalkyl or oxo ligands are assumed to occupy a site *trans* to a lone pair of electrons. A similar structure has been proposed for the di-substituted anion $Ph_2TeF_3^-$, and a phenyl substituent must occupy a site *trans* to a lone pair of electrons in order to account for the stereoselective synthesis of *cis*-Ph_2TeF_4 in the halide-catalyzed oxidative-fluorination of Ph_2TeF_2 with XeF_2. The *cis* isomer can then be converted to *trans*-Ph_2TeF_4 by means of fluorine-bridged intermediates [18].

$$Ph_2TeF_2 \quad + \quad F^- \quad \underset{-C_{Te(4)F(0)}}{\overset{+C_{Te(4)F(0)}}{\rightleftharpoons}}$$



(43)

Addition of fluoride ion to silicon, and related elements, also occurs in the gas phase, where the first step is the formation of a pentacoordinated fluorosilicate, e.g Me_4SiF^- or $(MeO)_4SiF^-$, followed by a variety of decomposition pathways which, however, generally retain the strong Si–F bond [292,313,314].

In all of these fluoride-induced reactions, the formation of adducts or intermediates is favored by the large fluoride ion affinity of main group compounds, as determined by ICR measurements, e.g. BF_3 (301 kJ mol^{-1}), PF_5 (356 kJ mol^{-1}) and SiF_4 (251 kJ mol^{-1}) [68]; or by lattice energy calculations, e.g. BF_3 (385 kJ mol^{-1}), PF_5 (423 kJ mol^{-1}) and AsF_5 (464 kJ mol^{-1}) [53]. In some cases, however, the fluoride ion is bound by short O–H–F hydrogen bonds, rather than by direct bonding to the main group element, as found in the structures of $Te(OH)_6 \cdot NaF$ and $Te(OH)_6 \cdot 2KF$ [315].

D. BOND DISSOCIATION, –C AND –C^c

In most instances, the high E–F bond dissociation energy of main group fluorides precludes direct bond cleavage. Although this bond energy depends, among other factors, on the nature of the substituents in the molecule, as well as on the occupancy of fluorine ligands in axial or equatorial sites, changes in substituents or site occupancy have only a moderate effect on the E–F bond length of typical main group fluorides, as demonstrated in Table 4. The difference between axial and equatorial E–F bond lengths in most cases is less than 5%, although larger differences of 8 and 9% are found in SbF_5^{2-} and SF_5^-, respectively. Such changes in bond length/strength are presumably too small to allow rapid

TABLE 4

Typical E–F bond lengths in four-, five- and six-coordinate fluorides

Species	E–F ax (mean)	E–F eq (mean)	Ratio ax/eq	Ref.
PF_5	157.7	153.4	1.03	[76]
$MePF_4$	161.2	154.3	1.04	[316]
SiF_5^-	166.0	162.2	1.02	[317]
$PhSiF_4^-$	169.1	162.6	1.04	[317]
$PhMeSiF_3^-$	169.5	162.1	1.05	[318]
$Ph_2SiF_3^-$	170.5	166.2	1.03	[317]
SF_4	164.6	154.5	1.07	[319]
SF_5^-	155.9	171.8	0.91	[309]
SeF_4	177.1	168.2	1.05	[320]
TeF_4	190	179	1.06	[321]
TeF_5^-	186.2	195.3	0.95	[322]
Ph_3TeF_3	192.4	196.0	0.98	[186]
Ph_3TeF_2OH	195.8	201.6	0.97	[187]
SbF_5^{2-}	191.6	207.5	0.92	[323]
IF_5	184.4	186.9	0.99	[324]
XeF_5^+	181.3	184.3	0.98	[309]

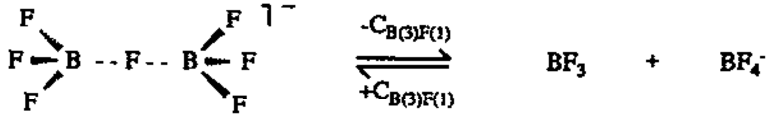
cleavage of strong E–F bonds under the usual experimental conditions, instead, further changes in coordination number and electron count will be required before bonds are sufficiently weakened to be cleaved under mild thermal conditions, i.e. spontaneously.

(i) Cleavage of fluorine-bridges, E--F--E, –C

Fluorinated compounds may formally be divided into F^-, $F^{\cdot}$, F^+ and e^- donors or acceptors. In most reactions, the transfer of a fluorine ion or atom is assumed to involve a fluorine-bridged intermediate, but the transfer of an electron can occur with or without a net transfer of a ligand, as discussed in connection with the inner-sphere mechanism of electron transfer [325,326].

Significant changes in E–F bond length/strength are associated with the formation of a fluorine bridge. For those typical neutral and ionic compounds listed in Table 5, there is a lengthening of the bridging bonds of between 3 and 64%, therefore, rapid bond cleavage appears reasonable in those intermediates with sufficiently weakened bridging bonds.

The cleavage of a weak bridging bond may be illustrated by the dissociation of $B_2F_7^-$, which is a rapid process at –100°C but can be stopped at –155°C [232,340]. The weak B--F--B bridging bond contains 8-F-2 fluorine and 8-B-4 boron, but the stable B–F terminal bonds contain 8-F-1 fluorine and 8-B-4 boron.



(44)

With a stronger Lewis acid such as aluminum, bridging bonds are also weakened. As seen in Table 5, the aluminum–fluorine bond in monomeric AlF_3 (163 pm) is lengthened in bridged species such as $Me_3Al–F–AlMe_3^-$ (178.2 pm), $Et_3Al–F–AlEt_3^-$ (182 pm), or $[Me_2AlF]_4$ (181.0 pm) [341]. Despite a lengthening of about 9–12%, however, the bridging Al–F–Al bond, with 8-Al-4 aluminum and 8-F-2 fluorine, remains too strong for rapid cleavage, and aluminum fluorides are rigid under mild conditions, in fact, $[Me_2AlF]_4$ and $[Et_2AlF]_4$ remain tetrameric under most experimental conditions [342].

A relatively small increase of 3% is observed in the length of the bridging B–F bond in $Cu(PPh_3)_3$--F–BF_3 (Table 5), and this small increase accurately reflects the experimental observation that bond cleavage occurs at the transition metal site, rather than at boron.

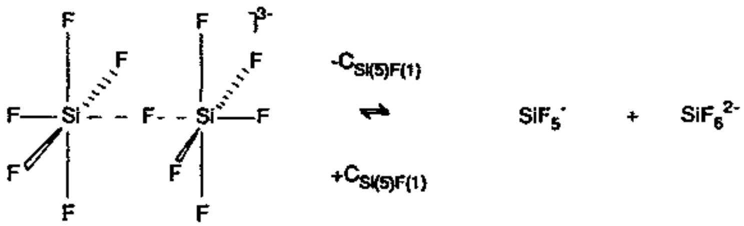
Bridged Si--F--Si intermediates such as **64** are responsible for rapid intermolecular fluorine exchange in four-, five- and six-coordinate silicon fluorides, and Arrhenius plots for the SiF_5^-–SiF_6^{2-} and $MeSiF_3$–$MeSiF_4^-$ systems gave E_a = 21 and 23 kJ mol^{-1}, respectively. In the absence of further data, these values provide a crude estimate of the strength of the silicon–fluorine bridge bond [17]. Fluorine-bridged silicates have been identified recently by X-ray crystallography [37].

TABLE 5

Bond lengths (pm) and ratio of terminal and bridging element-fluorine bonds

Compound	E–F	E--F--E'	E--F--E/E–F	Ref.
SiH_3F	159.3	–		[327]
$H_3Si–F–SiH_3^+$ (calcd)	–	177.9	1.12[a]	[234]
o-$C_6H_4(SiPhF_2)_2F^-$	160.1–165.7	189.8–206.5	1.22	[37]
$P_2F_{11}^-$ (calcd)	156.7–157.2	183.1	1.17	[235]
$F_2C(SF_3)_2F^-$	160.7–172.9	211.7	1.27	[255]
AlF_3 (monomer)	163	–	–	[328]
$Me_3Al–F–AlMe_3^-$	–	178.2	1.09[b]	[329]
$Et_3Al–F–AlEt_3^-$	–	182.0	1.12[b]	[330]
$F_2Sn–F–SnF_2^-$	207–208	222	1.07	[331]
$F_5Sb–F–SbF_5^-$	178-196	200	1.07	[332]
$FXe–F–XeF^+$	190	214	1.13	[333]
$F_5Xe–F–XeF_5^+$	180–186	221–226	1.22	[334]
$Cu(PPh_3)_3F–BF_3$	135	139	1.03	[335]
$Ag(CNR)_2(\mu$-$F)_2PF_4$	151	156	1.03	[336]
SeF_3^+	166 (ave)	243 (ave)	1.46	[337]
TeF_3^+	183–186	254–269	1.42	[338]
ClF_3 (–100°C)	157.0–174.3	270.6–274.0	1.64	[339]
BiF_5 (chains)	190	211	1.11	[131]

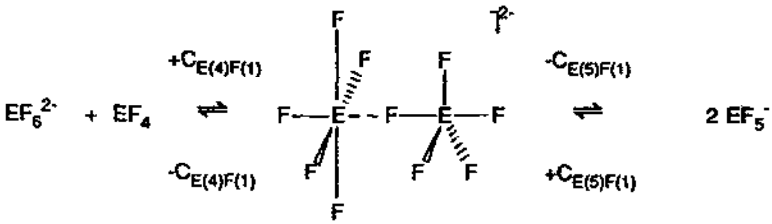
[a]Compared to Si–F bond length in SiH_3F. [b]Compared to Al–F bond length in AlF_3.



64

(45)

Symmetrical fluorine-bridged E–F–E intermediates such as **64** are ideal for dynamic NMR study, but synthetic applications generally require an unsymmetrical intermediate E--F--E' with a favorable equilibrium constant. The synthesis of pentafluorides by the reaction of four- and six-coordinate fluorides of Si, Ge and Sn must involve an unsymmetrical intermediate with 10-E-5 and 12-E-6 elements, as shown in eqn. (46).



(46)

E = Si [17][343], E = Ge [344], E = Sn [345]

An unsymmetrical fluorine-bridged P–F--Si intermediate can account for the synthesis of $PhPF_5^-$ in the reaction of $PhPF_4$ and SiF_5^- [346],

$$PhPF_4 + SiF_5^- \underset{-C_{P(5)F(1)}}{\overset{+C_{P(5)F(1)}}{\rightleftharpoons}} PhPF_4\text{-}F\text{--}SiF_5^- \underset{+C_{Si(4)F(1)}}{\overset{-C_{Si(4)F(1)}}{\rightleftharpoons}} PhPF_5^- + SiF_4 \qquad (47)$$

and cleavage of a bridging Si--F–C bond is a convenient way of forming carbon–fluorine bonds in the reaction of difluorotrimethylsilicate with perfluoro olefins or ketones [300].

$$CF_2{=}C(CF_3)_2 \overset{Me_3SiF_2^-}{\rightleftharpoons} Me_3FSi\text{--}F\text{-}CF_2C(CF_3)_2^- \underset{+C_{C(3)F(1)}}{\overset{-C_{C(3)F(1)}}{\rightleftharpoons}} Me_3SiF + (CF_3)_3C^- \rightleftharpoons \text{etc.} \qquad (48)$$

Difluorotrimethylsilicate can also be used to prepare sulfur–fluorine compounds, via a Si--F–S intermediate, but in liquid sulfur dioxide, the initial product SO_2F^- undergoes rapid intermolecular fluorine exchange, although exchange is stopped in acetonitrile as solvent [3471.

$$SO_2 \overset{Me_3SiF_2^-}{\rightleftharpoons} Me_3FSi\text{--}F\text{-}SO_2^- \underset{+C_{Si(4)F(1)}}{\overset{-C_{Si(4)F(1)}}{\rightleftharpoons}} Me_3SiF + SO_2F^- \underset{-SO_2}{\overset{SO_2}{\rightleftharpoons}} O_2S\text{–}F\text{–}SO_2^- \qquad (49)$$

Bridging P--F–Sb bonds are undoubtedly responsible for the rapid reaction of pentafluorohydridophosphate anion with excess antimony pentafluoride [348].

$$HPF_5^- \underset{-SbF_5}{\overset{SbF_5}{\rightleftharpoons}} F_5Sb\text{-}F\text{--}PHF_4^- \underset{+C_{P(5)F(1)}}{\overset{-C_{P(5)F(1)}}{\rightleftharpoons}} SbF_6^- + HPF_4 \underset{-SbF_5}{\overset{SbF_5}{\rightleftharpoons}} HPF_3\text{–}F\text{-}SbF_5 \underset{+C_{P(4)F(1)}}{\overset{-C_{P(4)F(1)}}{\rightleftharpoons}} HPF_3^+ + SbF_6^- \underset{-SbF_5}{\overset{SbF_5}{\rightleftharpoons}} Sb_2F_{11}^- \qquad (50)$$

Stable 8-S-3 sulfur cations can be prepared from 10-S-4 sulfuranes such as SF_4 [349], CF_3SF_3 or $(CF_3)_2SF_2$ [350] by reaction with Lewis acids SbF_5, AsF_5, PF_5 and BF_3, and these reactions presumably involve intermediates with S--F–E bridging bonds.

$$(CF_3)_2SF_2 \overset{SbF_5}{\rightleftharpoons} (CF_3)_2FS\text{--}F\text{-}SbF_5 \underset{+C_{S(3)F(1)}}{\overset{-C_{S(3)F(1)}}{\rightleftharpoons}} (CF_3)_2SF^+ + SbF_6^- \qquad (51)$$

Bridging S--F–As bonds can account for the formation of $FSO_2N{=}SF_4$, as a result of fluoride abstraction from $F_5SNSO_2F^-$ by arsenic pentafluoride [351]. An impurity-catalyzed sulfur–fluorine bond cleavage process in organosulfur fluorides such as R_2NSF_3 and Ph_2SF_2 [39,157,158] is most likely due to the presence of Lewis acids such as BF_3 and SiF_4 from the H_2O-HF-glass system [26], and rapid exchange may be attributed to bridged S--F–B and S--F--S intermediates, as postulated in eqn. (52).

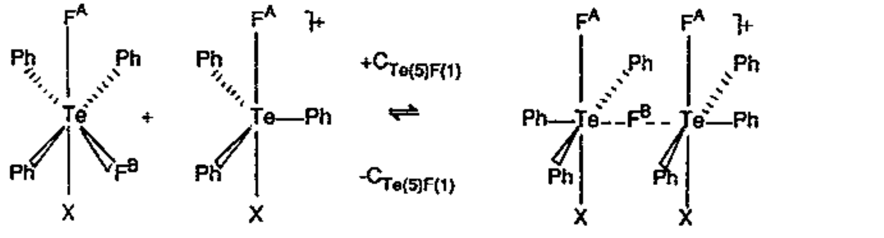
$$R_2NSF_3 \overset{BF_3}{\rightleftharpoons} R_2NSF_2\text{--}F\text{-}BF_3 \underset{+C_{S(3)F(1)}}{\overset{-C_{S(3)F(1)}}{\rightleftharpoons}} R_2NSF_2^+ + BF_4^- \underset{-R_2NSF_3}{\overset{R_2NSF_3}{\rightleftharpoons}} R_2NF_2S\text{--}F\text{--}SF_2NR_2^+ \tag{52}$$

The addition of AsF_5 to RuF_6^{2-} leads to tetrameric RuF_4 [352], presumably as a result of Ru--F–As bridged intermediates, and the reaction of TeF_4 with a rhodium complex to give $L_4RhTeF_3^+TeF_5^-$ has been described [353], while SF_4 reacts with an iridium compound to give $L_4Ir(F)SF_3$ [354]. On the basis of exchange studies with the radiotracer fluorine-18, it was established that anions SbF_6^- or AsF_6^- are kinetically more inert than anions PF_6^- or BF_4^- towards the hexafluorides of molybdenum, tungsten or uranium [355]. The hydrolysis of fluoroanions such as PF_6^-, BF_4^- or AsF_6^- undoubtedly requires a bridged intermediate for fluoride abstraction; indeed, hydrolysis is catalyzed by typical hard acids such as Be^{II}, Al^{III}, Zr^{IV} and Th^{IV} [356].

The relative strength of bridging bonds, i.e. E--F–E' versus E–F--E', can often be inferred from the identity of reaction products. For example, the fact that nitrosyl fluoride reacts with XeF_4 but not with XeF_5^- [33] implies that in intermediates of the type ON--F–XeF_4 and ON–F--XeF_5^-, the former bridged intermediate leads to the formation of XeF_5^-, but the latter reverts to starting materials NOF and XeF_5^- without any formation of XeF_6^{2-}.

In some anions, either fluorine or hydrogen bridging is feasible, but an X-ray structure analysis proved that the anion O_2FSO–H–$OSFO_2^-$ contains a short hydrogen bond [357]. Hypofluorous acid, HOF, where either O–H--F or O–H–O bonding is possible, has O–H--O hydrogen bonds in the solid state [358], and the fluorosilonate anion R_2FSiO–H–$OSiFR_2^-$ (R = mesityl) is hydrogen-bonded rather than fluorine-bridged [359].

Small differences in the strength of E--F--E' bridging bonds are expected to lead to substantial differences in rates of bond dissociation, however, such differences may not always be observable because of rapid scrambling of non-equivalent fluorines. The latter situation is encountered in the $PhPF_3H$–$PhPF_4H^-$ and $PhPF_4$–$PhPF_5^-$ systems, where rapid P–F bond cleavage may involve either axial or equatorial fluorines, but information about selective bond cleavage is lost because of an accompanying exchange of axial and equatorial fluorines [44,346]. In order to circumvent this problem, any five-coordinate species must be non-fluxional, and this is generally the case in tri-substituted fluorides R_3EF_2, as discussed in a previous section, consequently, site-selective E–F bond cleavage can be observed in a series of triphenyltellurium(VI) fluorides, e.g. *mer*-Ph_3TeF_3, *mer*-Ph_3TeF_2Cl or *mer*-Ph_3TeF_2OH. In each molecule, only the Te–F^B bond is cleaved, but not the Te–F^A bond, as verified by ^{19}F and ^{125}Te NMR. A rigid and planar Ph_3Te moiety in **65–67** presumably prevents scrambling of non-equivalent fluorines in all reactants and intermediates [2,186,187].

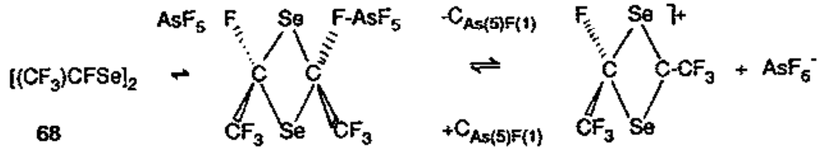


65 **66** **67** X = F^A, Cl, OH (53)

The selective nature of bond dissociation can also be demonstrated in mixtures containing neutral and anionic or cationic species. For example, in the Ph_3TeF_3–$Ph_3TeF_2^+$–PF_6^- system, bond cleavage involves only the tellurium species, however, on addition of PF_5, rapid exchange occurs among the phosphorus species PF_5 and PF_6^- [186]. Selective P–F bond cleavage has also been postulated in adducts of PF_4^+ [26]. In the XeF_6–SbF_5 system, selective Sb–F bond cleavage occurs, without involvement of cationic XeF_5^+, as demonstrated by the AB_4 ^{19}F NMR spectrum of rigid XeF_5^+, together with a single fluorine line arising from fluorine exchange between SbF_6^- and SbF_5 [360].

$$\mathrm{XeF_6} \underset{-\mathrm{SbF_5}}{\overset{\mathrm{SbF_5}}{\rightleftharpoons}} \mathrm{F_5Xe{-}{-}F{-}SbF_5} \underset{+C_{Xe(5)F(1)}}{\overset{-C_{Xe(5)F(1)}}{\rightleftharpoons}} \mathrm{F_5Xe^+} + \mathrm{SbF_6^-} \underset{-\mathrm{SbF_6^-}}{\overset{\mathrm{SbF_5}}{\rightleftharpoons}} \mathrm{Sb_2F_{11}^-} \qquad (54)$$

Carbon–fluorine bonds are generally cleaved in the presence of a strong Lewis acid [361], and those conditions which favor intermediates of the type C--F–E, rather than C–F--E, are of importance for synthetic applications. The carbon–fluorine bond in **68** is cleaved rapidly at –60°C on addition of arsenic pentafluoride in liquid SO_2; cleavage of a C--F–As bond in intermediate **69** leads to cation **70**, which can be identified by NMR [362].



68 **69** **70** (55)

Three successive C--F–Bi bridges are presumably cleaved as all fluorines from one trifluoromethyl group of 2,4,6-$(CF_3)_3C_6H_4ONa$ are replaced in the presence of $BiCl_3$ [363], but for the cleavage of stronger carbon–fluorine bonds, other mechanistic features are important, as discussed in the next section.

A bridging C–F--B bond is found in a boron trifluoride–ferracyclopentadiene complex [364]. Cleavage of an aromatic carbon–fluorine bond occurs during oxidative-addition of a tungsten complex, but the multistep reaction also involves transfer of fluorine by a six-center step and loss of solvent from the tungsten complex [365].

Fluorine transfer reactions can be studied in the gas phase, where pentacoordinate silicon anions and fluorine-bridged intermediates appear to play the same sole as they do in solution [366].

$$Me_4Si \underset{}{\overset{F^-}{\rightleftharpoons}} Me_4SiF^- \overset{Me_3SiC_3H_5}{\rightleftharpoons} Me_4Si\text{--}F\text{-}SiMe_3(C_3H_5)^- \underset{+C_{Si(4)F(1)}}{\overset{-C_{Si(4)F(1)}}{\rightleftharpoons}} Me_4Si + SiMe_3(C_3H_5)F^- \quad (56)$$

(ii) Cationic intermediates

An important characteristic of main group fluorides EF_n is their amphoteric nature, which promotes the intermediacy of cationic and anionic species [367,312], according to eqn. (57).

$$EF_{n+1}^- \underset{F^-}{\rightleftharpoons} EF_n \overset{MF_5}{\rightleftharpoons} EF_{n-1}^+ + MF_6^- \quad (57)$$

For some elements, an extensive series of ionic and neutral species has been identified, for example, PF_4^+, $PF_4^{\cdot}$ and PF_4^- [98,153,368], or $Me_2PF_2^+$, Me_2PF_3, and $Me_2PF_4^-$ [369], or $CF_3SF_2^+$, CF_3SF_3, $CF_3SF_4^+$, $CF_3SF_4^-$, and CF_3SF_5 [370]. Additionally, odd-electron species such as $PF_2^{\cdot}$, $PF_4^{\cdot}$, $SF_3^{\cdot}$ and $SF_5^{\cdot}$ have been characterized by ESR and studied by MO methods [371,372]. If all these intermediates, in turn, are capable of electron transfer reactions, then a multitude of reactive intermediates, of assorted geometry, coordination number and electron count, are available for bringing about chemical transformations.

Fluorinated cations are bridged in the solid state to neutral or anionic fluorides, as illustrated by the structure of $XeF_2 \cdot XeF_5 \cdot AsF_6$ in which the cation XeF_5^+ is bridged to XeF_2 and AsF_6^- [373]. Cationic fluorine-bridged intermediates are responsible for rapid bond cleavage in a variety of systems, such as dissociation of $Xe_2F_{11}^+$ to XeF_5^+ and XeF_6 [374], or fluorine exchange in the Ph_3TeF_2X–Ph_3TeFX^+ (X = F, Cl, OH) system [2,186,187].

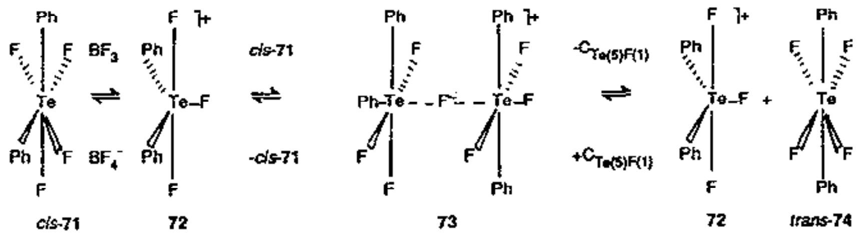
A rapid equilibrium between xenon oxyfluoride species in dilute HF solution [375] presumably involves cationic fluorine-bridged intermediates,

$$XeO_2F^+ \quad + \quad XeO_2F_2 \quad \underset{-C_{Xe(3)F(1)}}{\overset{+C_{Xe(3)F(1)}}{\rightleftharpoons}} \quad FO_2Xe\text{--}F\text{--}XeO_2F^+ \tag{58}$$

and rapid cleavage of As--F--As bonds occurs when R_3AsF_2 is treated with PF_5 or BF_3 [376].

$$R_3AsF_2 \quad + \quad R_3AsF^+ \quad \underset{-C_{As(4)F(1)}}{\overset{+C_{As(4)F(1)}}{\rightleftharpoons}} \quad R_3FAs\text{–}F\text{–}AsFR_3{}^+ \tag{59}$$

Octahedral *cis* and *trans* isomers of a variety of main group fluorides have been reported, including tellurium fluorides, e.g. *cis*- and *trans*-$F_2Te(OTeF_5)_4$ [377] and *cis*-$(C_6F_5)_2TeF_4$ [378], and *cis* and *trans* sulfur fluorides [162,379], and related derivatives [380–383]. The isomerization of geometrical isomers is catalyzed by Lewis acids, as demonstrated by the SbF_5 catalyzed isomerization of *trans*- to *cis*-$F_2Te[C_6H_4C(CF_3)_2O]_2$ [384], or the SbF_5, PF_5 and BrF_3 catalyzed isomerization of *trans* to *cis*-$F_2S[C_6H_4C(CF_3)_2O]_2$ [385]. In the catalyzed isomerization of *cis*- to *trans*-Ph_2TeF_4, the cation $Ph_2TeF_3{}^+$ **72** is assumed to be the chain carrier, converting *cis*-**71** to *trans*-**74** via a fluorine-bridged cation **73** [18], as shown in eqn. (60).



(60)

A modest shortening (strengthening) of the fluorine–element bond generally accompanies the formation of a cation, for example, the N–F bond in $NF_4{}^+$ (130 pm) [74] is shorter than in NF_3 (136.5 pm) [386]. The Cl–F bond in $ClF_2{}^+$ (156.5–156.8 pm) is shorter than in ClF_3 (157.0–174.3 pm), and the secondary bridging Cl--F bonds in $ClF_2{}^+$ (226.3–229.7 pm) are also shorter than the secondary bonds in tetrameric ClF_3 (270.6–274.0 pm) [339,387]. A comparison of experimental and calculated bond lengths in xenon and krypton difluorides shows that the Xe–F and Kr–F bonds are shortened by 10 pm in the cations XeF^+ and KrF^+; this decrease in bond length is offset to a small extent by solvation, as illustrated by a bond lengthening of 1.6 pm in solvated cations $HCNXeF^+$ and $HCNKrF^+$ [88].

In view of the strengthening of E–F bonds in cations, their cleavage becomes more difficult and alternative processes more feasible. Thus a carbon–sulfur bond is cleaved in cation RSF_4^+, rather than a sulfur–fluorine bond, during the reaction of $MeSF_5$ or $EtSF_5$ with arsenic or antimony pentafluoride [388]. This reaction is accompanied by an overall reduction of 12-S-6 sulfur to 8-S-3 sulfur as cation SF_3^+ and fluoroalkane are formed.

$$CH_3SF_5 + AsF_5 \xrightarrow{-70^\circ C} CH_3SF_4^+\,AsF_6^- \xrightarrow{20^\circ C} SF_3^+ + CH_3F \qquad (61)$$

An analogous reaction of arsenic pentafluoride with *trans*-CF_3SF_4Cl gives the cation SF_2Cl^+ and CF_4 [389], and a carbon–selenium bond is cleaved as organoselenium(VI) fluorides decompose to selenium(IV) fluorides and fluorocarbons, e.g. CF_3SeF_5 to SeF_4 and CF_4 [390]. Arsenic pentafluoride also facilitates the rapid reaction at –78°C of CF_3IF_4 to give $IF_2^+AsF_6^-$ and CF_4 [391].

Occasionally, the central element is reduced even though a Lewis acid is not deliberately added, as illustrated by the conversion of $^nBu_3BiF_2$ to $^nBu_2BiF$ and ^nBuF, or the conversion of $C_6F_5AsF_4$ to AsF_3 and C_6F_6 at temperatures above –78°C [392], however, it seems reasonable to propose that bismuth(V) and arsenic(V) fluorides are sufficiently strong Lewis acids to abstract a fluoride ion via intermediate **75** and generate a cationic intermediate.

$$C_6F_5AsF_4 \underset{}{\overset{C_6F_5AsF_4}{\rightleftharpoons}} \underset{\textbf{75}}{C_6F_5AsF_3\text{–}F\text{–}AsF_4C_6F_5} \underset{+C_{As(4)F(1)}}{\overset{-C_{As(4)F(1)}}{\rightleftharpoons}} C_6F_5AsF_3^+ + C_6F_5AsF_5^- \rightleftharpoons \text{etc.} \qquad (62)$$

In the presence of SiF_4, the postulated bromine(V) species R_3BrF_2 gives as the final product a reduced bromine(III) compound $R_2Br^+SiF_5^-$, along with fluoroalkane [393], and CH_3IF_2 decomposes to CH_3F and IF in glass apparatus [22,376].

Tellurium–carbon bond cleavage and reduction of a tellurium cation has been proposed for the conversion of Bu_4TeMe^+ to Bu_3TeMe, and for the reaction of a biphenylene tellurium cation $(C_6H_4\text{–}C_6H_4)_2TeCH_3$ [211].

The details of the cleavage of carbon–element bonds in cations REF_n^+, as well as the formation of fluoroalkane, are not entirely clear but could involve, presumably, either attack of a suitable F^- or $F^\cdot$ donor on the organic substituent, or a reduction of cation REF_n^+ to radical $REF_n^\cdot$, followed by interaction with a suitable F^- or $F^\cdot$ donor. Organofluoro cations REF_n^+ can thus function as either R^+ or $R^\cdot$ donors. Among the difficulties of identifying aryl-element cations is the rapid fluorination of the aryl group, as well as the influence of traces of Lewis acids on the formation of these cations [394].

If both carbon–element and fluorine–element bonds in a cation REF_n^+ are sufficiently robust, then alternative processes may prevail, such as the reduction of the Lewis acid. Thus arsenic pentafluoride is reduced by $Te(CF_3)_2$ to give arsenic trifluoride and $(CF_3)_2TeF^+AsF_6^-$ [395]. Cationic species are reasonable intermediates in these reactions, as postulated in eqn. (63).

$$Te(CF_3)_2 \overset{AsF_5}{\rightleftharpoons} (CF_3)_2Te\text{-}AsF_5 \overset{AsF_5}{\rightleftharpoons} (CF_3)_2TeAsF_4\text{--}F\text{-}AsF_5 \underset{+C_{As(5)F(1)}}{\overset{-C_{As(5)F(1)}}{\rightleftharpoons}} (CF_3)_2TeAsF_4^+ \rightarrow (CF_3)_2TeF^+ + AsF_3 \tag{63}$$

The alkylating properties of a mixture of methyl fluoride and antimony pentafluoride in sulfur dioxide, which generates the species $MeF–SbF_5$, $MeOSO^+$ and $Sb_2F_{11}^-$ [127,396], may be rationalized by a sequence of steps involving cationic and fluorine-bridged intermediates, although the details of the methyl transfer step are not specified in eqn. (64).

$$MeF \overset{SbF_5}{\rightleftharpoons} MeF\text{-}SbF_5 \overset{SbF_5}{\rightleftharpoons} MeF\text{-}SbF_4\text{--}F\text{-}SbF_5 \overset{-C_{Sb(5)F(1)}}{\rightleftharpoons} MeF\text{-}SbF_4^+ \ (+\ SbF_6^-) \overset{SO_2}{\longrightarrow}$$

$$MeOSO^+ + SbF_5 \overset{SbF_6^-}{\rightleftharpoons} Sb_2F_{11}^- \tag{64}$$

The fluoromethane–antimony pentafluoride system, with its net transfer of R^+ to sulfur dioxide, bears some resemblance to the difluorine–antimony pentafluoride system and its transfer of F^+ to xenon under mild conditions to give $XeF^+Sb_2F_{11}^-$ [397]. A similar mechanism, involving cationic and fluorine-bridged intermediates, may be suggested for the cleavage of the fluorine–fluorine bond in F_2, as postulated in eqn. (65)

$$F_2 \overset{SbF_5}{\rightleftharpoons} FF\text{-}SbF_5 \overset{SbF_5}{\rightleftharpoons} FF\text{-}SbF_4\text{--}F\text{-}SbF_5 \underset{+C_{Sb(5)F(1)}}{\overset{-C_{Sb(5)F(1)}}{\rightleftharpoons}} FF\text{-}SbF_4^+ \ (+\ SbF_6^-) \overset{Xe}{\rightleftharpoons} Xe\text{-}F\text{--}F\text{-}SbF_4^+$$

$$\underset{+C_{F(1)F(1)}}{\overset{-C_{F(1)F(1)}}{\rightleftharpoons}} XeF^+ + SbF_5 \overset{SbF_6^-}{\rightleftharpoons} Sb_2F_{11}^- \tag{65}$$

Oxidation of elemental sulfur and selenium by AsF_5 or SbF_5 is facilitated by the presence of traces of halogens, Cl_2, Br_2 or I_2 [398], and oxidative-chlorination of CF_3SCl to $CF_3SCl_2^+$ is carried out with either Cl_2/AsF_5, or $Cl_2F^+AsF_6^-$ in SO_2 [399].

If the cleavage of carbon–element bonds in cations REF_n^+ is a reversible process, then the formation of carbon–element bonds may occur under those conditions which favor cationic intermediates. Indeed, tellurium–carbon bonds are formed under cationic reaction conditions, i.e. $(C_6F_5)_2TeF_2$ to $Te(C_6F_5)_3^+$ [400], and the formation of a carbon–iodine bond occurs in the reaction of pentafluorophenyldifluoroiodine with tris(pentafluorophenyl)boron [401]. The formation of $(C_6F_5)_2IF$ could involve a cationic intermediate, $C_6F_5IF^+$, although details of the aryl transfer step are not specified in eqn. (66).

$$C_6F_5IF_2 + B(C_6F_5)_3 \underset{-C_{B(3)F(1)}}{\overset{+C_{B(3)F(1)}}{\rightleftharpoons}} C_6F_5IF{-}F{-}B(C_6F_5)_3 \underset{+C_{I(2)F(1)}}{\overset{-C_{I(2)F(1)}}{\rightleftharpoons}} C_6F_5IF^+ + B(C_6F_5)_3F^- \xrightarrow{C_6F_5IF_2} (C_6F_5)_2IF \text{ etc.} \tag{66}$$

The recent synthesis of organoxenon compounds also occurs under reaction conditions which favor cationic intermediates, since the reaction with xenon difluoride occurs in the presence of a Lewis acid such as $B(C_6F_5)_3$ [401,402].

An equilibrium between main group fluorides of different oxidation states is occasionally a rapid process, as illustrated by the behavior of arsenic pentafluoride and phosphorus trifluoride. At −130°C, the adduct $F_3P{:}AsF_5$ is stable, but this adduct dissociates between −130 and −78°C, and above −78°C only oxidized PF_5 and reduced AsF_3 are present [98]. The multistep pathway of eqn. (67) postulates that only two types of bonds are cleaved, namely, donor-acceptor bonds P^{III}--As^V and P^V--As^{III} in the adducts $AsF_5{:}PF_3$ and $PF_5{:}AsF_3$, and fluorine-bridged bonds As--F--As and As--F--P.

$$AsF_5 \underset{-PF_3}{\overset{PF_3}{\rightleftharpoons}} F_3P{:}AsF_5 \underset{-AsF_5}{\overset{AsF_5}{\rightleftharpoons}} F_3P{:}AsF_4{-}F{-}AsF_5 \underset{+AsF_6^-}{\overset{-AsF_6^-}{\rightleftharpoons}} F_3PAsF_4^+ \underset{-AsF_6^-}{\overset{AsF_6^-}{\rightleftharpoons}} F_5As{-}{-}F{-}PF_3AsF_4 \underset{+AsF_5}{\overset{-AsF_5}{\rightleftharpoons}}$$

$$F_4P{-}AsF_4 \underset{-AsF_5}{\overset{AsF_5}{\rightleftharpoons}} F_4PAsF_3{-}F{-}AsF_5 \underset{+PF_5}{\overset{-AsF_6^-}{\rightleftharpoons}} F_4PAsF_3^+ \underset{+PF_5}{\overset{AsF_6^-}{\rightleftharpoons}} F_5As{-}{-}F{-}PF_4AsF_3 \underset{+AsF_5}{\overset{-AsF_5}{\rightleftharpoons}} F_5P{:}AsF_3 \underset{+PF_5}{\overset{-PF_5}{\rightleftharpoons}} AsF_3 \tag{67}$$

A redox reaction also occurs between SbF_5 and PF_3 at room temperature, but the reaction is complicated by further reaction of the products with SbF_5 [98].

A reduction of phosphorus(V) to phosphorus(III) is illustrated by the conversion of $PhPF_3H$ to $PhPF_2$ in the presence of triethylamine, and this reduction is accompanied by a rapid phosphorus–fluorine bond cleavage process in the $PhPF_3H$–$PhPF_4H^-$ system. As outlined in eqn. (68), fluoride abstraction from the neutral hexacoordinated adduct $PhF_3HP{:}NEt_3$ can generate the anion $PhPF_4H^-$, and the latter anion then undergoes rapid fluorine exchange with phosphorane $PhPF_3H$. Deprotonation of the cation $PhF_2HP{-}NEt_3^+$ by triethylamine then leads to $PhPF_2$ and Et_3NH^+, eqn. (69). The overall stoichiometry of eqns. (68) and (69) is well established, and the details of the fluorine exchange process are in agreement with ^{1}H and ^{31}P NMR experiments [44]

$$PhPF_3H \xrightleftharpoons[-NEt_3]{NEt_3} PhF_3HP\text{-}NEt_3 \xrightleftharpoons[-PhPF_3H]{PhPF_3H} PhF_2HP\text{-}NEt_3^+ + PhPF_4H^- \xrightleftharpoons[-PhPF_3H]{PhPF_3H} PhF_3HP\text{--}F\text{--}PF_3HPh^- \quad (68)$$

$$PhF_2HP\text{-}NEt_3^+ \xrightarrow{NEt_3} PhPF_2 + Et_3NH^+ + Et_3N \quad (69)$$

In a somewhat more complex system, $PhPF_2HOMe$–MeOH–pyridine, an NMR study showed that cleavage of P–F, P–H and P–O bonds occurred, but attempts to measure the relative rates of bond cleavage were unsuccessful because of the limited stability of the samples above 10°C [109,403].

The disproportionation of organophosphorus(III) compounds, i.e. RPF_2 to RPF_4 and $(RP)_n$ [404], or R_2PF to R_2PPR_2 and R_2PF_3 [405], is a method of forming phosphorus–phosphorus bonds. Hydrogen fluoride catalyzes these reactions [404] and, since hydrogen fluoride is known to form stable phosphoranes such as R_2PHF_2 and RPF_3H, these phosphoranes are reasonable intermediates in disproportionation reactions. If the phosphorane forms a Lewis acid-base adduct $PhPF_3H{:}PPhF_2$ which in turn loses a fluoride ion, then a cation and anion would be generated in a process analogous to that of eqn. (68). A different outcome is expected, however, because of the presence of P–P bonds in the intermediates, leading eventually to stable cyclic $(RP)_n$ products. All phosphoranes and cations are presumably solvated, and it is interesting that disproportionation of $PhPF_2$ is faster in acetonitrile solution and leads exclusively to hexameric $(PhP)_6$, rather than pentameric $(PhP)_5$ [406].

Organofluorosulfur cations are also implicated in the reactions of xenon difluoride with alkyl sulfides or sulfur-containing amino acids or biotin [407,408]. This reaction probably proceeds via a sulfurane R_2SF_2 which is converted to the cation R_2SF^+ by a Lewis acid such as BF_3 [409], or by contact with borosilicate glass [26]. Deprotonation of the cation, followed by transfer of fluorine from sulfur to carbon, then gives the final α-fluorinated product, FCH_2SR, eqn. (70). As in other cations, it is implicitly assumed that the S–F bond in $CH_3(R)SF^+$ is strengthened relative to the parent sulfurane, but this may be accompanied by a weakening of the C–H bond (hyperconjugation) so that deprotonation by base or fluoride ion can occur more readily via a bridged C--H-base intermediate.

$$CH_3SR \xrightarrow{XeF_2} CH_3(R)SF_2 \xrightleftharpoons[BF_4^-]{BF_3} \overset{H}{|}CH_2(R)SF^+ \xrightleftharpoons{base} baseH^+ + CH_2{=}S(R)F \longrightarrow FCH_2SR \quad (70)$$

Oxidative fluorination with xenon difluoride is carried out more effectively if the salts are used, e.g. $XeF^+AsF_6^-$, $Xe_2F_3^+AsF_6^-$[333] or $XeF^+SbF_6^-$ [410]. Reactions of xenon difluoride are catalyzed by Lewis acids such as BF_3 and $R_2O{:}BF_3$ [19,411], or $B(OR)_3$ [412]; some reactions are catalyzed by hydrogen fluoride, but since xenon difluoride itself is stable in anhydrous HF, the effect of hydrogen fluoride must be less direct and may involve the formation of Lewis acids as a result of interaction with metal or glass surfaces [18,26]. Those reactions of xenon difluoride that are catalyzed by hydrogen fluoride are inhibited by fluoride ion because of the formation of FHF [333].

Oxidation of xenon with AgF_2 is carried out in the presence of fluoride ion acceptors such as AsF_5 or BF_3, and oxidation occurs, presumably, via cationic and solvated AgF^+. Undesirable precipitation of Ag^I salts is prevented by ensuring that all reagents are scrupulously dry [413].

$$2\,AgF_2 + 2\,BF_3 + Xe \rightarrow 2\,AgBF_4 + XeF_2 \tag{71}$$

The formation of ionic species in redox reactions of organoiodine halides is also illustrated by the reaction of $PhICl_2$ in acetonitrile, in which tin(II) chloride is converted to the stronger Lewis acid tin(IV) chloride [394].

$$PhICl_2 \xrightarrow{SnCl_2} PhI + SnCl_4 \xrightarrow{PhICl_2} PhICl^+ + SnCl_5^- \xrightarrow{MeCN} SnCl_5(MeCN)^- \tag{72}$$

Somewhat paradoxically, anions may be required for the synthesis of cations, as demonstrated by the reaction of arsenic pentafluoride with cesium chloride [398]. In this reaction, a hexacoordinate adduct AsF_5Cl^- probably undergoes fluoride abstraction by AsF_5. A series of bond cleavages via halogen-bridged intermediates, accompanied by the addition of Cl^- gives, eventually, the stable products $CsAsF_6$ and $AsCl_4^+AsF_6^-$. If KBr is used as a source of halide ion, then AsF_5 is reduced to AsF_3.

$$6\,AsF_5 + 4\,CsCl \rightarrow 4\,CsAsF_6 + AsCl_4^+AsF_6^- \tag{73}$$

Fluorocations such as XeF^+ are formally donors of F^+ in the synthesis of other fluorocations, as illustrated in eqn. (74) [410],

$$XeF^+AsF_6^- + RSR \rightarrow R_2SF^+\,AsF_6^- + Xe \tag{74}$$

but a direct transfer of F^+ via intermediate $R_2S{-}F{-}Xe^+$ is unlikely for the reasons discussed above, namely, a strengthening of E–F bonds in cations as compared to the neutral fluorides. If that is the case, then cleavage of a xenon–fluorine bond during oxidative fluorinations may require a further change in coordination number or electron count, perhaps involving an electron transfer process. Free radicals have been detected by ESR under conditions where fluorocations are also present, for example, the $NF_3^{\cdot+}$ radical cation has been observed during the decomposition of NF_4^+ salts [414], and polyphenyl radical cations have been observed during reactions of xenon difluoride with aromatic compounds [19,415]. Radical intermediates have been postulated for the reaction of xenon difluoride with P–O [416], Si–N and Si–S [417] compounds, and fluorination with transition metal fluorides may also involve radical cations [418]. Some fluorinations are postulated to require successive electron transfer steps, as well as proton and fluoride ion transfer [419].

A quantitative scale of the oxidizing strength of a variety of oxidative fluorinators has been developed recently. The oxidizer strength depends not only on the number of fluorine ligands and the oxidation state and electronegativity of the central atom but also on the presence of free valence electron pairs on the central atom and the geometry of the oxidizer [420].

(iii) Odd-electron intermediates

Substantial changes in bond strength often accompany a change in electron count as ions REF_n^+ or REF_n^- are converted to a radical $REF_n^{\bullet}$. Such appears to be the case in organofluorosilanes, where a silicon–carbon bond remains intact despite the rapid cleavage of bridging Si--F--Si bonds in systems containing $RSiF_3$, $RSiF_4^-$ and $RSiF_5^{2-}$ [17]. Many hexacoordinated organofluorosilicates $RSiF_5^{2-}$ are stable in aqueous and non-aqueous solvents, but rapid silicon–carbon bond cleavage does occur under mild conditions if one-electron oxidizing agents are added, such as Cu^I, Ag^I, Pd^{II}, Hg^I, Hg^{II}, Tl^{III}, Bi^{III}, and *N*-bromosuccinimide [58,421].

Electron transfer from $RSiF_5^{2-}$ to tetracyanoethylene (TCNE) has been investigated by electron spin resonance, which confirms the presence of the $TCNE^{\bullet -}$ radical anion, but $RSiF_5^{\bullet -}$ was not detected [422]. Although a fluorine-bridged intermediate may facilitate the electron transfer process, the fluorine ligand is not transferred and the electron affinity of TCNE is evidently greater than its fluoride ion affinity.

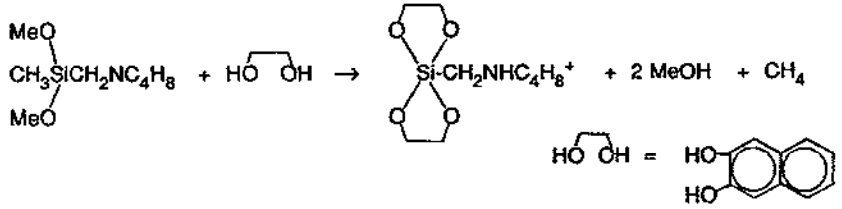
$$RSiF_5^{2-} + (NC)_2C{=}C(CN)_2 \rightleftharpoons [RSiF_5\text{--}TCNE]^{2-} \rightleftharpoons RSiF_5^{\bullet -} + TCNE^{\bullet -} \qquad (75)$$

Organopentafluorosilicates behave as a typical source of $R^{\bullet}$ and give, under various conditions, coupled products R–R, protonated products RH, organoelement derivatives R_2Hg, R_3Sb or R_3Bi, and halocarbons RX [58,423], and these results provide additional support for the existence of intermediate $RSiF_5^{\bullet -}$. A study of the stereochemistry of bromination at carbon in norbornylpentafluorosilicates suggests that Br^- or $Br^{\bullet}$ attacks $RSiF_5^{\bullet -}$, with inversion at carbon, but this process is accompanied by cleavage of the silicon–carbon bond to generate $R^{\bullet}$ and SiF_5^-, with racemization at carbon [424].

The fluoride-induced weakening of a stable silicon–carbon bond in organosilanes is thus seen to be a multistep process involving distinct silicon species, $RSiF_3$, $RSiF_4^-$, $RSiF_5^{2-}$, and $RSiF_5^{\bullet -}$, as shown in eqn. (76).

$$\begin{array}{ccccccccc} \mathrm{RSiF_3} & \xrightarrow{F^-} & \mathrm{RSiF_4^-} & \xrightarrow{F^-} & \mathrm{RSiF_5^{2-}} & \xrightarrow{-e^-} & \mathrm{RSiF_5^{\cdot -}} & \rightarrow & \mathrm{etc.} \\ \text{8-Si-4} & & \text{10-Si-5} & & \text{12-Si-6} & & \text{11-Si-6} & & \end{array} \qquad (76)$$

Silicon–carbon bond cleavage in $RSiF_3$ occurs under mild conditions in the presence of Me_3NO [425]. The cleavage of a methyl–silicon bond and the formation of methane at 0°C in high yield takes place in the presence of diols such as 2,3-dihydroxynapthalene [426], as shown in eqn. (77), and some of the mechanistic features that accompany the weakening of a Si–C bond can be gleaned from this reaction: higher coordinate silicon intermediates, acyclic-cyclic equilibria involving 5-center steps, electron-delocalizing ligands, and hydrogen-transfer reactions.



(77)

A change in electron count is accompanied by significant changes in geometry and bond lengths, for example, there is an average lengthening of 8.3% in the axial and equatorial P–F bonds in trigonal bipyramidal PF_5 (153.4–157.7 pm) [76] as rectangular pyramidal $PF_5^{\cdot -}$ (164–173 pm, calcd.) is formed, and the unpaired electron resides in an apical position, according to ab initio calculations [427]. The loss of a fluorine atom from PF_5 is calculated to result in an average lengthening of only 0.7% as $PF_4^{\cdot}$ (154.1–159.2 pm) is formed. For the fluorophosphoranyl series $H_nPF^{\cdot}_{4-n}$, calculations show that fluorines prefer axial sites and hydrogens prefer equatorial sites, and there is progressive contraction of the P–F bonds with increasing fluorine substitution, as also observed in fluorophosphines and fluorophosphonium ions [428]. In these fluorophosphoranyl radicals, the electron resides in an equatorial site, but with aromatic ligands the unpaired electron may be centered on the ligand [429]. Calculations of odd-electron fluorides of the main group elements show geometries which usually are close to those predicted by VSEPR theory, with the unpaired electron occupying the same position as does a lone pair of electrons [371].

Without electron transfer, the effects on silicon–carbon and silicon–fluorine bond lengths with increasing fluorine substitution are known. For example, the silicon–carbon bond in Me_3SiF (184.8 pm) is shortened by 1.1% in the trifluoro derivative $MeSiF_3$ (182.8 pm) [430], and ab initio calculations indicate a lengthening of the silicon–carbon bond, up to 5.5%, along the series CH_3SiF_3 (185.6 pm), $CH_3SiF_4^-$ (189.8 pm) and $CH_3SiF_5^{2-}$ (195.9 pm), with a lengthening of the silicon–fluorine bond, up to 8.7%, along the same series, CH_3SiF_3 (165.2 pm), $CH_3SiF_4^-$ (169.8–176.0 pm) and $CH_3SiF_5^{2-}$

(176.0–179.6 pm) [431]. These differences in bond length are presumably correlated with the bond length/strength in the bridged intermediates where bond cleavage occurs.

The apicophilicity of ligands in phosphoranyl radicals is similar to that in phosphoranes, and five-membered rings are attached to axial and equatorial sites [429]. An ESR study of the stereoisomerization of a 9-P-4 phosphoranyl radical, containing a perfluoropinacol ligand, has been reported [432].

Odd-electron intermediates are involved in the cleavage of other carbon–element bonds under mild conditions, for instance, the carbon–iodine bond, ~213 kJ mol^{-1} [433] is cleaved at room temperature if suitable nucleophiles and electron donors such as nitronate, thiolate, malonate and sulfinate are added to perfluoroalkyl iodides and alkenes [434,435].

$$R_fI \; + \; \overset{Nuc:^-}{\rightleftharpoons} \; [R_f\text{-}I\text{--}Nuc]^- \; \overset{-Nuc\bullet}{\rightleftharpoons} \; R_f\text{-}I^{\bullet -} \; \overset{-I^-}{\rightleftharpoons} \; R_f\bullet \; \overset{R_2C=CR_2}{\rightleftharpoons} \; R_fCR_2CR_2\bullet \rightleftharpoons \text{etc.} \qquad (78)$$

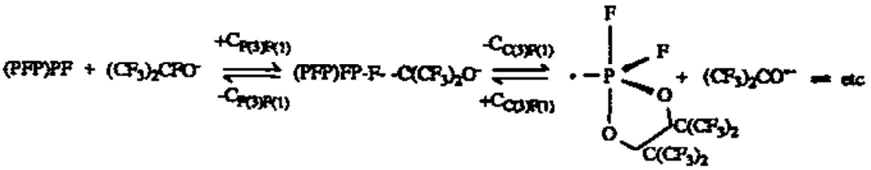
Perfluoroalkylation also occurs in the presence of electron mediators such as zinc-methyl viologen or enzymes [436]. Similar reactions are initiated by UV irradiation, electrochemically, by peroxides or azo compounds [437] and by copper [438], but without an initiator, reactions of perfluoroalkyl iodides with olefins generally require temperatures in excess of 160°C.

Trifluoromethylation with CF_3Br occurs under mild conditions in the presence of the radical anion $SO_2^{\bullet -}$, and the source of the latter species is either $Na_2S_2O_4$ or SO_2 and zinc [439]. The reaction of CF_3Br can also be carried out with electrochemically-generated radical anions [440].

$$CF_3Br \; + \; SO_2^{\bullet -} \; \underset{-C_{Br(1)S(2)}}{\overset{+C_{Br(1)S(2)}}{\rightleftharpoons}} \; F_3C\text{--}Br\text{-}SO_2^{\bullet -} \; \underset{+C_{C(3)Br(1)}}{\overset{-C_{C(3)Br(1)}}{\rightleftharpoons}} \; CF_3\bullet \; + \; BrSO_2^{\bullet -} \rightleftharpoons \text{etc.} \qquad (79)$$

Electron transfer between difluorodihalomethane CF_2X_2 and zinc and cadmium metals, and the formation of a radical anion $CF_2X_2^{\bullet -}$, has been proposed as the first step in the preparation of (trifluoromethyl)cadmium and -zinc reagents [441], and the subject of one-electron transfer reactions in the redox chemistry of main group compounds has been reviewed [442]

In some reactions, the perfluoro anion $(CF_3)_2CFO^-$ behaves as a typical fluoride ion donor, but the anion can also be a source of fluorine atoms in the oxidation of certain phosphorus(III) compounds, as illustrated in eqn (80) This reaction is accompanied by dimerization of the hexafluoroacetone ketyl $(CF_3)_2CO^{\bullet -}$ and fluoride ion transfer to give $(PFP)PF_4^-$ as the final product, hence, the overall reaction involves transfer of both $F^\bullet$ and F^- [303]



(80)

Fluoro substituents can stabilize free-radicals of the main group elements, e.g. $(CF_3)_2NO$ [443] or cyclic-$CF_3CSNSCCF_3$ [444], and direct addition of a radical is a common way of generating neutral odd-electron intermediates [445,446].

$$Me_3Si\bullet + CF_3C(O)OMe \underset{-C_{Si(3)O(1)}}{\overset{+C_{Si(3)O(1)}}{\rightleftharpoons}} Me_3SiO\dot{C}(OMe)CF_3 \tag{81}$$

$$t\text{-}BuO\bullet + (t\text{-}BuO)_3P \underset{-C_{P(3)O(1)}}{\overset{+C_{P(3)O(1)}}{\rightleftharpoons}} (t\text{-}BuO)_4P\bullet \rightarrow (t\text{-}BuO)_3PO + t\text{-}Bu\bullet \tag{82}$$

Fluoroanions AsF_6^-, SbF_6^- or $Sb_2F_{11}^-$ are stable towards radical cations such as O_2^+, Br_2^+, I_2^+, $C_6F_6^+$, $C_5H_5N^+$ [447–450] or cyclic-$CF_3CSSSCCF_3^+$ [451], and AsF_6^- is stable during the oxidation of $Te[N(SiMe_3)_2]_2$ to its radical cation [452].

N-Fluoropyridinium salts are convenient sources of F^+ and have found wide application as electrophilic fluorinating agents. Their reactions parallel those of other oxidizing agents, for example, organosulfur compounds and amino acids undergo α-fluorination with either pyF^+ [453] or XeF_2 [407,408]. Although pyF^+ is formally a F^+ donor, the increased N–F bond strength in fluoronitrogen cations [74] argues against a direct F^+ transfer reaction, instead, a single electron transfer from a suitable electron donor may be required before a weakened N--F–E bond can be cleaved [454], as postulated in eqn. (83).

$$R_3C^- + Fpy^+ \underset{-C_{C(3)F(1)}}{\overset{+C_{C(3)F(1)}}{\rightleftharpoons}} R_3C\text{--}Fpy \underset{+C_{C(3)F(1)}}{\overset{-C_{C(3)F(1)}}{\rightleftharpoons}} R_3C\bullet + Fpy\bullet \overset{R_3C^-}{\rightleftharpoons} R_3C\text{-}F\text{--}py^{\bullet-} \underset{+C_{C(3)F(1)}}{\overset{-C_{C(3)F(1)}}{\rightleftharpoons}} R_3CF + py^{\bullet-} \rightleftharpoons \text{etc.} \tag{83}$$

A recent study using an ion trap mass spectrometer has shown that a halogen cation radical $Cl_2^{\bullet+}$ will accept an electron from a donor such as benzene [455].

$$Cl_2^{\bullet+} + C_6H_6 \rightleftharpoons Cl_2\text{--}C_6H_6^{\bullet+} \rightleftharpoons C_6H_6^{\bullet+} + Cl_2 \tag{84}$$

(iv) Solvated intermediates

If a solvent interacts weakly with all reactants and intermediates, then rates in solution are expected to be very similar to those in the gas phase [456]. If the solvent interacts weakly with an anion, then the reactions of the anion will closely resemble those in the gas phase, as demonstrated by the similarity of the reactions of fluoride ion with silicon or sulfur compounds in solution or in the gas phase [68,457]. For solvent adducts of moderate strength, the solvent must participate actively in the overall mechanism by stabilizing and dispensing key intermediates.

Equilibria involving the solvent can be monitored conveniently by NMR. For example, the ^1H NMR spectrum shows that the equilibrium of eqn. (85) is shifted to the right as acetonitrile is replaced by the less basic solvent chloroform, but both of these solvents compete less effectively for the hydrogen bond than the anion F_5TeO^-, which forms a relatively stable hydrogen-bonded adduct $F_5TeO–H–OTeF_5^-$ [458].

$$F_5TeOH\text{--}NCCH_3 \underset{+C_{N(1)H(1)}}{\overset{-C_{N(1)H(1)}}{\rightleftharpoons}} F_5TeOH + CH_3CN \quad (85)$$

Krypton difluoride, a powerful oxidizer [459], can be stabilized as a solvated cation, $HCN–KrF^+$ [460], and loss of $^{129}Xe–^{14}N$ coupling in nitrile adducts of XeF^+ above –30°C, in the case of the less basic perfluoroalkyl nitriles C_2F_5CN and C_3F_7CN, is a measure of the weakening of the Xe–N bond in these solvated cations [461].

$$RC{\equiv}N\text{-}XeF^+ \underset{+C_{Xe(1)N(1)}}{\overset{-C_{Xe(1)N(1)}}{\rightleftharpoons}} XeF^+ + RC{\equiv}N \quad (86)$$

$R = H, R, R_f$

That perfluoropyridine forms an adduct with XeF^+, i.e. $C_5F_5N–Xe–F^+$ [462], underlines the view that fluorocations are poor F^+ donors, because XeF^+ does not transfer F^+ to pyridine even though pyF^+ is known to be a stable cation. Evidently, any fluorine-bridged intermediate such as $C_5F_5N\text{--}F–Xe^+$ must be cleaved consistently at the weakest N--F bond, but $C_5F_5N–XeF^+$ is sufficiently stable to be observed in solution.

Ethers and other basic solvents can regulate the concentration of Lewis acid catalysts such as BF_3 by means of dissociation of the adducts base:BF_3 [3], and equilibrium concentrations of stronger Lewis acids such as antimony pentafluoride can be maintained in sulfur dioxide solution by dissociation of the octahedral adduct SbF_5:OSO [463]

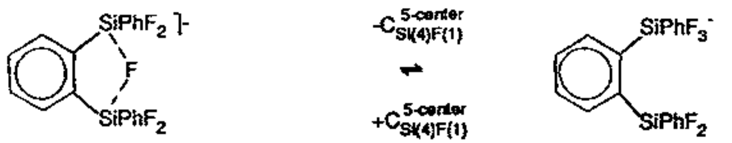
$$F_3B\text{-}OR_2 \underset{+C_{B(3)O(2)}}{\overset{-C_{B(3)O(2)}}{\rightleftharpoons}} BF_3 + R_2O \qquad (87)$$

Solvents also stabilize odd-electron species, for example, the $SO_3F^{\cdot}$ radical [464], which can be observed in liquid, gaseous and solid phases, forms a hydrogen-bridged radical in a fluorosulfuric acid solution of bis(fluorosulfuryl)peroxide [465], eqn (88). An analogous hydrogen-bonded anion, $O_2FSO\text{–}H\text{–}OSFO_2^-$ is also known [357].

$$SO_3F\cdot + HSO_3F \underset{-C_{O(1)H(1)}}{\overset{+C_{O(1)H(1)}}{\rightleftharpoons}} [O_2FSO\text{–}H\text{–}OSFO_2]^{\cdot} \rightleftharpoons HSO_3F + SO_3F\cdot \qquad (88)$$

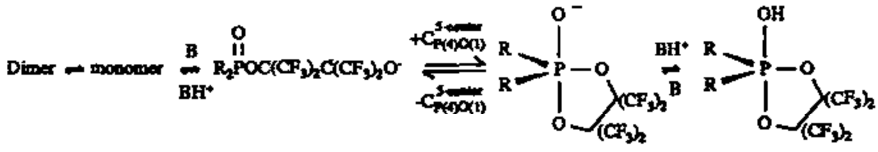
(v) Ring cleavage, $-C^c$

The cyclic fluorine-bridged silicate **76** is rigid at –80°C, but NMR studies show that as the temperature is raised, the cleavage of bridging Si--F--Si bonds is accompanied by rotation about the Si–C bond, as well as exchange of axial and equatorial fluorines. In the solid state, the fluorine bridge in **76** is unsymmetrical, with bond lengths of 189.8 and 206.5 pm, but the geometry about the silicon atoms is nearly trigonal bipyramidal with two fluorines in axial positions [37].



76 **77** (89)

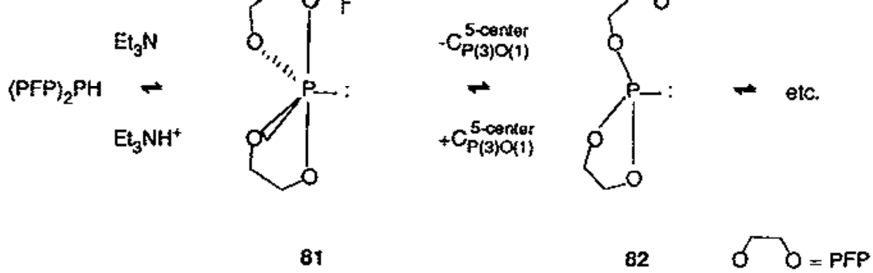
The cleavage of phosphorus–oxygen bonds in cyclic five-membered ring organophosphates is of interest because of the role of such intermediates in phosphate [244] and enzyme [466] hydrolysis reactions. Often, however, the phosphorus–oxygen bond of cyclic or acyclic derivatives is fairly robust, as in pentacoordinate $P(OR)_5$ or $RP(PFP)_2$, and it is not always clear which mechanistic features are responsible for a weakening of the phosphorus–oxygen bond. This problem has been studied in perfluoropinacol derivatives such as $R_2P(O)OC(CF_3)_2C(CF_3)_2OH$ (R = Me, Ph). The methyl derivative is a hydrogen-bonded dimer in the solid state, but deprotonation by bases such as triethylamine, pyridine, imidazole or DMSO increases the solubility in organic solvents and shifts the equilibrium of eqn. (90) towards cyclic pentacoordinated phosphorus [467]. A variable-temperature ^{19}F NMR study of the pyridine-catalyzed equilibration of trifluoromethyl groups in the phenyl derivative, gave the following reaction parameters: $\Delta H^{\ddagger} = 33.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -86$ J K^{-1} mol^{-1} [468].



78 79 80 (90)

The low reaction enthalpy of 33.5 kJ mol^{-1} implies that only weak bonds are cleaved in the equilibrium of eqn. (90), and these weak bonds are assumed to be hydrogen bonds, i.e. protonation-deprotonation and monomer-dimer equilibria, and a weak P–O bond in intermediate 79 that is specifically assigned to an axial site which is *trans* to a phosphoryl substituent. The selective cleavage of such a *trans* P–O bond was demonstrated more clearly in the analogous $Ph_2P(O)OC_6H_4OH$-base system, where the retention of the ABCD proton spectrum of the catecholyl ring during rapid equilibria provides strong evidence for the selective cleavage of this *trans* P–O bond [469]. Although reactions of organophosphates in organic and biochemical systems are complex multistep processes, some of the important mechanistic features can be identified in these model systems, namely, rapid five-center ring-opening and ring-closing steps, selective bond cleavage of weakened P–O bonds, equilibria between four-, five, and possibly six-coordinate phosphorus species, and protonation-deprotonation that is coupled to cyclic-acyclic equilibria.

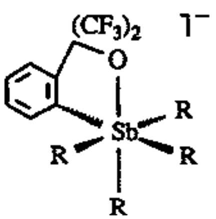
Deprotonation of hydridophosphoranes containing a perfluoropinacol ligand leads to anionic 10-P-4 phosphoranide **81**, and the rapid cyclic-acyclic equilibrium of eqn. (91) then interconverts **81** and **82**. The phosphoranide **81** has a TBP structure with a lone pair of electrons in the equatorial plane and two unequal axial P–O bonds, with one axial P–O (202 pm) bond being 14% longer than the other axial P–O (177 pm) bond. The longer P–O bond is hydrogen bonded to the cation Et_3NH^+ in the solid state [470].



81 82 (91)

Phosphoranides with the ligands $C_6H_4C(CF_3)_2O$, $OCPh_2C(O)O$ or OCR_2CR_2O [203,471–473] undergo similar five-membered ring equilibria. Unequal axial bonds are found in PCl_4^- (211.8 and 285.0 pm) [474] and in PBr_4^- (252.7 and 262.0 pm) [475] in the solid state.

The close connection between protonation-deprotonation and cyclic-acyclic equilibria is further demonstrated by compound **83**, in which protonation of the oxygen–antimony bond leads to ring opening [476]. Protonation of the cyclic silatrane **84** lengthens (weakens) the axial silicon–oxygen bond by up to 17 pm, but shortens the silicon–nitrogen bond by 10.2 pm, as compared to the unprotonated analogue [477]. A lengthening of the protonated Si–N (189 pm) bond is also observed in **85**, as compared to the remaining equatorial Si–N (ave 169 pm) bonds or axial Si–N (173 pm) bond [478].



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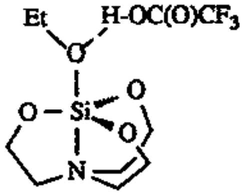
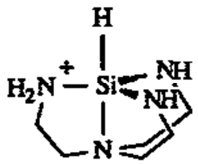


84



85

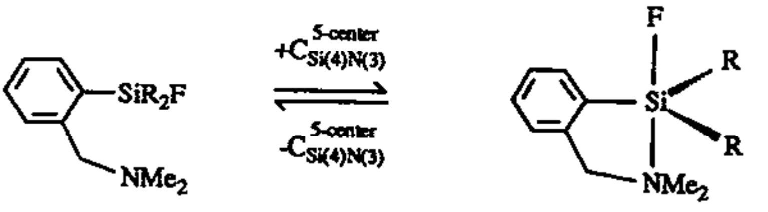
Cleavage of a silicon–nitrogen bond in silatranes $XSi(OCC)_3N$ is acid catalyzed [479]. Protonation and ring opening is also observed in the acid-catalyzed cleavage of catecholyl derivatives of silicon [480] and in the acid-catalyzed hydrolysis and reversible ring opening of the spirophosphorane $PhP(OCMe_2CMe_2O)_2$ [481].

Cyclic-acyclic equilibria provide a low energy pathway of stereoisomerization, and recent examples include compounds of silicon [482], antimony [483], bismuth [484] and iodine [485]. The rate of de-methylation of five-membered-ring methoxysulfuranes has been investigated [486].

Deprotonation can be induced by the addition of fluoride ion, as illustrated by the effect of fluoride ion on the solubility of succinic acid. Each fluoride ion dissolves one additional succinic acid molecule and forms a linear OH–F–HO hydrogen-bonded system [487]. Phthalic acid dissolves completely, but two fluoride ions are required per phthalic acid molecule, and an intramolecularly hydrogen-bonded anion is formed [488].

$$C_6H_4(COOH)_2 + 2F^- \longrightarrow C_6H_4(COO)_2H^- + FHF^- \quad (92)$$

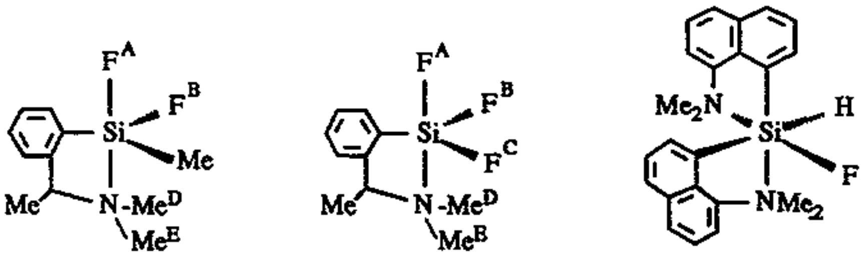
Equilibria involving five-membered rings have been used to estimate the stability of pentacoordinated silicon chelates, and to establish the site preference of ligands in a trigonal bipyramid, i.e. apicophilicity. The details of the trajectory of bond formation, as well as relative bond strength, can be probed experimentally in fluorosilanes such as **86**, where chelation places a nitrogen donor atom in an axial site in trigonal bipyramidal **87**, as shown in eqn. (93). An apicophilicity series was established for these intramolecularly coordinated compounds: H < alkyl < aryl < OR, NR_2 < F ~ SR < Cl, OCOR. It was also demonstrated that, except for hydrogen, the stability of a pentacoordinated chelate of silicon is primarily related to the nature of the most apicophilic ligand in the *trans* position; hydrogen, however, preferentially occupies an equatorial site [489].



(93)

86 **87**

With a chiral ligand, ring-closure generates non-equivalent fluorines in **88** and **89**, and the low temperature ^{19}F NMR spectrum of rigid **89** shows three fluorine signals, while the ^{1}H NMR spectrum shows two N-methyl groups. As long as the nitrogen atom is coordinated at silicon, the two methyls are diastereotopic because rapid inversion at the nitrogen is now hindered.



88 **89** **90**

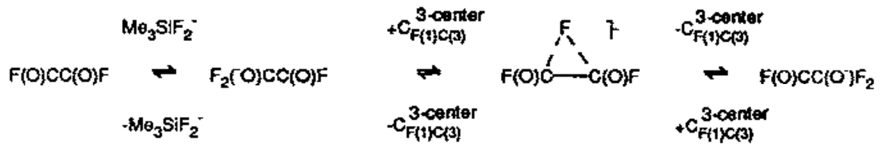
As the temperature is raised, the axial and equatorial fluorines in **89** become equivalent ($\Delta G^{\ddagger} = 54.8$ kJ), but the barrier is lower than that responsible for equivalence of the N-methyl groups ($\Delta G^{\ddagger} = 66.1$ kJ). The corresponding barriers for **88** are $\Delta G^{\ddagger} = 39$ kJ and $\Delta G^{\ddagger} = 49.4$ kJ, respectively [489]. Typical energy barriers for silicon compounds which contain a five-membered ring are given in Table 6. The higher energy pathway is identified with cleavage of the silicon-nitrogen bond in the five-membered chelate ring, while the low energy pathway is assigned to axial-equatorial exchange, and the latter process presumably involves interaction with donor atoms, as discussed in a previous section for the analogous intermediates $D{:}R_2SiF_3^-$ and $D{:}RSiF_4^-$. Six-coordination has been established in related silicon adducts such as **90**, although the geometry at silicon may deviate considerably from that of an ideal octahedron [490], however, the silicon atom is in an octahedral environment in the six-coordinate catecholyl derivative $(C_6H_4O_2)_2Si(C_6H_4CH_2NMe_2)$. Even heptacoordination can be observed in cyclic silicon, germanium [491] and tin adducts [492].

TABLE 6

Axial-equatorial exchange and cleavage of five-membered ring in some silicon compounds

Compound	Axial-equatorial exchange $\Delta G^{\ddagger}$ (kJ mol^{-1})	Cleavage of five-membered ring $\Delta G^{\ddagger}$ (kJ mol^{-1})	Ref.
$Me_2NCH_2C_6H_4SiNpMeF$		43.1	[489]
$Me_2NCH_2C_6H_4SiMeHF$		48.1	[489]
$Me_2NCH_2C_6H_4SiMeF_2$		37	[489]
$Me_2NCH_2C_6H_4SiMeFCl$		49.4	[489]
$Me_2NCHMeC_6H_4SiMe_2F$		40.6	[489]
$Me_2NCHMeC_6H_4SiF_3$	54.8	66.1	[493]
$Me_2NCHMeC_6H_4SiF_2Me$	39	49.4	[489]
o-$C_6H_4(SiPhF_2)_2F^-$	42.7	38	[37]

Cleavage of bonds in cyclic intermediates has been investigated by ab initio calculations which corroborate an open structure for the oxalyl fluoride adduct **91**, but a bridged intermediate **92** allows rapid fluorine transfer by an intermolecular route [494].



91 **92** (94)

(vi) Analogy between F and H catalysis

Attention has been drawn to the analogy between F^- and H^+ induced reactions, as illustrated by the chemistry of carbanions and carbocations [495]. Both F^- and H^- ions add to boron compounds, i.e. 1,8-bis(dimethylboryl)naphthalene, to form five-membered rings containing B--F--B or B--H--B bridges [496], while H^+ adds to the Lewis base analogue, i.e. 1,8-bis(dimethylamino)naphthalene and forms a N--H--N bridge [497] Fluoride and hydride ions both add to organosilanes to generate pentavalent silicon anions [498], and the fluoro- and hydridosilicates undergo similar reactions in solution and in the gas phase [314,499]. SiH_5^- has been characterized in the gas phase and hydride transfer among the silanes closely resembles fluorine transfer among the fluorosilanes and fluorosilicates, as illustrated in eqn. (95).

$$Et_3SiH_2^- + SiH_4 \underset{-C_{Si(4)H(1)}}{\overset{+C_{Si(4)H(1)}}{\rightleftharpoons}} Et_3SiH\text{--}H\text{-}SiH_4^- \underset{+C_{Si(4)H(1)}}{\overset{-C_{Si(4)H(1)}}{\rightleftharpoons}} Et_3SiH + SiH_5^- \qquad (95)$$

Hydrogen compounds may be classified formally as H^-, H^+, $H^{\cdot}$, or e^- donors and acceptors, analogous to the classification of fluorinated compounds. The phosphorane

$(C_6H_4-C_6H_4)_2PH$, for example, can lose its hydrogen as a proton, a hydride or a hydrogen atom, with each species opening up its unique reaction pathway [500]. Hydrogen-bridged species are reasonable intermediates in all these reactions, and hydrogen-bridge bonding can show considerable variation, with bond strengths varying from <30 kJ mol^{-1} to >50 kJ mol^{-1} and, in some cases, greater than 100 kJ mol^{-1} [501].

Impurities also affect the study of proton transfer reactions, and the purification of reagents, choice of solvent, and chemical treatment of glassware have been emphasized on numerous occasions [502].

If proton transfer reactions are diffusion controlled in the direction of formation of a bridged intermediate, but slower and controlled by the rate of bond rupture as the bridged intermediate breaks down, then the mechanism of hydrogen transfer may be very similar to that proposed for fluorine transfer.

$$NH_3 \quad + \quad NH_4^+ \quad \underset{-C_{N(3)H(1)}}{\overset{+C_{N(3)H(1)}}{\rightleftharpoons}} \quad H_3N\text{--}H\text{--}NH_3^+ \tag{96}$$

The effectiveness of F and H catalysis may be related, at least partly, to the weakness of the bridging bonds, E--F--E or E--H--E, as compared to the terminal bonds, E–F or E–H. A bridged intermediate provides a means of rapid transfer of fluorine or hydrogen substituents, but any subsequent intermediate contains only terminal E–F or E–H bonds. Since the latter are among the strongest single bonds, the focus of reactivity is naturally directed elsewhere, until another bridged intermediate allows loss of a fluorine or hydrogen substituent, thus completing the catalytic cycle.

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