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INORGANIC CHEMISTRY OF HEXAFLUOROACETONE

M. WITT, K. S. DHATHATHREYAN, and H. W. ROESKY

Institut für Anorganische Chemie der Universität Göttingen,
D-3400 Göttingen, Federal Republic of Germany

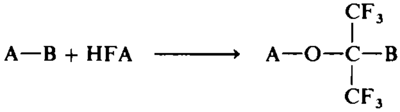
I. Introduction

Hexafluoroacetone (HFA) was discovered by Fukuhara and Bigelow in 1941 (109), but more than two decades passed before HFA gained wide interest in inorganic, organic, and technical chemistry. The chemical and physical properties of HFA were reviewed by Krespan and Middleton (*168*) in 1967 and more recently by Middleton (*185*).

The difference in reactivity compared to organic ketones is caused by the strong electron-withdrawing effect of the fluorine atoms in HFA, which leads to an electron-deficient carbonyl group. This is manifested in the inability to protonate the oxygen atom in super acidic media (*203*).

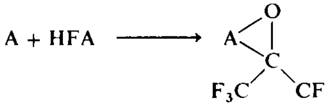
Depending on the nature of the reaction partners, there are various pathways leading to different products:

i. Insertion into activated single bonds:



$$\mathrm{A{-}B + HFA \longrightarrow A{-}O{-}\underset{CF_3}{\overset{CF_3}{C}}{-}B} \qquad (1)$$

ii. Oxidative addition to low-valent atoms (with ligand displacement in organometallic compounds) and multiple bonds to yield heterocycles of different size and geometry:



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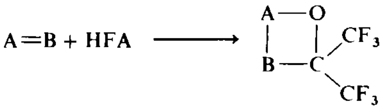

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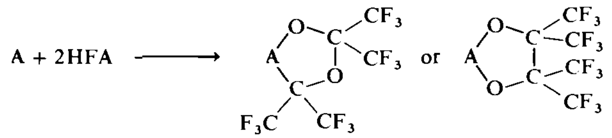

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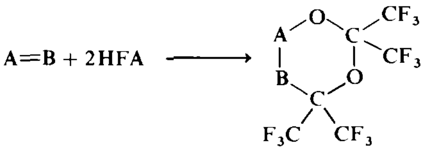

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In addition to these common types of reactions, several syntheses are known in which HFA causes changes in the substrate (e.g., isomerization of nitriles to isonitriles) or rearrangements of initially unstable products. However, only few exceptions to the above-mentioned examples have been found so far in HFA chemistry.

This article deals mainly with synthetic "inorganic" aspects of HFA chemistry. Reaction conditions and spectroscopic data are mentioned if necessary for structural and mechanistic considerations. Particular attention has been drawn to literature coverage since 1966; earlier works reviewed by Krespan and Middleton (*168*) have been included only for completion of some sections.

II. Reactions of HFA with Compounds of Group IV Elements

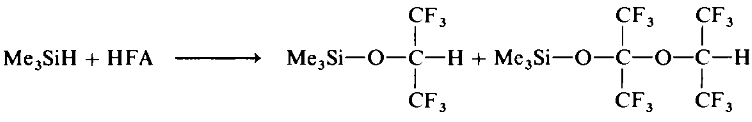
The chemistry of group IV elements and HFA is dominated by insertion reactions according to Eq. (1). Cycloadditions involving the elements of group IV are rather seldom observed.

A. SILICON

1. Reactions with Si—H Bonds

Under free radical conditions HFA adds to a variety of silanes containing Si—H bonds to form hexafluoroisopropoxysilanes (*143a*, *156*). Ionic conditions (dark, liquid phase, low temperatures) lead in the case of trimethylsilane to adducts **1** and **2** (*73*, *156*).[1]

[1] Abbreviations: Me, CH_3; Et, C_2H_5; Pr, C_3H_7; *i*-Pr, $CH(CH_3)_2$; Bu, C_4H_9; *t*-Bu, $C(CH_3)_3$; Ph, C_6H_5; Cp, η^5-cyclopentadienyl; COD, 1,5-cyclooctadiene; Hfp, hexafluoroisopropyl; Pfp, perfluoropinacolyl; Py, pyridine; Ar, aryl; Al, alkyl; acac, acetyl acetonate.



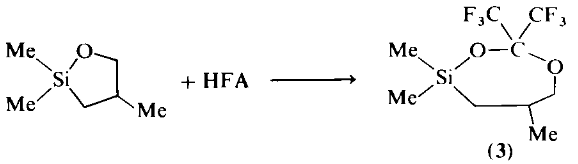
$$\mathrm{Me_3SiH + HFA \longrightarrow Me_3Si{-}O{-}C(CF_3)_2{-}H + Me_3Si{-}O{-}C(CF_3)_2{-}O{-}C(CF_3)_2{-}H} \quad (6)$$

(1) (2)

A mechanism proceeding via abstraction of a hydride ion by HFA with formation of isopropoxide ion as the initial step, followed by reversible addition of another molecule of HFA, has been proposed. The resulting anions combine with the Me_3Si cation to yield **1** and **2** (*158*). The "1:1 adduct" of **1** with HFA reported by Cullen and Styan (*73*) has been proved by Janzen and Willis (*158*) to be identical with **2**.

2. *Reactions with Si—O Bonds*

Similarly, hydroxy- and alkoxysilanes are attacked by HFA to form hemiketals and ketals (*35*, *157*). A 1,3,4-dioxasilepane (**3**) is accessible by insertion of HFA into the Si—O bond of a 1,2-oxasilolane (*67*) [Eq. (7)] via nucleophilic attack of oxygen at the carbonyl carbon atom (*35*). Attempts to synthesize perfluoroisopropoxysilanes from alkylhalogenosilanes with HFA in the presence of KF via intermediate perfluoroisopropoxide ion proceed with elimination of HFA and formation of the corresponding fluorosilanes (*208*).

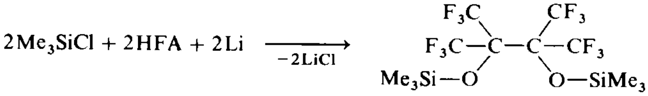


(3)

(7)

A silene was assumed to be involved in the reaction of dichlorodimethylsilane with two equivalents of lithium and HFA to yield a 1,3,4-dioxasilolane (*34*). Further investigations showed the mechanism, as well as the structure assigned, to be incorrect.

Frye *et al.* (*108*) obtained bis(trimethylsilyl) oxyperfluoropinacolate (**4**) and 2,2-dimethyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxasilolane (**5**) by reacting HFA, lithium, and the corresponding chlorosilanes.



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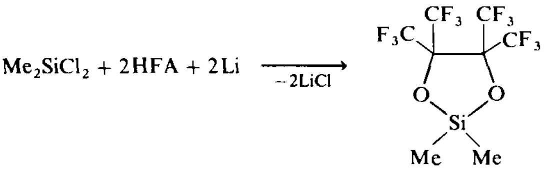


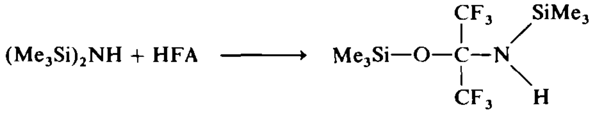
(9)

(5)

The structure of **5** was confirmed by metathesis of dimethyldiacetoxysilane with perfluoropinacol (*108*). The reactions according to Eqs. (8) and (9) proceed via the alkali salts of perfluoropinacolate dianion, which in the case of sodium can be obtained as a pure white powder (*153*). Compound **4** is also accessible by reaction of HFA and bis(trimethylsilyl)mercury under mild conditions (*153*). As the reaction rate is increased by UV radiation, formation of trimethylsilyl radicals is assumed to be the first step.

3. *Reactions with Si—N Bonds*

HFA inserts into one Si—N bond of hexamethyldisilazane at 50°C in a sealed tube with formation of **6** (*254*). However, no products have been obtained in the reactions of HFA with heptamethyldisilazane and a cyclic trisilazane (*2*).



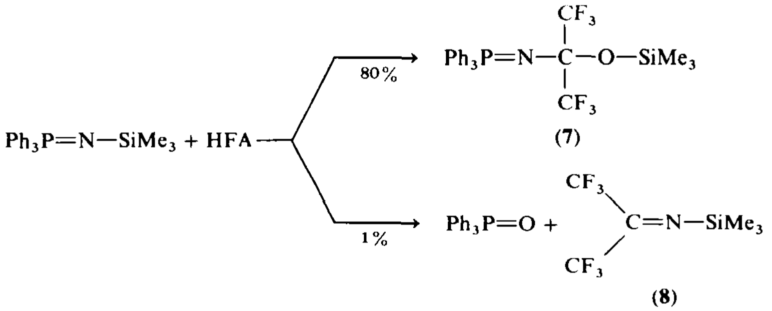
$$(Me_3Si)_2NH + HFA \longrightarrow Me_3Si{-}O{-}\underset{CF_3}{\overset{CF_3}{C}}{-}N(SiMe_3)H \qquad (10)$$

(6)

A polymeric 2:1 addition product is formed with a 1,3-diaza-2-silolidine (*2*).

Further examples of insertion into Si—N bonds have been found in the reactions of HFA with dimethylaminotrimethylsilane, phenylaminotrimethylsilane (*2*), azidotrimethylsilane (*1*, *270*), and bis(trimethylsilyl)carbodiimide (*102*). All products show the insertion of HFA only in one of the Si—N bonds.

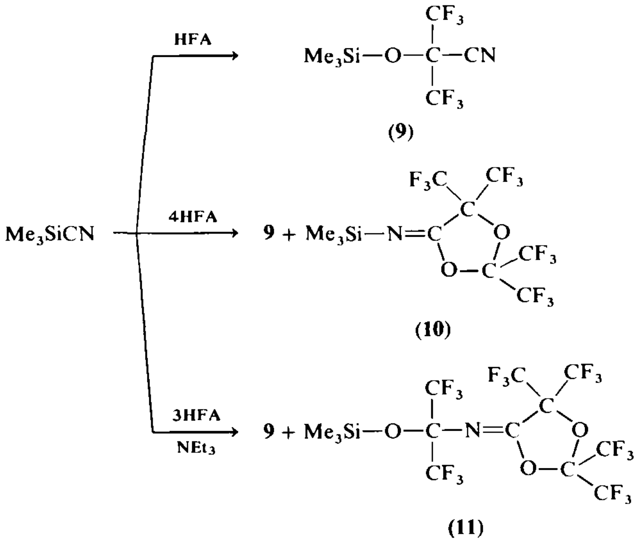
HFA also cleaves the Si—N bond in trimethylsilylaminotriphenyliminophosphorane to form **7** in high yield. A minor side reaction results in the formation of **8**. The nitrogen-oxygen exchange prevails with the corresponding tin compound (*vide infra*). Unlike its tin analogue, **8** does not add another molecule of HFA (*1*). In contrast to organic fluoroimines, ^{19}F NMR of **8** shows only one signal, suggesting a very low nitrogen inversion barrier.



(11)

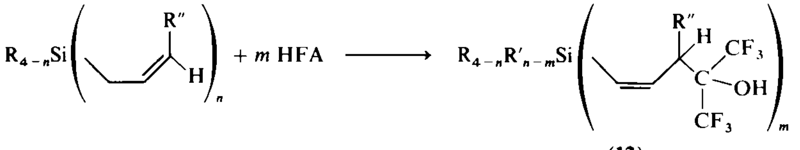
4. *Reactions with Si—C Bonds*

HFA and cyanotrimethylsilane react stoichiometrically with formation of the substituted cyanhydrin **9** (*175*). Increasing the molar ratio of the reactants to 4:1 yields, in addition to **9**, compound **10**, with nitrile-isonitrile equilibrium competing with direct attack of HFA (*242*). The five-membered ring is also formed in the reaction of organic iso-nitriles with HFA (*188*). The same structural feature in addition to insertion has been found when triethylamine is present as a catalyst, as well as minor amounts of **9** (*83*, *242*).



(12)

Abel and Rowley (*4*) have done extensive work on the interaction of HFA and silanes with allylic substituents. At 100°C the reaction occurs according to Eq. (13). Decreasing the temperature leads to the formation of oxetane **13**.

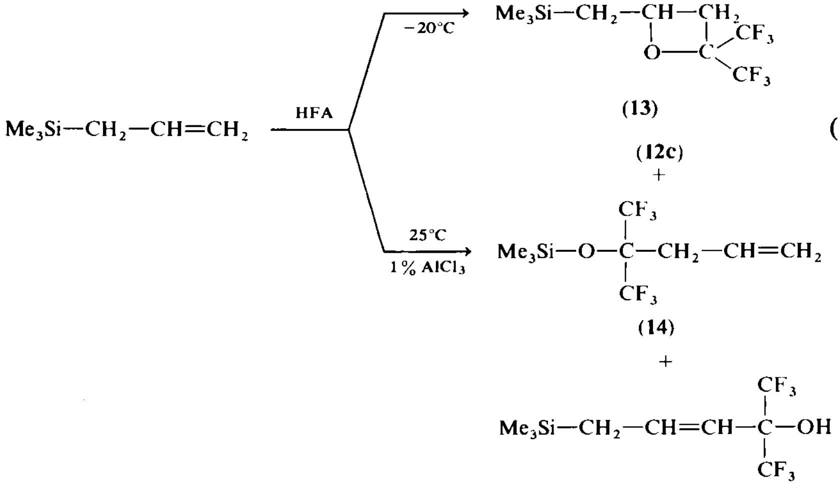


(12)

(13)

12	R	R′	R″	*n*	*m*
a	Ph		H	1	1
b	Me		Me	1	1
c	Me	CH_2CHCH_2	H	1-4	$\leq n$

Catalytic amounts of $AlCl_3$ yield, in addition to **12c** ($n = 1$), an insertion product into the Si—C bond (**14**) and an alcohol without isomerization of the double bond (**15**).



(13)

(12c)

(14)

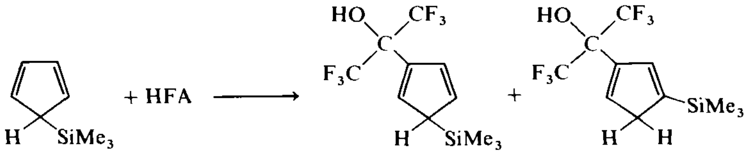
(15)

(14)

Mechanisms of these reactions have been discussed in detail (*4*). Interestingly, the phenyl-substituted 2-butenylsilane failed to react with HFA even at 140°C. These observations have been explained by a mechanism involving a six-center intermediate with significant polar contribution to the transition state.

The reaction of HFA with substituted vinyltrimethylsilyl ethers in the presence of Lewis acids with subsequent hydrolysis provides a good route to alcohols containing the hexafluoroisopropyl group (*148*).

Cyclopentadienyltrimethylsilane yields the two isomeric alcohols **16a** and **16b**.



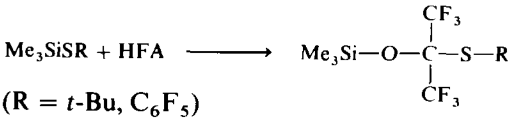
(16a) **(16b)**

(15)

A series of carbonyl compounds including HFA has been found to react with a silirene with ring expansion to yield 1,2-oxasilolenes (*248a*).

5. *Reactions with Si—S Bonds*

HFA causes fission of Si—S bonds in acyclic (*109*) and cyclic (*6*) silthians.

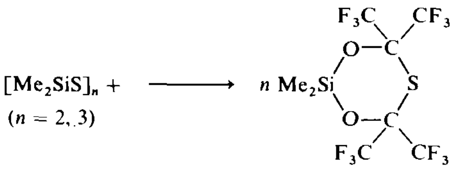


$$Me_3SiSR + HFA \longrightarrow Me_3Si{-}O{-}C(CF_3)_2{-}S{-}R$$

$(R = t\text{-}Bu, C_6F_5)$

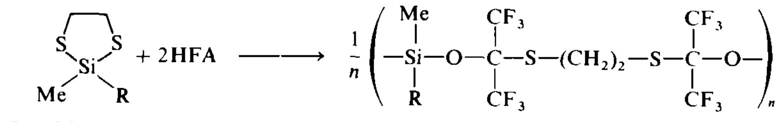
(17)

(16)



(18)

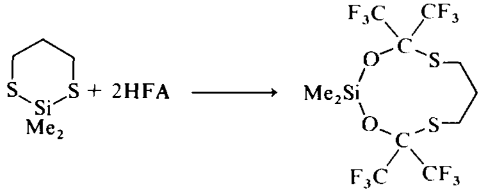
(17)



(19)

(18)

In contrast to Eq. (*18*), the homologue dithiasilacyclohexane forms a monomeric heterocycle (**20**) (*6*).

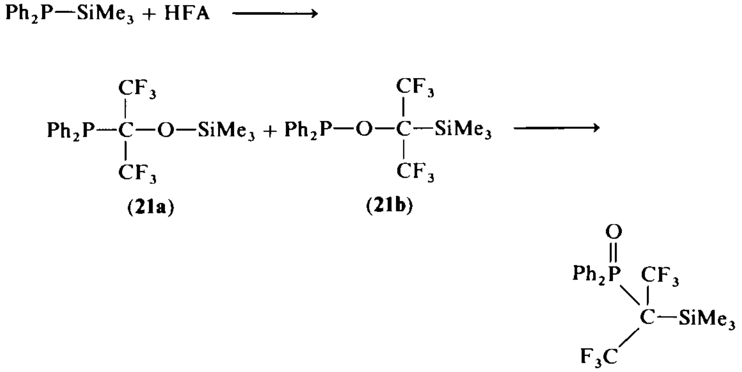


(20)

(19)

6. *Reactions with Si—P and Si—As Bonds*

The action of HFA on a silylphosphane has been reported (*5*). Both possible insertion modes have been found. Compound **21b** undergoes an intramolecular Arbuzov rearrangement, which is evident from the large ^{19}F-^{31}P and ^{1}H-^{31}P coupling constants (*5*).



(**21a**) (**21b**) (**21c**) (20)

Similarly, permethylated silaarsanes with one to three arsenic atoms bound to silicon suffer bond cleavage, but only the silyl ethers analogous to **21a** are formed (*3*).

7. *Miscellaneous*

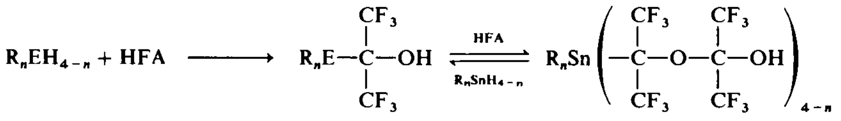
Bell and co-workers (*24*, *25*) have investigated the generation of trifluoromethyl radicals from photolysis of HFA in the presence of silanes. Abstraction of the proton is observed in the case of trichlorosilane (*24*), while methyl(fluoro)silanes lead to the formation of CF_3H, C_2F_6, and CF_2CH_2(*25*).

B. GERMANIUM AND TIN

The reactions of germanium and tin compounds with HFA are very similar to those of silicon compounds. But because of differences in polarity and bond strengths some reactions yield products different from those of their silicon analogues.

1. *Insertion into E—H Bonds*

The action of HFA on tin and germanium hydrides has been reported (*73*). In the case of tin, double insertion has been observed, the products of which can be cleaved by excess hydride to form the monoaddition product (*73*).



$$R_nEH_{4-n} + HFA \longrightarrow R_nE{-}C(CF_3)_2{-}OH \underset{R_nSnH_{4-n}}{\overset{HFA}{\rightleftharpoons}} R_nSn\left({-}C(CF_3)_2{-}O{-}C(CF_3)_2{-}OH\right)_{4-n}$$

(22) **(23)**

(R = Me; n = 2, 3)

(21)

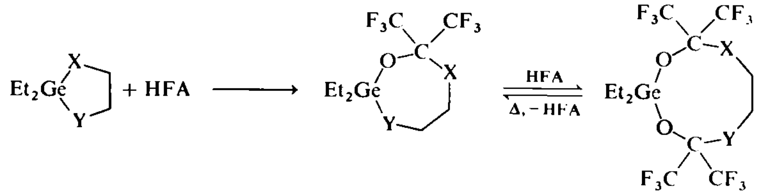
E	R	n
Ge	Me	3
Sn	Me	2, 3
	Bu	3

The reversibility of the last step in Eq. (21) in contrast to Eq. (6) is further evidence for the ionic mechanism proposed by Janzen and Willis (*158*), since trialkylsilicon compounds form cations more easily.

2. *Reactions with Ge—O Bonds*

Reactions of open-chain and cyclic germoxanes and cyclic germadioxanes with HFA have been investigated.

Insertion of one molecule of HFA in the Ge—O bond of methoxytriethylgermane (*87*), hexaethyldigermoxane (*87*), some 1,2-oxagermetanes (*22*), and 1,2-oxagermolanes (*22*, *182*) has been reported. 2,2-Diethyl-1,3,2-dioxagermolane can add either one or two molecules of HFA. The bis adduct **25a** releases one molecule of HFA on heating (*85*).



(22)

(24) **(25a)**

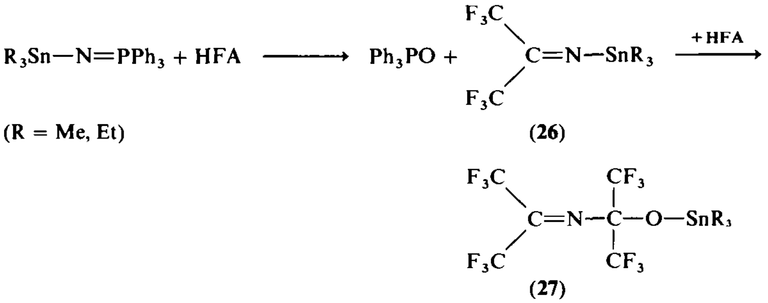
24, 25	**a**	**b**	**c**
X	O	NMe	NMe
Y	O	O	NMe

3. *Reactions with E—N Bonds*

The same reactions have been found for *N*-methyl-substituted 2,2-diethyl-1,3,2-oxaazagermolidine (*86*) and 2,2-diethyl-1,3,2-diazagermolidine (*172*); dimethylamino(tri-*n*-butyl)germane and dimethylamino(trimethyl)stannane also undergo insertion into the E—N bond (*2*).

In analogy to the corresponding silicon compound, bis(tri-*n*-butyl)stannylcarbodiimide adds only one molecule of HFA (*102*).

Whereas in Eq. (11) (*vide supra*) P=N bond breaking plays only a minor role, in the homologous trialkylstannyltriphenylphosphorane/HFA reaction, the ketimines **26** are the only detectable products which insert another HFA molecule into the Sn—N bonds (*1*).



(26)

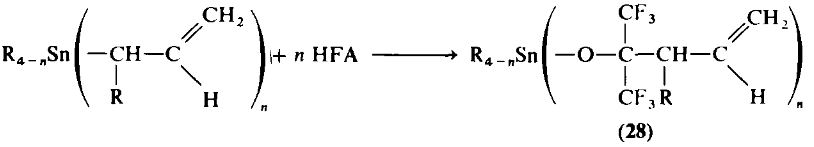
(27)

(23)

Although ketimines (e.g., **8**, **26**) generally have a low inversion barrier, the three ^{19}F NMR signals of **27** collapse only at 100°C to form two signals (*1*).

4. *Reactions with Sn—C Bonds*

In sharp contrast to the reactions of allyl- and cyclopentadienylsilanes with HFA [Eqs. (13)-(15)], where alcohol formation and double bond isomerization prevail, the corresponding tin systems exhibit only Sn—C bond rupture without shifting the double bond (*4*).

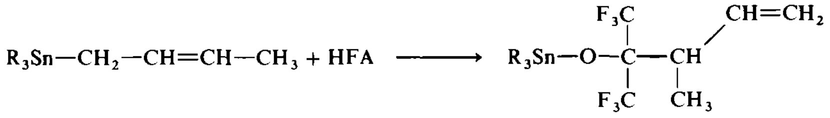


(28)

(24)

R	R′	*n*
Ph	H	1
Me	H	1, 2
Me	Me	1

An interesting skeletal rearrangement has been found in the triphenyl-2-butenylstannane/HFA system (*4*).



$$R_3Sn{-}CH_2{-}CH{=}CH{-}CH_3 + HFA \longrightarrow R_3Sn{-}O{-}\overset{F_3C}{\underset{F_3C}{C}}{-}\underset{CH_3}{CH}{-}CH{=}CH_2$$

(R = Me, Ph) (**29**)

(25)

While cyclopentadienyltrimethylstannane forms two valence isomers under the influence of HFA, the double bond in 1-indenyltrimethylstannane is not shifted (*4*).

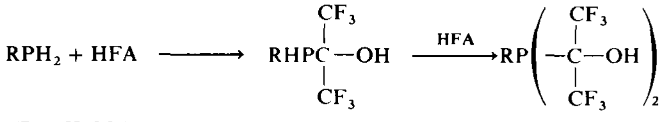
III. Reactions of HFA with Compounds of Group V Elements

A. PHOSPHORUS

HFA has been found to be a versatile reagent in phosphorus chemistry. Insertion reactions into P—E bonds (Section III,A,1, 2, 6, and 7) as well as oxidative ring formation and reactions in the coordination sphere of phosphorus (Section III,A,9) are described. Reactions involving an Si—P bond are discussed in Section II,A,6.

1. Insertion into P—H and P—O Bonds

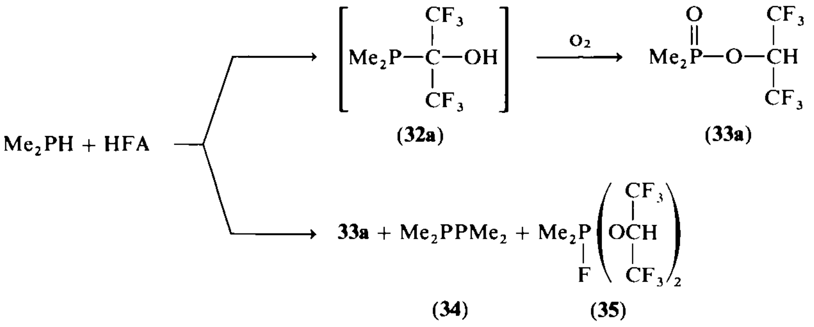
The reaction of HFA with phosphanes has been reported by Bruker *et al.* (*43*) and reinvestigated by Röschenthaler (*227*).



$$RPH_2 + HFA \longrightarrow RHP\overset{CF_3}{\underset{CF_3}{C}}{-}OH \xrightarrow{HFA} RP\left(-\overset{CF_3}{\underset{CF_3}{C}}{-}OH\right)_2 \qquad (26)$$

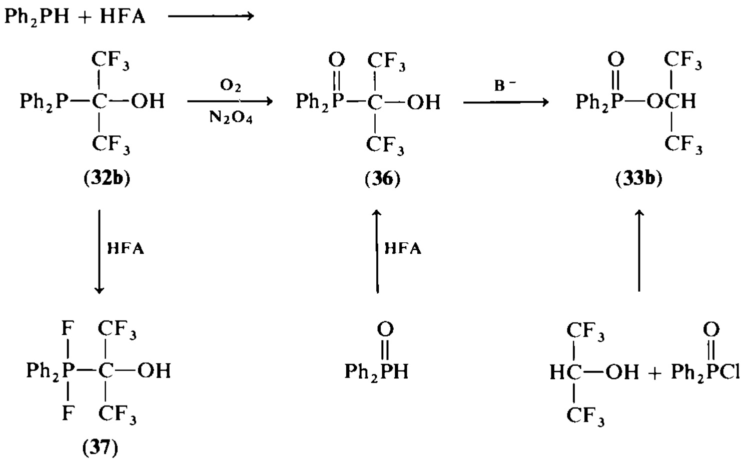
(R = H, Me) (**30**) (**31a**, R = H; **31b**, R = Me)

Both observed the monoaddition products **30**, but the phosphanediols **31** have been found only by Röschenthaler (*227*). While the methylated compound **31b** decomposes above 45°C, the phosphane derivative **31a** has been found to be air-stable. Dimethylphosphane was claimed by Bruker and co-workers (*43*) to yield the alcohol **32a**, which could not be confirmed (*227*). Instead, the oxidation product **33a** has been found together with a diphosphane **34** and fluorophosphorane **35** (*227*).



(27)

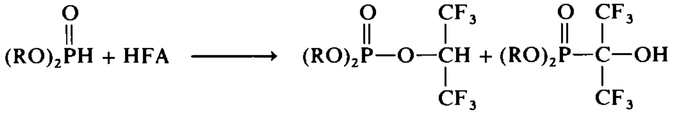
The primary addition product from HFA and diphenylphosphane (**32b**) has been unambiguously characterized by several groups (*97*, *155*). It is easily oxidized by atmospheric oxygen and dinitrogen tetroxide (*97*, *155*) to form phosphonous acid ester **33b** via phosphane oxide **36** (*155*), which can also be synthesized from HFA and diphenylphosphane oxide. Kinetics of the base-catalyzed rearrangement have been studied (*154*). Further action of HFA on **32b** yields difluorophosphorane **37** (*155*). A dipolar intermediate with tetracoordinated phosphorus has been postulated by Stockel (*260*) in the formation of **33b** and **33c** ($R = c\text{-}C_6H_{11}$).



(28)

Compound **33b** is also accessible from hexafluoropropanol and chlorodiphenyloxophosphorane (*97*). Thermal decomposition of **33b** yields tetraphenyldiphosphane and hexafluoropropanol.

Depending on the substituents, different product distributions of phosphonic **36d**–**f** and phosphoric acid esters **33d**–**f** have been found in the reaction of HFA and phosphinic acid esters (*152*).

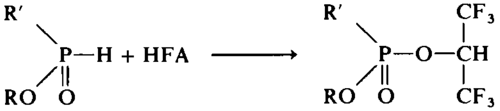


$$\mathrm{(RO)_2\overset{O}{\overset{\|}{P}}H + HFA \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{—}O\text{—}CH(CF_3)_2 + (RO)_2\overset{O}{\overset{\|}{P}}\text{—}C(CF_3)_2\text{—}OH} \qquad (29)$$

(33c–e) **(36c–e)**

	R	YIELD (%)	
		33	36
d	Me	94	6
e	Et	88	12
f	Bu	5	95

Only O-addition products **33d**, **e**, **g**, and **h** have been found by Ivin *et al.* (*149*) in a series of reactions of HFA with phosphinates and phosphinites.

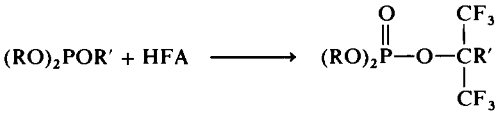


$$\mathrm{R'(RO)P(O)\text{—}H + HFA \longrightarrow R'(RO)P(O)\text{—}O\text{—}CH(CF_3)_2} \qquad (30)$$

(33)

33	**d**	**e**	**g**	**h**
R	Me	Et	*i*-Pr	Et
R′	OMe	OEt	*i*-PrO	Me

Formation of **33i** (*37*) and **33j** (*104*) from oxidative rearrangement has been reported. Triethylamine has been employed as a catalyst in the formation of **33j**. No reaction has been found with $\mathrm{P(OCH(CF_3)_2)_3}$ (*226*).

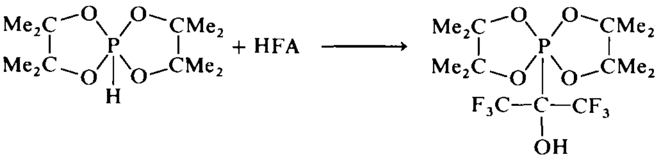


$$\mathrm{(RO)_2POR' + HFA \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{—}O\text{—}CR'(CF_3)_2} \qquad (31)$$

(33)

	33i	**33j**
R	$\mathrm{—OCMe_2CMe_2O—/2}$	$\mathrm{—OCH_2CF_2CF_2H}$
R′	$\mathrm{—OC(O)—C_6H_2Me_3}$	H

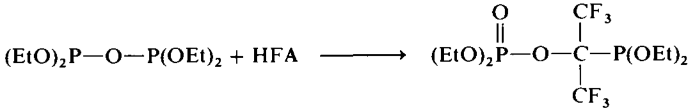
The reaction of a spirobicyclic phosphorane with HFA leads to the formation of the alcohol **38** (*113*).



(38)

(32)

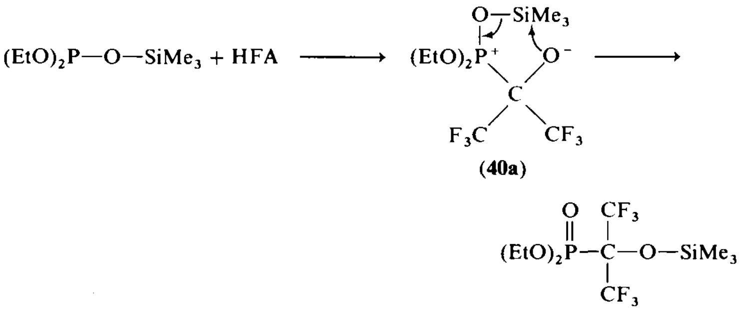
Insertion of HFA into P—O—P (*106*) and P—O—Si bonds (*161*, *211*) of phosphites results in the formation of **39** and **40**. A mechanism involving a dipolar intermediate **40a** [Eq. (34)] has been discussed for the silicon compound **40** (*161*, *211*).



$$(EtO)_2P{-}O{-}P(OEt)_2 + HFA \longrightarrow (EtO)_2\overset{\overset{\large O}{\|}}{P}{-}O{-}\underset{\underset{\large CF_3}{|}}{\overset{\overset{\large CF_3}{|}}{C}}{-}P(OEt)_2$$

(39)

(33)

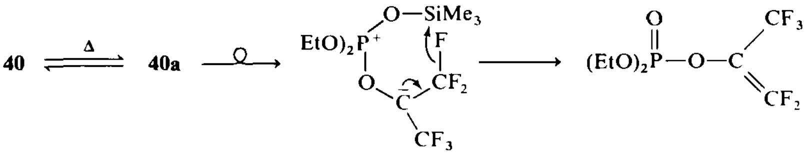


(40a)

(40)

(34)

No spectroscopic evidence for the structure of **40** (e.g., P–F coupling constants) has been reported; the mechanism has been verified by Evans *et al.* (*98*) in the reaction of silyl phosphites with a wide variety of different ketones. At elevated temperatures C—O inversion has been postulated, and a vinyl phosphate **41** is formed with elimination of trimethylfluorosilane (*161*).



(40b) **(41)**

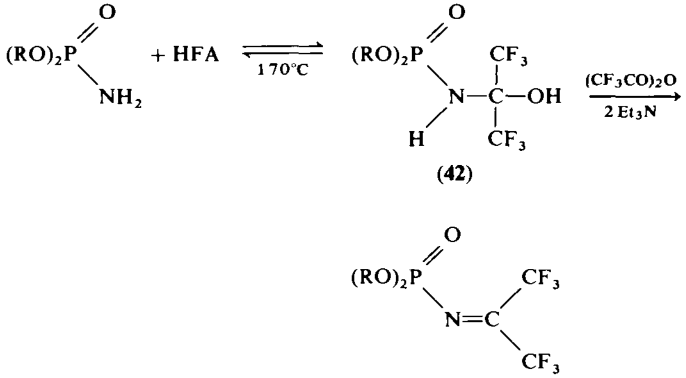
(35)

Ketal formation is observed when a pentaoxophosphorane is reacted with HFA (*251*).

2. *Reactions Involving P—N Bonds*

The reaction of the aminophosphanes *t*-Bu_2PNH_2 and F_2PNH_2 results in the formation of hexafluoroacetoneimine and phosphoric acid derivatives with and without addition of HFA. With aminodifluorophosphane, the expected formation of a 1,3,2-dioxaphospholane (see Section III,A,4) has been observed (*263*).

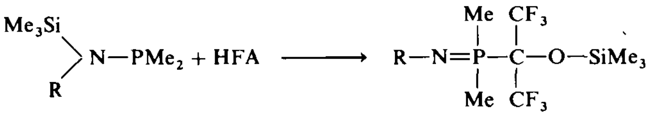
Phosphoric acid ester amides suffer insertion into the N—H bond (*170*). Dehydration of **42** with trifluoroacetic acid anhydride and triethylamine yields the ketimide **43**. Decomposition of **42** at 170°C leads to recovery of the starting material.



(42) (36)

(R = Me, Et, Pr, *i*-Pr, Bu) (43)

Silyl group migration has been observed in the reaction of silyl-substituted aminophosphanes to yield iminophosphoranes **44**. A mechanism has been discussed (*198*, *201*).

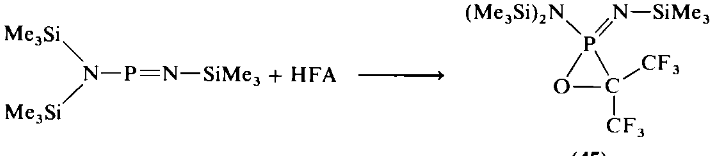


(37)

(R = SiMe₃, *t*-Bu) (44)

The reaction of HFA with tris(dimethylamino)phosphane leads mainly to the formation of tris(dimethylamino)difluorophosphorane and a smaller amount of hexamethylphosphoric acid triamide, although indirect evidence for the formation of 1,3,2-dioxaphospholanes (Section III,A,4) has been found (*217*).

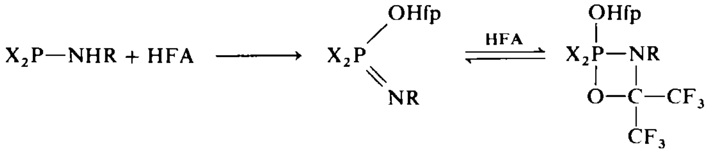
An oxaphosphirane **45** is accessible from HFA and a silylated amino-iminophosphane via [2 + 1] cycloaddition (*230*).



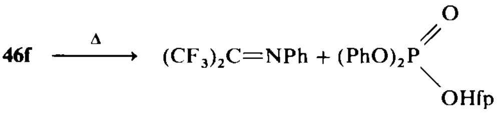
(45)

(38)

A series of oxaazaphospetidines **46**, **49**, and **51** has been synthesized, starting from primary and secondary P(III) amines. The reaction proceeds by hydrogen migration with intermediate formation of iminophosphoranes **47** (*91*, *263*), from activated iminophosphoranes (*246*, *250*) and cyanates and thiocyanates (*91*, *176*, *239*), with preceding [3 + 2] cycloaddition involving formation of a phosphorus-nitrogen double bond. Although pseudohalides of phosphorus are treated in a subsequent section, we include these examples in this section due to their analogy to the present topic.



(47) **(46)**



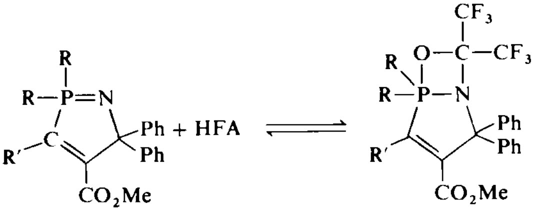
(48) **(33k)**

(39)

46, 47	a, b	c, d	e	f
R	H, Me	Me, *t*-Bu	H	Ph
X	OHfp	F	Pfp/$_2$	OPh
Reference	*106a*	*106a*	*263*	*91*

The X-ray structures of **46a** and **e** show slight distortion from trigonal-bipyramidal geometry at the phosphorus atom (*106a*, *263*). The axial positions are occupied by oxygen atoms; the oxygen-phosphorus distances are relatively short due to the electron-withdrawing effect of the CF_3 groups (*263*).

Thermal decomposition of **46f** at 130°C yields **48**, **33k**, and **47f** in reversal of its formation (*91*).



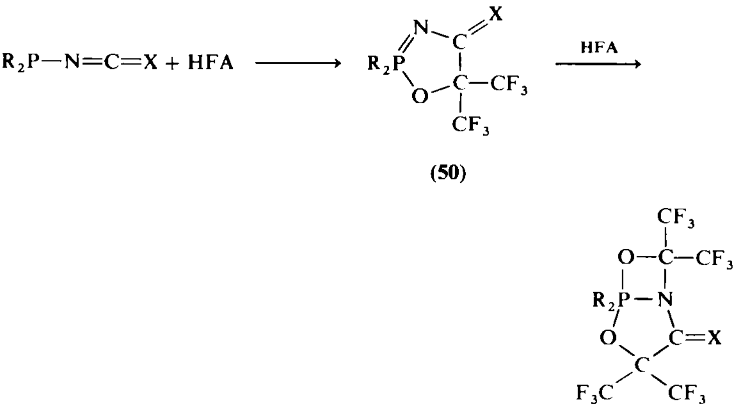
(49)

(40)

49	a	b	c
R	Ph	Me	Ph
R′	H	CO_2Me	CO_2Me

The adducts **49a**–**c** are crystalline solids, which in solution are in equilibrium with their precursors (*246*, *250*). The X-ray structure of **49b** has been reported (*250*).

Similar bicyclic phosphoranes **51** are formed in the reactions of phosphorus isocyanates and isothiocyanates with HFA (*91*, *176*, *239*) via intermediate formation of oxazaphospholinones and -thiones **50**.



(50)

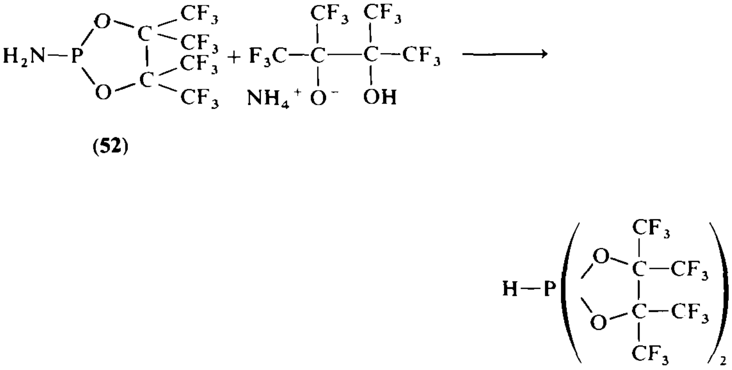
(51)

(41)

50, 51	a	b	c	d	e	f
R	OEt	OEt	OPh	NCO	NCS	OMe
X	O	S	O	O	S	O
Reference	*91*	*91*	*91*	*239*	*239*	*166*

Pudovik and co-workers (*166*) found the reaction [Eq. (41)] to stop at the stage of the five-membered ring **50f** when excess dimethoxycyanatophosphane reacts with HFA. The same bicyclic system (**51g**, R = Ph, X = S) has been found in the reaction of the $Hg(SCN)_2$—HFA adduct **192** (Section V, F) with diphenylchlorophosphane (*241*, *242*).

The reaction of monoammonium perfluoropinacolate with 2-amino-1,3,2-dioxaphospholane (**52**) provides a spirocyclic phosphorane **53** with hydrogen attached to phosphorus, with evolution of ammonia occurring (*263*).



(**52**)

(**53**)

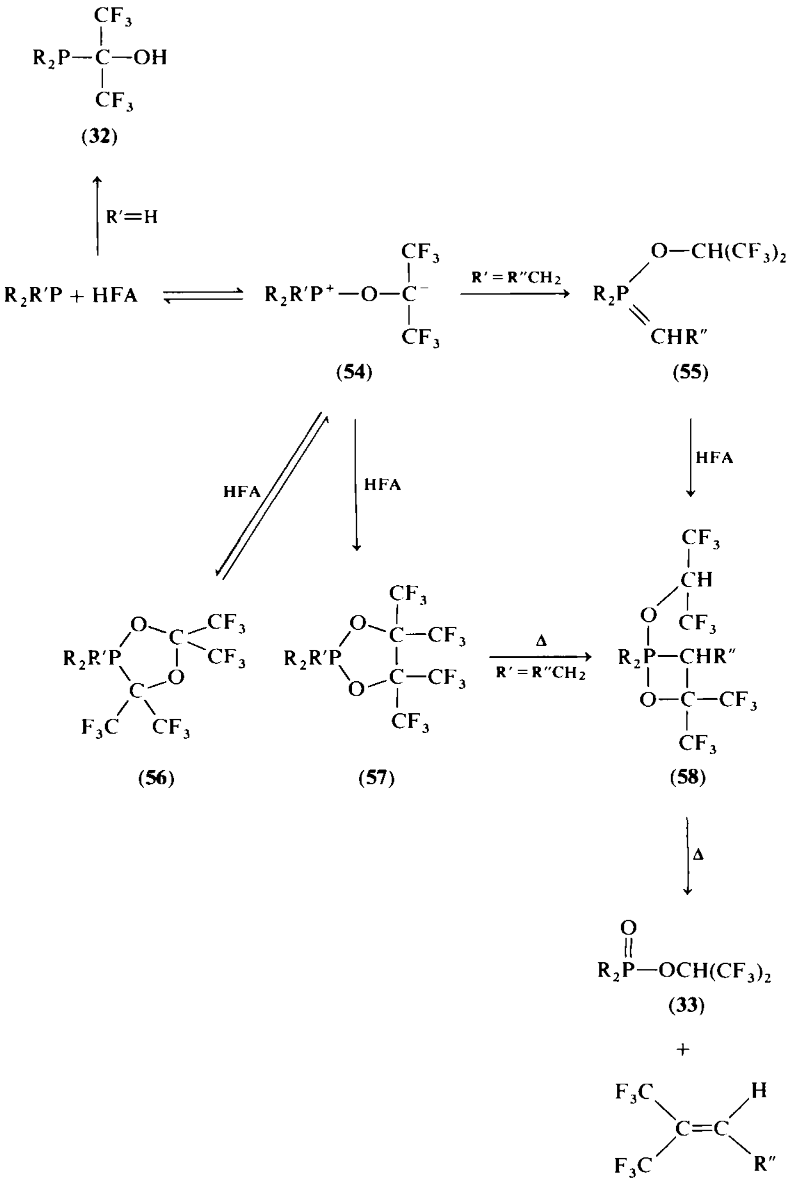
(42)

P-substituted derivatives **53a–g** have been obtained by metathesis of phosphorus(V) dihalides and dilithium perfluoropinacolate (see Section III,A,6). A similar compound, in which one ring bears methyl groups, has been prepared in an analogous fashion (*32*).

3. 1,3,4-Dioxaphospholanes

In contrast to trivalent phosphorus compounds with activated bonds, where insertion occurs, phosphanes bearing only alkyl, aryl, alkoxy, aryloxy, secondary amino, thio, and halogeno ligands are oxidized by HFA. Earlier work was reviewed by Ramirez (*216*) in 1970 and Hellwinkel (*139*) in 1972. The following scheme [Eq. (43)] shows all reactions occurring in the phosphane/HFA system.

The primary intermediates (dipolar 1:1 adducts **54**) can add another molecule of HFA to form five-membered rings. 1,3,4-λ^5-Dioxaphospholanes **56** are the kinetically favored products from reactions of trivalent phosphorus compounds with HFA, but normally rearrange below ambient temperatures to yield the thermodynamically stable 1,3,2-λ^5-dioxaphospholanes **57**.

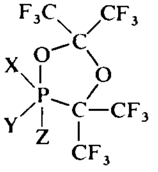


(43)

A series of stable heterocycles **56** is listed in Table I.

TABLE I

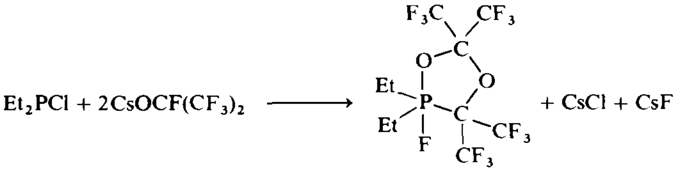
1,3,4-λ^5-DIOXAPHOSPHOLANES STABLE AT ROOM TEMPERATURE



(56)

56	X	Y	Z	Reference
a	Me	Me	F	*117, 226*
b	Me	Me	Cl	*117*
c	Me	F	F	*226*
d	Et	Et	Cl	*278*
e	Pr	Pr	Cl	*9, 278*
f	Ph	$CMe_2CMe_2CH_2$		*89, 204*
g	Ph	SCH_2CH_2O		*90*
h	OPh	OCH_2CH_2O		*32*
i	Cl	$CMe_2CHMeCMe_2$		*32*
k	Me	NMeC(O)NMe		*282, 283*
l	NMe_2	o-$C_6H_4CH_2O$		*74*

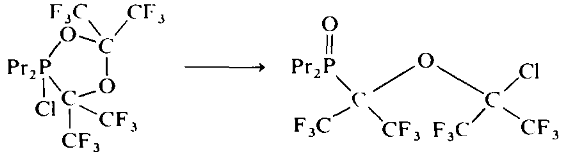
The fluoro-substituted compounds **56a** and **c** are the only examples where all three isomers **56**, **57**, and **58** are formed together under identical conditions (*226*). Compounds **56a–e** are converted into the corresponding oxaphosphetanes **58** by gentle heating. The isomeric five-membered rings **57** are also formed in the case of **56a**, and **c**; **56f** and **h** behave similarly. The spirophosphoranes **56g** and **56k** show remarkable stability: Decomposition occurs only at 150°C (*90, 283*). The structure of **56g** with two oxygen atoms occupying the axial positions has been confirmed by X-ray diffraction (*89*). Compound **56i** slowly regenerates the starting materials at room temperature (*32*). Ligand exchange reactions with **56c** yield derivatives otherwise inaccessible (*9, 278*). Compound **56m** can be synthesized from diethylchlorophosphane and cesium perfluoropropylate at room temperature [Eq. (44)], as well



(56m)

(44)

as by halogen exchange in **56d** with CsF (*278*). The *n*-propyl derivative **56e** slowly rearranges at ambient temperature to form **59** (*278*).


(45)

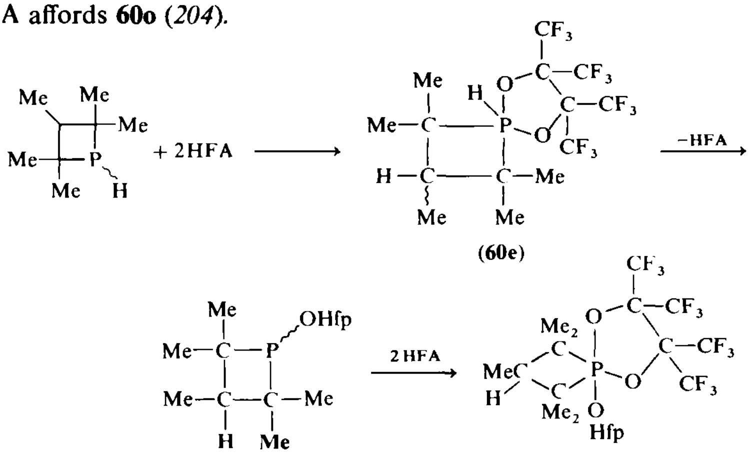
(56e) **(59)**

4. 1,3,2-Dioxaphospholanes

The majority of the publications in the field of oxidative addition of HFA to tertiary phosphanes deal with the formation and properties of 1,3,2-λ^5-dioxaphospholanes **57** (*60, 61*). These compounds are generally stable when the α carbon atoms do not bear hydrogen atoms. Heterocycles with α hydrogen atoms are stable up to about 70°C; at this temperature the isomeric phosphetanes are formed. The syntheses of some sterically hindered phosphoranes require drastic conditions.

The compounds **57** (*60, 61*) formed according to Eq. (43) are listed in table II; the substituent Z normally occupies the second axial position, and the perfluoropinacolyl bridge has—with exceptions—axial-equatorial conformation. Spirocyclic phosphoranes **60** are shown in Table III.

The reaction of HFA with 2,2,3,4,4-pentamethyl-λ^3-phosphetane has been investigated (*204*). A crystalline 2:1 adduct has been obtained. NMR studies indicate two isomers of the dioxaphospholane **60e** relative to the position of the 3-methyl group. Compound **60e** slowly decomposes to yield diastereomeric phosphites **62** with the same isomeric composition. Further action of HFA affords **60o** (*204*).



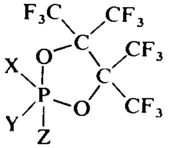
(60e)

(46)

(62) **(60o)**

TABLE II

1,3,2-λ^5-DIOXAPHOSPHOLANES



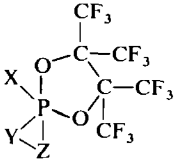
(57)

57	X^a	Y	Z	References
	i. X = Y = Z			
a-j		Me, Et, Bu, Ph, Tpo, OMe, OEt, OPh, OCH$_2$CF$_2$CF$_2$H		*97, 104, 110–112, 151, 162, 218, 221–223, 244, 259, 262*
	ii. X = Y ≠ Z			
k-m, be, bf	Me		Ph, F, OSiMe$_3$ Cl, N$_3$	*222, 226, 277*
n, o	Et		Ph, OMe	*97, 218, 222, 223*
p, q	*t*-Bu		Cl, OHfp	*75*
r-u	Ph		OEt, OHfp, Hfp, Cl	*97, 151, 221*
v, w	OMe, O*i*-Pr		F	*88, 119*
x, y	OEt, NEt$_2$		Cl	*278*
	iii. X ≠ Y = Z			
z-ai	Me, Et, *t*-Bu, Ph, OMe, NEt$_2$, NAll$_2$, NTmc$_2$, N(*t*-Bu)SiMe$_3$, N(SiMe$_3$)$_2$		F	*75, 88, 92, 115, 116, 119, 121, 232*
aj-am	Me		Ph, Tpo, OMe, OHfp	*97, 218, 226, 262*
an-ao	Et		Ph, OMe	*97, 218*
ap-as	Ph		OMe, OBuO, OHfp, OPh	*97, 151, 212, 218, 222, 223*
at-au	NMe$_2$, NEt$_2$		OHfp	*107*
av	C(CF$_3$)$_2$OP(O)(OEt)$_2$		OEt	*106*
	iv. X ≠ Y ≠ Z			
aw	Me	—(CH$_2$)$_3$—	OSiMe$_3$	*166*
ax, ay	Me	*t*-Bu	OHfp, Cl	*68*
az	Me	OEt	Cl	*184*
ba	*t*-Bu	OHfp	F	*57*
bb, bc	Ph, C$_6$H$_4$-*p*-Me	NEt$_2$	F	*68*
bd	OEt	NEt$_2$	Cl	*184*
bg-bi	*t*-Bu	NEt$_2$	F, Cl, OHfp	*107a*

[a] Tpo, 4-oxy-3,3,5,5-tetramethylpiperidyl; All, allyl; Tmc, 2,2,6,6-tetramethylcyclohexyl.

TABLE III

SPIROCYCLIC PHOSPHORANES[a]

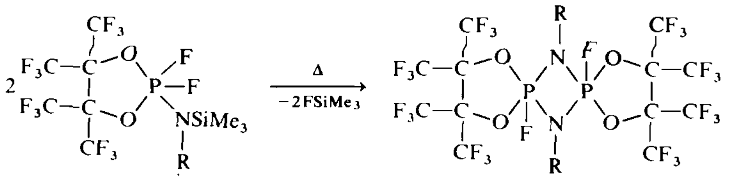


(60)

60	X	Y-Z	Reference
a	Ph	$CH_2CH_2CH_2$	*204*
b	Ph	$CH_2CMe_2CH_2$	*204*
c, d	Ph, C_6H_4-*p*-Br	$CMe_2CH_2CMe_2$	*89, 144*
e-t	H, Me, *i*-Pr, CH=CMe_2, *t*-Bu, 2-C_4H_4O, Ph, C_6H_4-*p*-Br, C_6H_4-*p*-OH, Cl, OHfp, OPh, NMe_2, $N(CH_2)_4$, $N(i\text{-}Pr)_2$, NMePh	$CMe_2CHMeCMe_2$	*89, 204, 205, 266*
u, v	OPh, SPh	OCH_2CH_2O	*32*
w-aa	OPh, OC_6H_4-*p*-Br, NMe_2, SPh, SePh	$OCMe_2CMe_2O$	*32, 159*
ab-ad	OPh, OC_6H_4-*p*-Br, NMe_2	*o*-OC_6H_4O	*32*
ae-ag	Ph, OPh, NMe_2	*o*-OC_6H_3ClO	*32*
ah	Ph	$OC(CF_3)_2C(CF_3)_2O$	*231*
ai	OPh	OCH_2CH_2NMe	*33*
aj-al	OPh, NMe_2, SPh	$NMeCH_2CH_2NMe$	*32, 33, 217*
am	OC_6H_4-*p*-Br	SCH_2CH_2O	*33*
an	OC_6H_4-*p*-Br	*o*-SC_6H_4O	*33*
ao	OPh	$O(CH_2)_3O$	*33*
ap	OC_6H_4-*p*-Br	$O(CH_2)_3NMe$	*33*

[a] Y-Z member of a ring, Z axial.

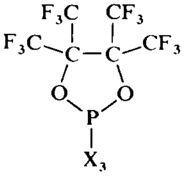
In addition to the compounds **57**, **60**, and **61** listed in Tables II-IV, further 1,3,2-λ^5-dioxaphospholanes are accessible via halogen exchange reactions (*106, 115, 229, 230, 232, 263, 263a, 277*) (*vide infra*), oxidative addition of α,β-diketones to λ^3-dioxaphospholanes (*32*), hydrolysis of silylamino compounds with HCl to yield unsubstituted amines (*121*), and thermal elimination of Me_3SiF from the silylaminofluoro derivatives **57ah** and **57ai** (*115, 118*).



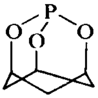
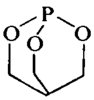
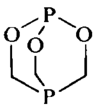
(47)

(57ah, 57ai) **(60aq**, R = *t*-Bu; **60ar**, R = $SiMe_3$)

TABLE IV
Phosphorane Cage Compounds

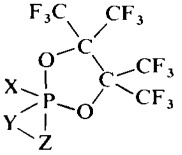


(61)

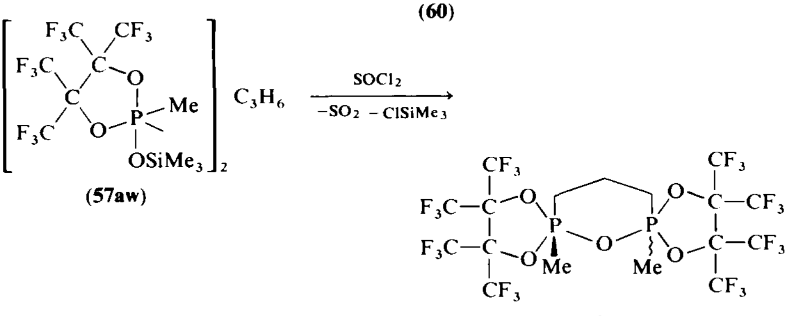
PX_3			Reference
 **(61a)**	 **(61b)**	 **(61c)**	*219, 223, 268, 269*

The X-ray structure of **60ar** has been reported and shows all rings having axial-equatorial conformation. This geometry is retained through pseudorotation processes, as shown from NMR studies (*118*). The chlorinated *t*-butyl-substituted derivative **60as** has been obtained similarly (*263a*) (*vide infra.*). Two isomers of the tricyclic system **60at**, in which phosphorus and nitrogen bear methyl groups, arise from photochemical nitrogen evolution via a tetracoordinated intermediate from azide **57bf** (*19a*).

The action of $SOCl_2$ on the bridged diphosphorane **57aw** yields a novel spirocyclic system (**60au**). The structure has been determined by X-ray analysis (*247*). All axial positions are shown to be occupied by oxygen atoms.



(60)

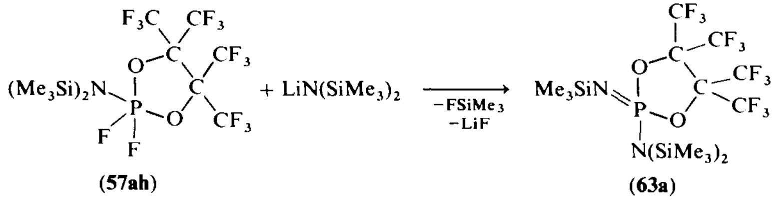


(57aw)

(60au)

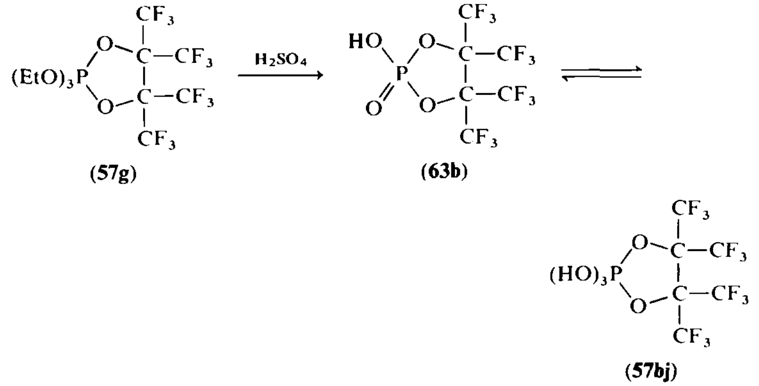
(48)

Four-coordinated phosphorus atoms are found in **63a** (*230*) [Eq. (49)] and **63b** (*110*) [Eq. (50)].



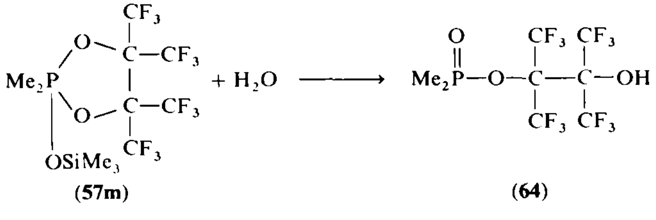
(57ah) **(63a)** (49)

Hydrolysis of **57g** yields the phosphoric acid ester **63b**, which on exposure to air forms the orthophosphoric acid **57bj**. Prolonged heating of **57bj** affords perfluoropinacol (*110*).



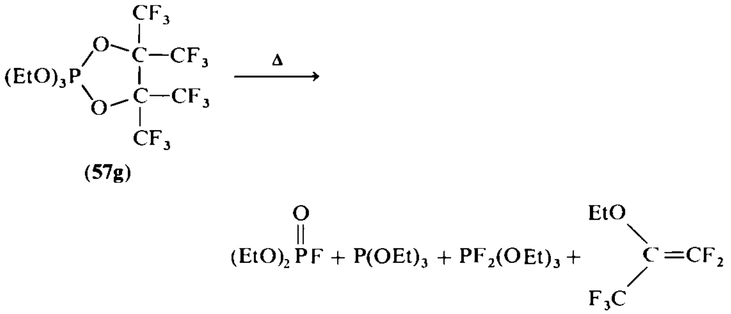
(57g) **(63b)** **(57bj)** (50)

The hydrolysis of various 1,3,2-dioxaphospholanes has been studied (*151, 212*) and is found to be a multistep process having a preliminary equilibrium with negative heat of reaction. Hydrolysis of **57m** proceeds via ring opening (*277*).



(57m) **(64)** (51)

Different behavior has been observed on heating dixoaphospholanes. With a few exceptions compounds bearing hydrogen on a carbon atom adjacent to phosphorus rearrange to 1,2-oxaphosphetanes (see Section III,A,5). At 160°C, **57d** (X = Y = Z = Ph) dissociates into the starting materials (*220*). Compound **57g** (X = Y = Z = OEt) loses one molecule of HFA at 165°C and forms several decomposition products (*220*)

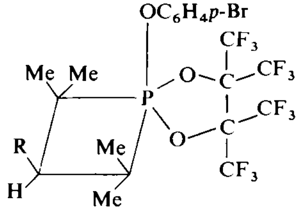


(57g)

(52)

Pseudorotation processes have been investigated by means of ESR in the case of the paramagnetic Tpo derivatives **57e** and **57ak** (*262*) and dynamic ^{19}F NMR studies. Values of $\Delta G^\ddagger$ have been determined for a number of dioxaphospholanes and are strongly dependent on substitution. Small alkyl and amino substituents (also cyclic) provide low isomerization barriers ($\Delta G^\ddagger \approx 40$ kJ mol^{-1}); the CF$_3$ groups become equivalent at $<0°C$ (*159, 204, 220, 223, 266*). Steric hindrance and conformational rigidity make pseudorotation more difficult: in a series of spiro- and polycyclic derivatives (*60, 61*) $\Delta G^\ddagger$ values of >90 kJ mol^{-1} have been found, as manifested in the nonequivalence of the CF$_3$ groups at 180°C (*32, 89, 204, 223, 268, 269*). Exchange of O and S in bridging phenylene ligands in **60ac,an** has no effect on the $\Delta G^\ddagger$ value (*33*). ^{13}C NMR spectroscopy of difluorodioxaphospholanes **57z**, **57ab–ad**, **57ai**, and **74g** have been reported (*116*).

In contrast to the trigonal-bipyramidal geometry of most derivatives, the spirophosphoranes **60d** and **60k** have a square-planar structure, as seen from X-ray analysis (*144*).

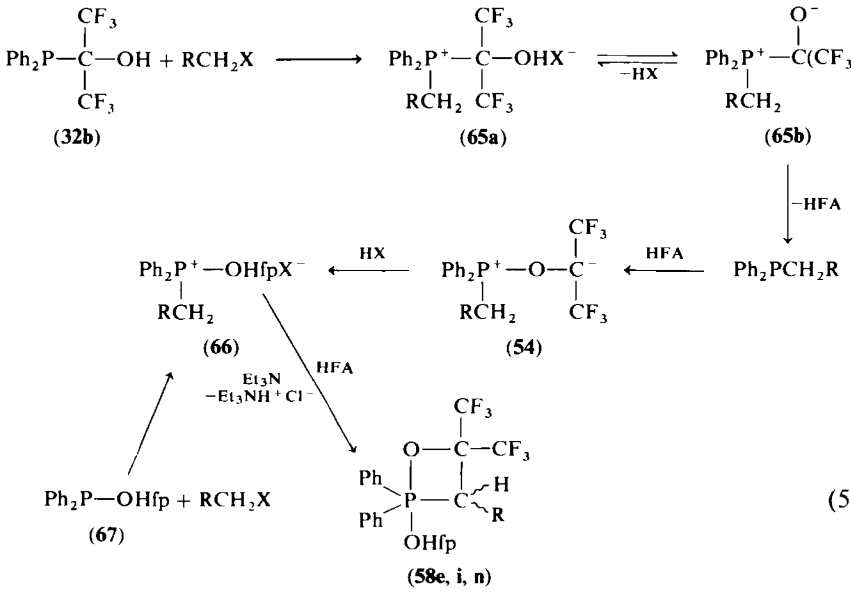


(R = H, Me) (60d, k)

5. *1,2-Oxaphosphetanes*

According to Eq. (43) the betaine **54** has a second possibility of stabilization. This is hydrogen migration from an α carbon to the carbonyl carbon bearing the negative charge with formation of a P=C double bond. The so-formed species (**55**) cannot be compared to stable Wittig reagents, which normally (cf. Section III,A,9) are not reactive toward HFA. No examples in which these intermediates (**55**) have been isolated are given in the literature. [2 + 2] Cycloaddition with HFA yields 1,2-λ^5-phosphetanes **58** with the oxygen ring atom always in an axial position.

A second access to these four-membered ring systems is the action of alkyl halides on the adduct of diphenylphosphane with HFA (**32b**) [Eq. (53)] (*96*).



(53)

58	e	i	n
R =	H	Me	Ph
X =	I	I	Br

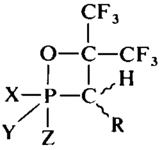
The extremely stable phosphonium salts **66** have been synthesized via the alternate route using diphenyl phosphite **67**, which is accessible from diphenylchlorophosphane and hexafluoroisopropanol, thus proving the last step of the reaction (*96*).

Phosphetanes available either from phosphanes and HFA or by thermal ring contraction of the corresponding dioxaphospholanes **56**, **57**, and **60** are listed in Table V.

With X ≠ Y and R ≠ H, formation of isomers has been observed; equilibration occurs on heating. Pseudorotation involves a trigonal-bipyramidal intermediate with the four-membered ring in the diequatorial position (*221*).

TABLE V

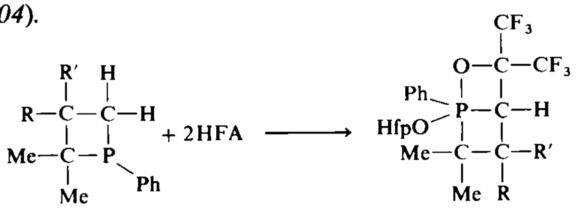
$1,2\text{-}\lambda^5$ – OXAPHOSPHETANES



(58)

58	X	Y	R	Reference
i.		**Z = OHfp**		
a	Me	Me	H	*69, 221*
b	Me	Ph	H	*69*
c	Me	OHfp	H	*226*
d	*t*-Bu	OHfp	H	*75, 92*
e	Ph	Ph	H	*69*
f	OMe	OMe	H	*69*
g	OHfp	OHfp	H	*226*
h	Et	Et	Me	*69, 218, 221*
i	Et	Ph	Me	*69, 218, 221*
j	Et	OMe	Me	*69, 218*
k	Et	OHfp	Me	*9*
l	Ph	Ph	Me	*69, 221*
m	*n*-Bu	*n*-Bu	*n*-Pr	*69*
n	OMe	OMe	Me	*69, 218*
	Y	Z	R	
ii.		**X = OHfp**		
o, p	Me	F, Cl	H	*117, 226*
q	*t*-Bu	Cl	H	*75, 92*
r, s	$CMe_2CHMeCMe_2$		H, Ph	*204*
t	F	F	H	*226*
u	Et	Cl	Me	*9*
v	OMe	OMe	Me	*69, 218*

Two fused four-membered rings are the main feature of the compounds **68a–c** (*89, 204*).



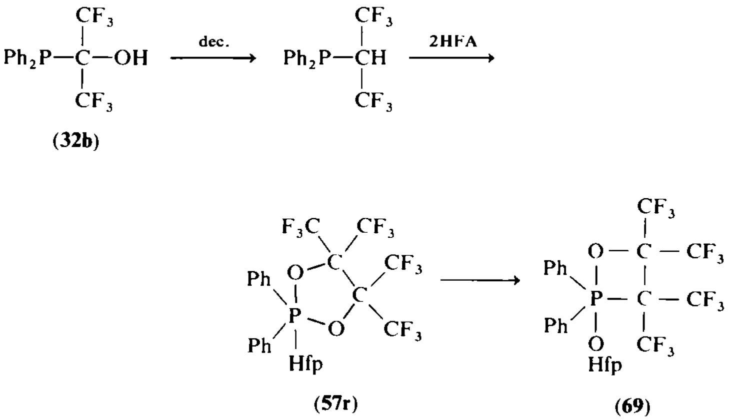
(54)

(R, R′ = H, H; H, Me; Me, Me)

(68)

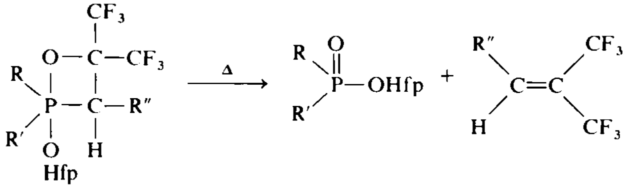
Compound **68c** is available from thermal rearrangement of dioxaphospholane **60k** (*204*).

Decomposition of the insertion product **32b** of HFA with diphenylphosphane [Eq. (28)] yields, in addition to the oxidation products **33b**, **36**, and **37**, tetraphenyldiphosphane and two cyclic compounds **57r** and **69** (*97*).



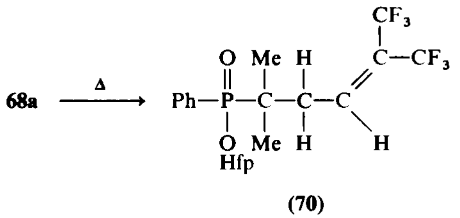
(**32b**) (**57r**) (**69**) (55)

The 1,2-λ^5-oxaphosphetanes **58** and **68** can be considered stable intermediates of the Wittig reaction. Pyrolysis of the parent compounds yields the corresponding olefins and oxophosphoranes, respectively, which have been reported in several publications (*204*, *220*, *221*, *226*).



(**58**) (**33**) (56)

Kinetics of formation and decomposition of **58** have been investigated (*221*). Pyrolysis of **68a** yields an ω-unsaturated phosphonous ester derivative **70** (*204*).



(**70**) (57)

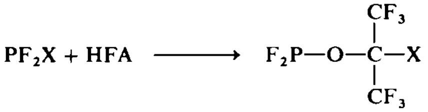
The tris-OHfp substituted oxaphosphetane **58g** is thermally stable up to 190°C (*226*).

Alcoholysis of **58g** has been studied (*218*). NMR studies show that the exchange of equatorial groups proceeds via a six-coordinated intermediate. Isomerization of equatorial substituents X and Y to R occurs at 120–140°C. Only one ^{19}F NMR signal for **58v** is observed at room temperature (*218*), which suggests that pseudorotation processes are rapid on the NMR time scale.

The X-ray structure of **58l** (X = Y = Ph, Z = OHfp, R = Me) has been reported. The two oxygen atoms are in axial positions (*183*).

6. *Reactions Involving Phosphorus–Halogen Bonds*

Only two examples are known in which HFA inserts into a phosphorus–halogen bond. While PF_2Cl, PF_3, and POF_2Br are inert even at elevated temperatures, insertion into the P—X bond is observed in PF_2Br and PF_2I (*177*).

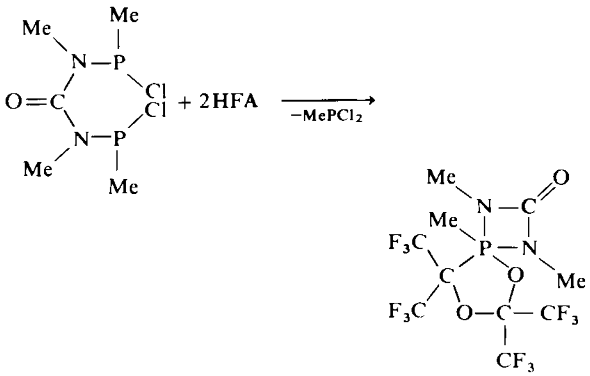


$$PF_2X + HFA \longrightarrow F_2P{-}O{-}\overset{CF_3}{\underset{CF_3}{C}}{-}X \qquad (58)$$

(X = Br, I) **(71)**

In contrast to reactions of other ketones with PCl_5, a temperature of 230°C is required to form 2,2-dichlorohexafluoropropane. The high activation energy might be due to the difficulty of coordinating the phosphorus atom by the oxygen atom of HFA (*100*).

Attempted oxidative addition of a urea-bridged diphosphane according to Eq. (43) with HFA leads to the spirophosphorane **56k** (*282*, *283*).



(59)

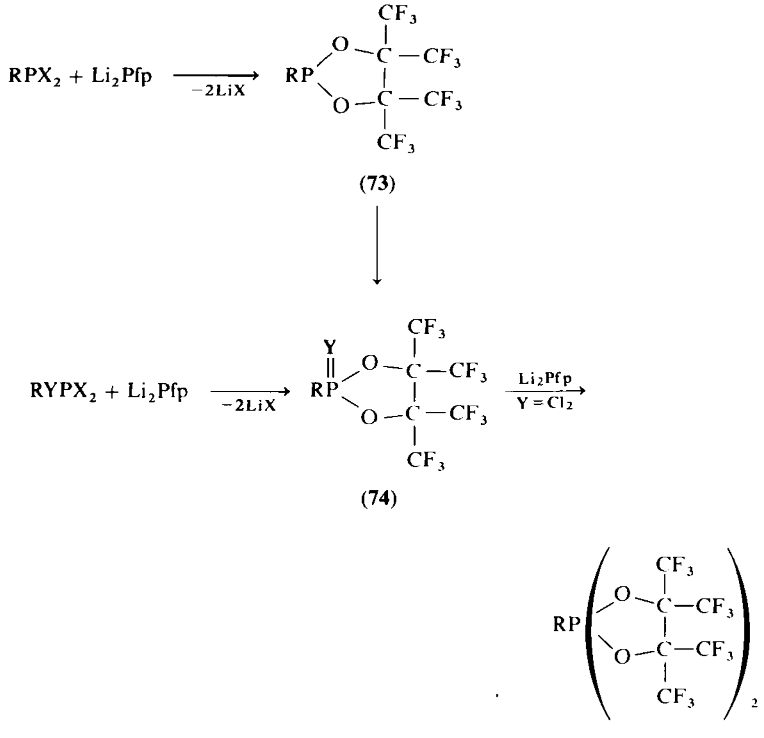
(56k)

Pyrolysis of the urea yields a 1,3,2-diazaphosphetanone, which is the actual precursor for the oxidation. The X-ray structure of **56k** shows nitrogen and oxygen to occupy the axial positions (*283*).

Most reactions of halophosphorus compounds do not involve direct attack of HFA. However, the reduced species dilithio perfluoropinacolate, accessible from HFA and lithium metal, is used as a precursor for λ^3- and λ^5-dioxaphospholanes [Eq. (60)] (Table VI).

λ^3-Dioxaphospholanes show no inversion at the phosphorus atom, which can be seen in the nonequivalence of the CF_3 groups (*273*). λ^3-Dioxaphospholanes **73** can be oxidized with halogens to form λ^5-dioxaphospholanes **74** (*228*). Exchange of the halogens in **73a–c** with suitable reaction partners (e.g., $LiNH_2$) yields substituted λ^3-phospholanes [e.g., **73g** (*263*)] (see also Section III,A,2).

Interestingly, POF_3 and $POBr_3$ yield not the tetracoordinated oxophosphoranes, but rather the pentacoordinated trihalogeno-λ^5-dioxaphospholanes, which is in sharp contrast to the formation of the chloro derivative **74i** (*228*).



(73)

(74)

(53a–g)

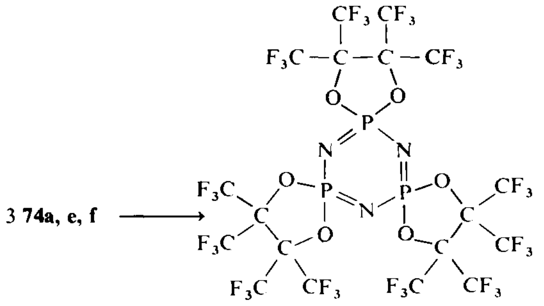
(60)

TABLE VI

1,3,2-DIOXAPHOSPHOLANES BY METATHESIS WITH PERFLUOROPINACOLATE

Compound	R		Reference
73a-**c**	F, Cl, Br		*228*
73d	OEt		*279*
73e	Ph		*64*
73f	CF_3		*273*
73g	NH_2		*263*, *263a*
73h-**l**	NMe_2, NEt_2, NH-*t*-Bu, $NHSiMe_3$, $N(SiMe_3)_2$		*263a*
53, **74**	R	Y	
a-**f**	NH_2, NMe_2, NEt_2, NH-*t*-Bu, $NHSiMe_3$, $N(SiMe_3)_2$	2Cl	*263a*
g	Ph	2F	*231*
h	OHfp	2Et	*9*
i	Cl	O	*228*
j-**l** (R = Y)	F, Cl, Br		*228*

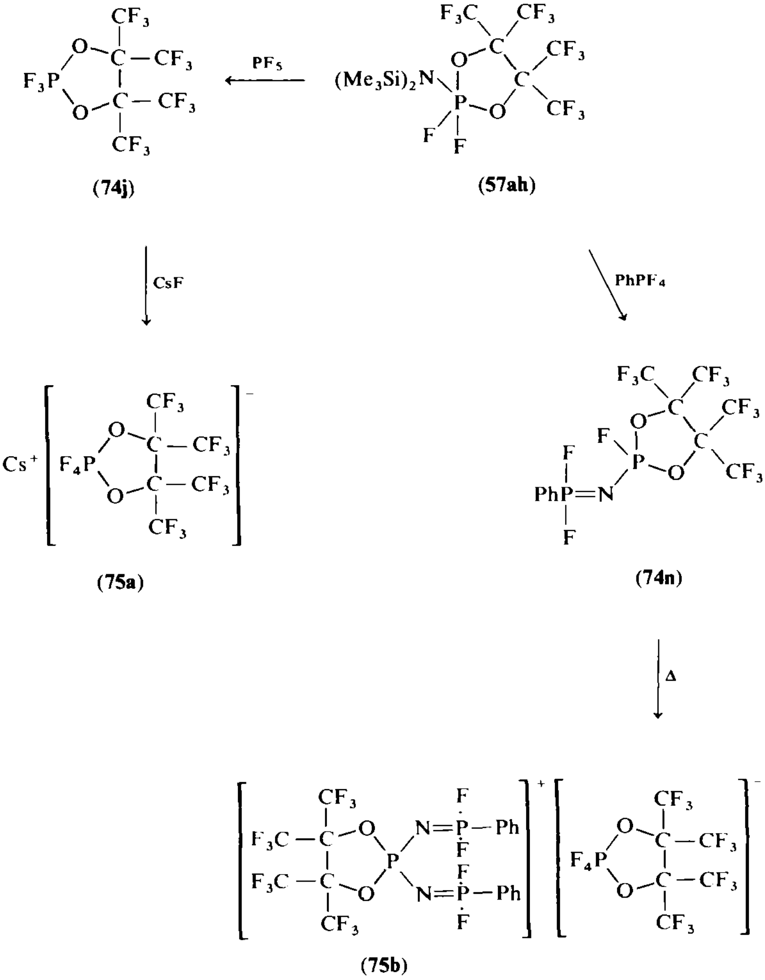
Thermolysis of **74d** yields a tricyclic system **60as** (see Section III,A,4). The derivatives **74a, e,** and **f** with two leaving groups on the nerogen atom form the phosphazene derivative **74m** on prolonged standing (*263a*) or heating in a sealed tube at 75°C (*263*).



(**74m**)

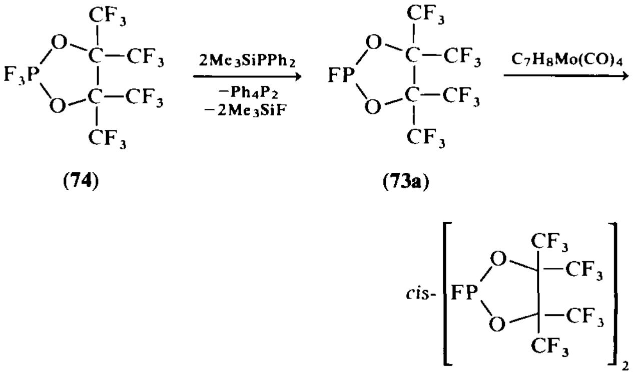
(61)

The trifluoro-substituted derivative **74j** is accessible via fluorine exchange in **57ah** with PF_5 (*229*).



(62)

On treatment with CsF, **74j** yields the salt **75a** (*119*). The same anion together with a cation containing a dioxaphospholane ring **75b** has been synthesized from thermolysis of the aminoiminodiphosphorane **74n** (*229*). Compound **74j** forms a stable donor-acceptor complex with trimethylphosphane (*119*). Reduction of **74j** with trimethylsilyldiphenylphosphane affords the λ^3-dioxaphospholane **73a**, which serves as a phosphane ligand in the molybdenum complex **76** (*229*). The phosphane ligands are in cis-positions.



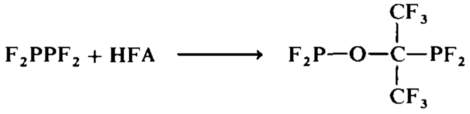
(74) (73a)

(76)

(63)

7. *Reactions with P—P Bonds*

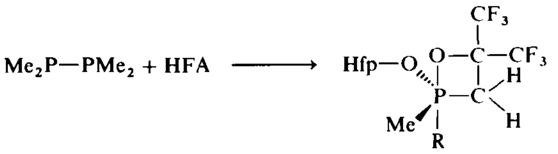
Only one report deals with insertion into a P—P bond. Tetrafluorodiphosphane adds one molecule of HFA to form 77 (*30*).



$$F_2PPF_2 + HFA \longrightarrow F_2P{-}O{-}C(CF_3)_2{-}PF_2 \qquad (64)$$

(77)

Röschenthaler and co-workers (*120*, *122*) have investigated the action of excess HFA on tetramethyldiphosphane. The resulting 1,2-oxaphosphetanes **58c,o,w** and their relative conformations have been studied with NMR.



(65)

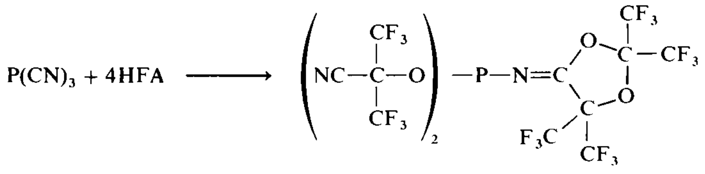
[R = F, OHfp, OC(CF$_3$)$_2$PMe$_2$] (**58c,o,w**)

Attempted reaction of the cyclic diphosphane 1,3,4,5-tetramethyl-1,3,4-λ^3,5-λ^3-diazadiphospholidinone with HFA did not result in oxidative addition; the complex mixture has not been separated (*283*).

8. *Insertion and Addition Reactions with Pseudohalides*

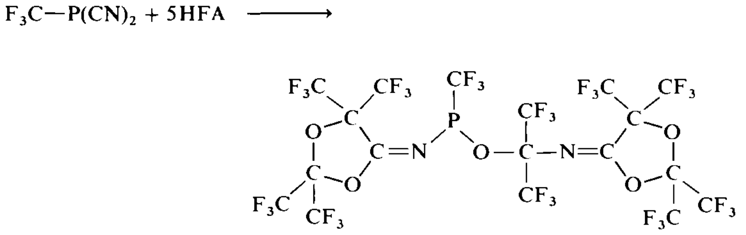
Depending on the substituents, a variety of reaction types have been observed in the reaction of HFA and pseudohalides of phosphorus(III). Most reactions do not proceed in the absence of a basic catalyst, of which triethylamine has proved the best. This catalyst is probably responsible for a nitrile-isonitrile equilibrium in solution; the formation of five-membered rings has also been found with organic isonitriles (*188*).

Insertion into two P—C bonds and isonitrile cycloaddition occur with phosphorus tricyanide (*240*).


(66)

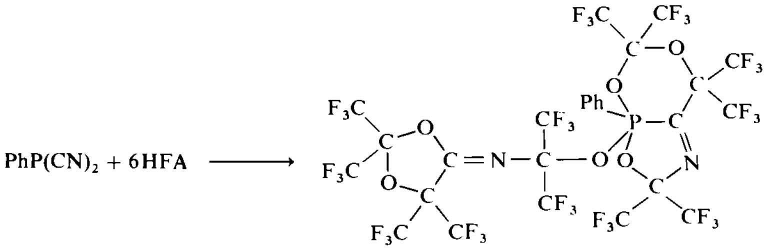
(78)

Substitution of one cyano group with a trifluoromethyl group and reaction with excess HFA lead to the formation of a chiral phosphane. The X-ray structure determination (**79**) shows only one enantiomer to be present in the solid state (*240*).


(67)

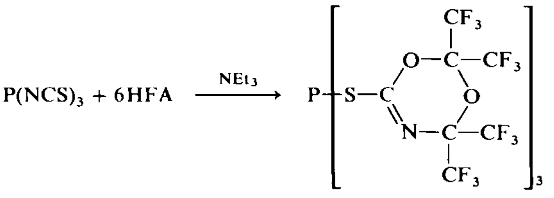
(79)

Again, an entirely different product geometry has been found in the reaction of phenyldicyanophosphane with HFA. X-Ray structure analysis of **80** shows the two cyclic oxygen atoms to occupy the axial positions (*241*).


(68)

(80)

Triisothiocyanatophosphane reacts with HFA, with complete isomerization of all ligands and formation of three dioxazine rings, in the presence of triethylamine as a catalyst (*240*).



(69)

(81a)

Uncatalyzed reactions of isocyanato- and isothiocyanatophosphanes [Eq. (41)] have been mentioned in Section III,A,2. The structure assignment of **81a** has been made on the basis of analogy with the homologous arsenic compound (**81b**), the X-ray structure of which has been determined.

9. Reactions with P—C Multiple Bonds and C—C Multiple Bonds Attached to Phosphorus

Wittig reactions have been found in several cases when HFA reacts with substituted methylenephosphoranes (*209*, *213*, *245*, *249*), by analogy with the

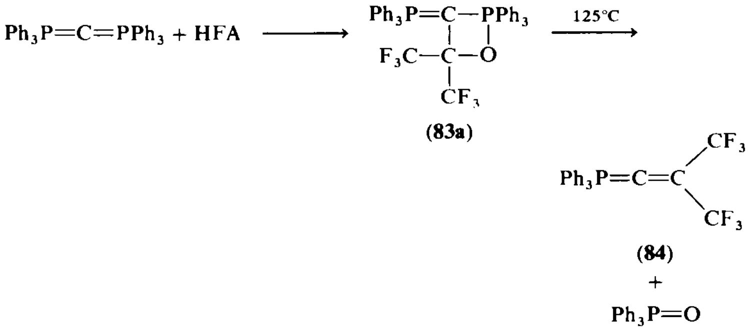
$$\mathrm{Ph_3P{=}CHR + HFA \longrightarrow Ph_3PO + (CF_3)_2C{=}CHR} \qquad (70)$$

(82)

[R = C(O)Me (*209*); CN, CO_2Me, COPh (*245*); CH_2SiMe_3 (*249*); SR′ (R′ = Me, Ph, CH_2Ph) (*213*)]

thermal decomposition of some 1,2-oxaphosphetanes (**58**) [Eq. (70)] (see Section III,A,5). Similarly, a phosphonium salt as a precursor of a steroid Wittig reagent yields partially fluorinated desmosterol (*141*).

The intermediate of a Wittig reaction has been isolated (*26*) and structurally characterized (*60*) from the reaction of HFA with a carbodiphosphorane.

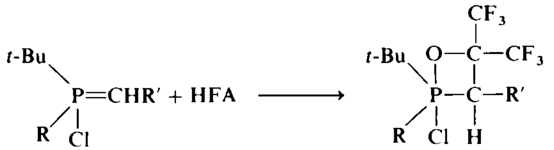


(83a)

(84)

(71)

The P—C bonds of **83** are essentially equivalent, suggesting contribution of polar forms. An extremely long P—O bond in contrast to **58l** indicates open chain mesomeric structures, stable due to electron delocalization (*60*). At 125°C a Wittig reaction occurs, and **84** is formed (*26*). The same type of [2 + 2] cycloaddition has been found with a series of *P*-(chloro)alkylidenephosphoranes. The oxaphosphetanes **83b-d** thermally eliminate hydrogen chloride to yield vinyloxophosphoranes (*165a*).



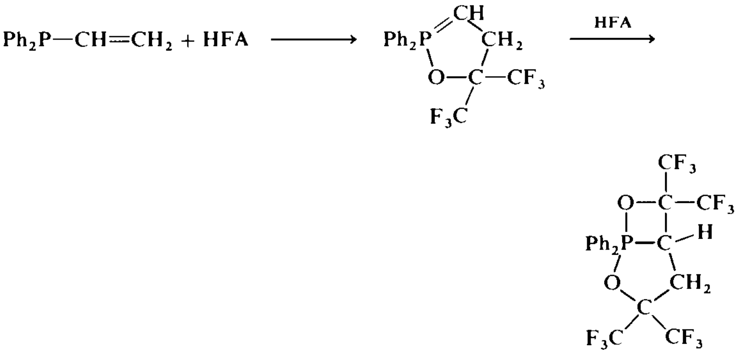
(83b-d)

(71a)

	b	**c**	**d**
R	*t*-Bu	Et_2N	Et_2N
R'	H	H	Me

No reaction has been observed with compounds containing a carbon-phosphorus triple bond (*290*).

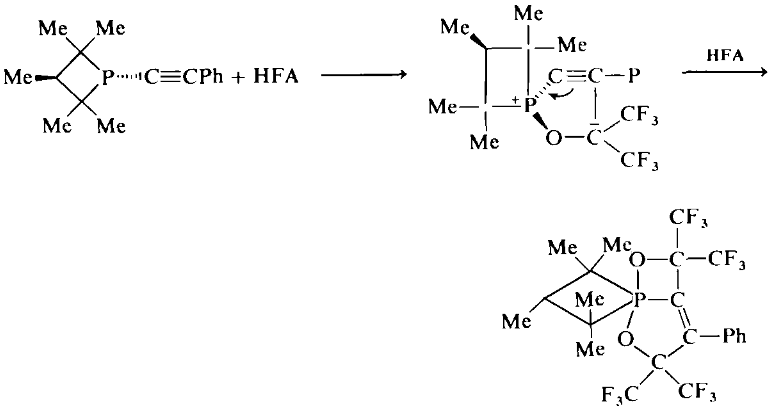
In analogy to the formation of **51** (Section III,A,2), diphenylvinylphosphane yields a bicyclic system **85** (*91*).



(85)

(72)

A similar dehydrated ring system **86** is accessible from 1-phenylethinyl-2,2,3,4,4-pentamethylphosphetane (*10*). A mechanism [Eq. (73)] has been reported. The X-ray structure of **86** shows the two oxygen atoms to occupy the axial positions (*10*).



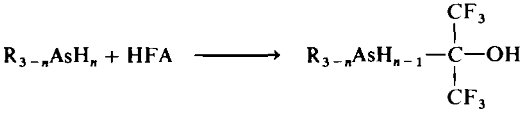
(86)

(73)

B. ARSENIC AND ANTIMONY

1. *Insertion and Addition Reactions*

Only a few reports deal with reactions of arsenic and antimony compounds with HFA. Several reports describe insertion of HFA into As—H bonds (*43*, *72*, *155*). In contrast to the heavier group IV elements, insertion leads to the formation of 2-arsanoperfluoropropanols **87**. This difference can be explained by assuming nucleophilic attack by the arsenic lone pair on the highly electrophilic carbonyl carbon.

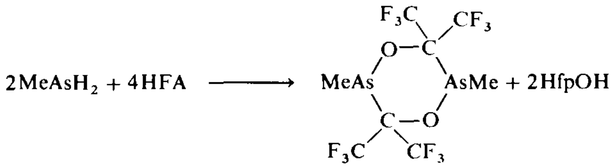


$$R_{3-n}AsH_n + HFA \longrightarrow R_{3-n}AsH_{n-1}\text{—}\underset{CF_3}{\overset{CF_3}{C}}\text{—}OH \qquad (74)$$

(87)

[R = Me, n = 3 (*43*), 2, or 1 (*72*); R = Ph, n = 1 (*155*)]

Reaction of two molecules of HFA with methylarsane probably yields a 1,4,2,3-dioxadiarsenane (**88**) with release of hexafluoroisopropanol; similar compounds have been found with aldehydes (*72*).



(88)

(75)

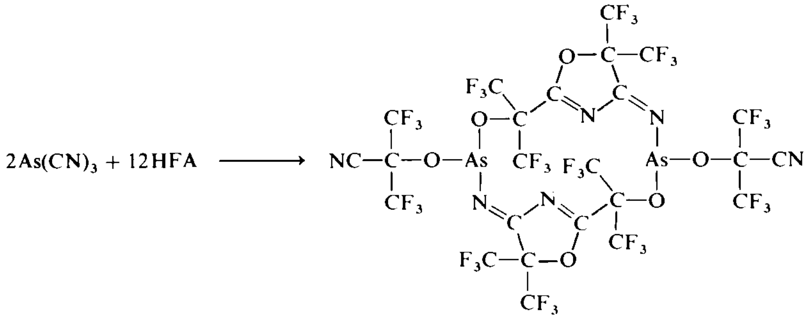
No formation of λ^5-dioxaarsolanes has been observed, probably due to the relative instability of the oxidation state (+V) of arsenic compared to phosphorus (*259*).

Tetramethyldiarsane and trimethylarsane form unstable, probably dipolar, 1:1 complexes as suggested by ^{19}F NMR spectroscopy. In the former a four-membered ring is formed with the two arsenic atoms acting as donor and acceptor sites (*72*). Tris(dimethylamino)stibane reacts with HFA with insertion into all three Sb—N bonds (*83*).

2. *Reactions with Pseudohalide Functions*

Triethylamine has been employed as a catalyst in the following reactions [Eqs. (76)-(78)].

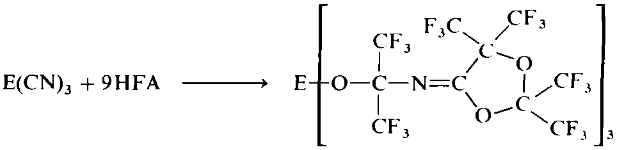
A 14-membered ring has been obtained in moderate yield from excess tricyanoarsane and HFA (*233*).



(76)

(89)

However, excess HFA leads to the formation of **90** (*83*) as well as the analogous reaction with tricyanostibane (*240*).

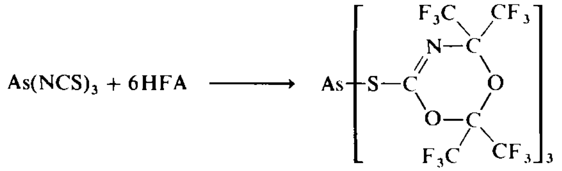


(77)

(E = As, Sb)

(90)

As in the case of cyanophosphanes (Section III,A,8), isomerization of the nitriles to the isonitriles is the initial step. While triisocyanatoarsane proved to be inert to HFA (*176*), the expected product **81b** with triisothiocyanatoarsane has been isolated (*240*). The structure of **81b** is reported.



(81b)

(78)

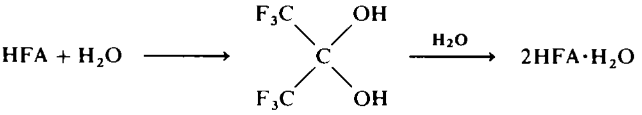
IV. Reactions of HFA with Compounds of Nitrogen and Group VI Elements

A. OXYGEN AND NITROGEN

Since the reactions of oxygen- and nitrogen-containing molecules with HFA are very similar, and several molecules contain both atoms which could serve as active centers, they are treated under one heading. Early work has been reviewed by Krespan and Middleton (*168*) and Gambaryan *et al.* (*111*).

1. Insertion into E—H Bonds

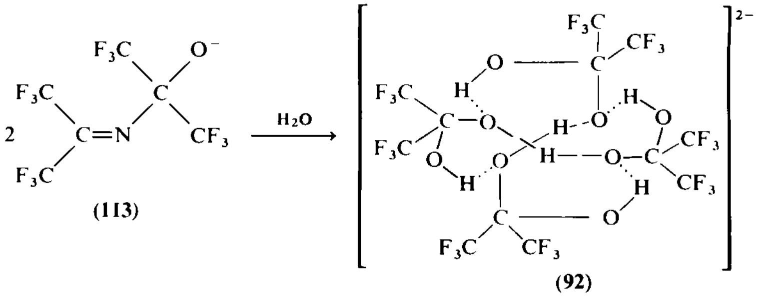
The exothermic reaction of HFA with a stoichiometric amount of water leads to the formation of a stable crystalline hydrate **91**; excess water affords a liquid sesquihydrate **91a** of unknown structure (*191*).



(91) (91a)

(79)

Despite its rather high acidity ($pK_a = 6.58$), **91a** is an excellent solvent for polymers like polyamides, -esters, -acetals, and -ols (*185*). Hydrolysis of the anionic species **113** (*vide infra*) in the presence of tetraphenylphosphonium chloride yields the tetrameric dianion **92**.

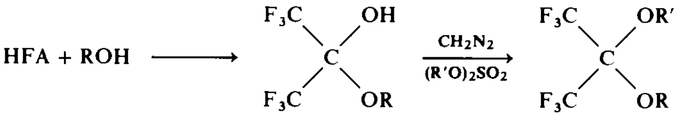


(113) (92)

(80)

The X-ray structure of **92** (*237*) shows fourfold symmetry with four asymmetrically bridging hydrogen atoms and two symmetrical bridges in the core of the molecule.

In analogy with Eq. (79), HFA forms unstable hemiketals **93a** which are converted into stable ketals **93b** with diazomethane (*163*) or dialkyl sulfates (*185*). The ketals **93b** are almost stable in 2 *M* HCl, only slight decomposition occurring.

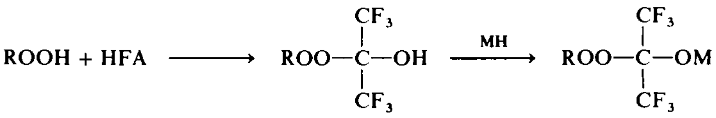


(81)

(93a) **(93b)**

^{19}F NMR spectra of HFA adducts with compounds containing active hydrogen atoms like alcohols **93a**, amines **95**, and thiols **126** have been reported (*173*). HFA also forms unstable ketal esters with a series of carboxylic acids. The equilibrium has been investigated by means of ^{19}F NMR spectroscopy (*206*).

In a similar fashion HFA inserts into the O—H and O—M (M = Li, Na) bond of peroxides (*11*, *12*, *57*). The hydroperoxides **94a** can be metallated with MH (*11*).



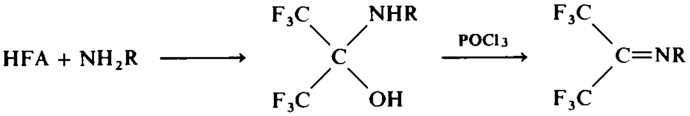
$$\text{ROOH} + \text{HFA} \longrightarrow \text{ROO}-\underset{\text{CF}_3}{\overset{\text{CF}_3}{\text{C}}}-\text{OH} \xrightarrow{\text{MH}} \text{ROO}-\underset{\text{CF}_3}{\overset{\text{CF}_3}{\text{C}}}-\text{OM} \qquad (82)$$

(94a) **(94b)**

[R = H, HOC(CF$_3$)$_2$, *t*-Bu, CF$_3$C(O)] (M = Li, Na)

These compounds are strong oxidizers, but less flammable than nonfluorinated peroxides.

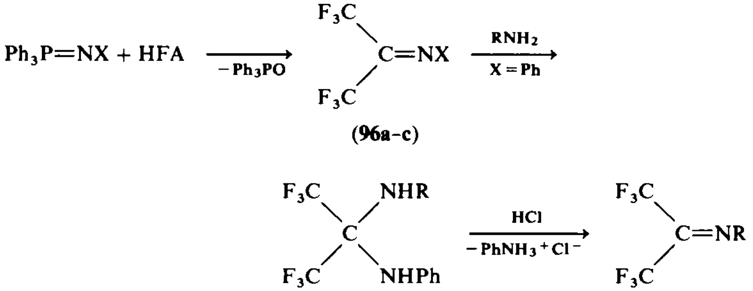
Hemiaminals are available from HFA and amines. A series of similar reactions has been carried out with ammonia (*187*, *189*), amines (*189*), aliphatic, aromatic (*258*), and fluoroaliphatic acid amides (*169*). The hemiaminals **95** can be dehydrated with phosphorus oxychloride in pyridine to form 2-hexafluoropropaneimines **96** (*187*).



(83)

(95) **(96)**

Hexafluoroacetoneazine (*47*, *276a*) and hexafluoroacetonebis(trifluoromethyl)hydrazone (*55*) have been synthesized similarly. Dehydration has been achieved with phosphorus oxychloride (*47*) or oleum (*276a*) for the ketazine and oleum for the hydrazone. *S*-Arylsulfinamides also react only via cleavage of an N—H bond (*46*). Derivatives of **96a** are available from (phenylimino)triphenylphosphorane via aminals **97** (*293*, *295*).



(96a–c)

(84)

[X = H, Ph, C(O)Ph; R = H, *i*-Bu, CH_2PH]

(96)

Compound **96a** (R = H) is also obtained from thermal decomposition of **97a** at 180°C or from the unsubstituted phosphoraneimine (*294*). Corresponding imides are found to react analogously (*294*). The same type of reaction has also been found with *N*-arylimino sulfoxides. Arylhexafluoropropaneimines are formed with HFA under the catalytic influence of CsF with evolution of SO_2 (*296*).

HFA reacts with trifluoroacetyl nitrite in the presence of potassium fluoride to yield potassium trifluoroacetate and heptafluoroisopropyl nitrite (*171*).

N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine reacts with HFA to form a blue charge-transfer complex. Though no ESR signal has been observed, one-electron transfer seems to be likely (*84*).

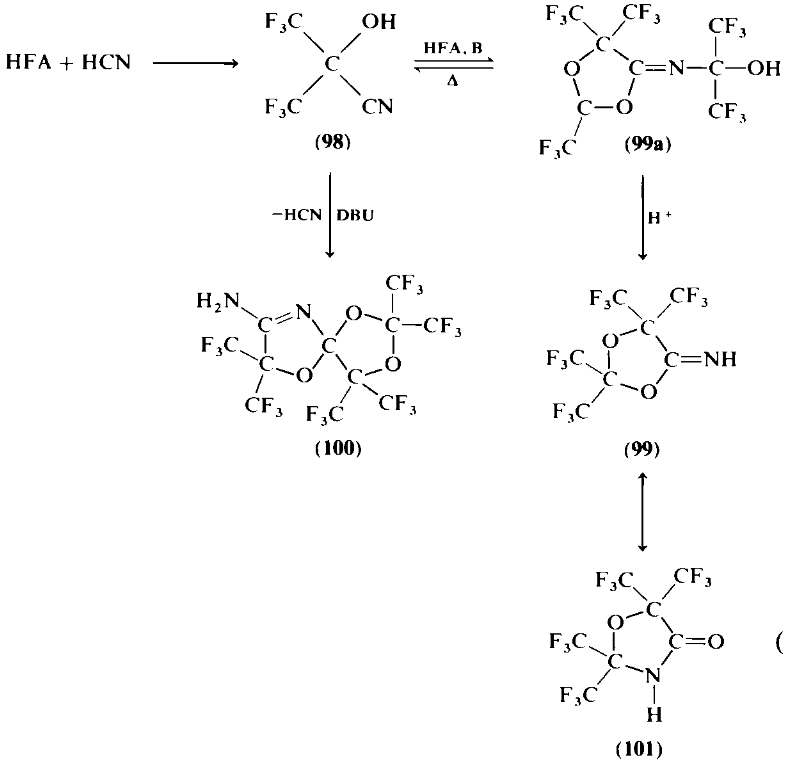
Pyridines and pyridine *N*-oxides are attacked by HFA in ortho positions in the presence of lithium-2,2,5,5-tetramethylpiperidide. The intermediate formation of a zwitterionic species in the case of the pyridines has been postulated (*265*).

Aldol condensation has been observed with acetone and acetophenone (*255*).

Photochemical reactions of HFA with perfluorinated carbon–oxygen compounds have been reported (*271*, *272*). HFA serves as a mild source of CO in the reaction with bis(trifluoromethyl) peroxide (*271*) to yield bis(trifluoromethyl) carbonate; with perfluoromethyl oxalate, CF_3 radicals are the reactive species to yield perfluoromethyl acetate (*272*).

2. *Reactions with Pseudohalides*

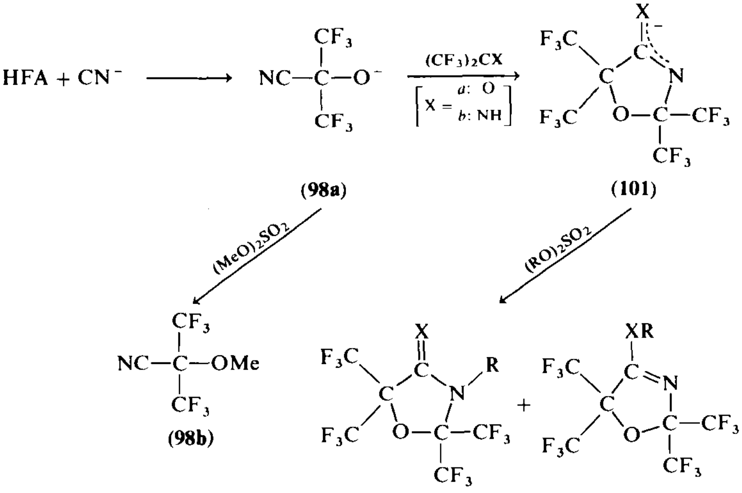
Like ordinary ketones, HFA forms a cyanohydrin **98** (*165*) with (*193*) and without (*210*) catalysis by bases like piperidine.



(85)

With excess HFA a dioxolaneimine **99a** is formed from a typical isonitrile reaction mentioned in previous sections. Acidification yields the unsubstituted five-membered ring **99**, which is the parent compound of alkylated dioxolanes **99b**-**e** available from isonitriles (R = Me, Et, *t*-Bu, *c*-C_6H_{11}) (*111*, *188*). Whether the imine structure **99** or the ketone structure **101** has to be assigned to the hydrolysis product is not known. The Chapman rearrangement has been proved in the following system [Eq. (86)] (*190*). Treatment of **98** with strong bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yields a spirocyclic compound **100** with elimination of HCN; the structure of **100** has been derived by spectroscopic methods (*193*). The reaction of **98** with HFA × H_2O (**91**) in sulfuric acid produces a 1,3-dioxolan-(4)one (*112*).

With sodium cyanide the anion of hexafluorocyanohydrin **98a** is formed. The structure of **98a** has been confirmed by etherification with dimethyl sulfate (*190*). Further action of HFA or hexafluoroacetoneimine on **98a** leads to the formation of ionic 1,3-oxazolidines **101a** and **101b** (*190*, *192*).



(98a) (101) (98b)

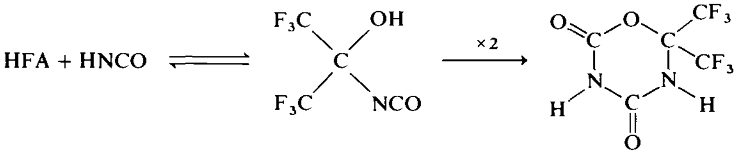
(86)

$R \overset{Me}{\underset{H}{=}} X = O^{101}{}^{c}_{d} X = NH^{e}_{f}$

Compound **101a** is generated from an unstable intermediate by a Chapman rearrangement. Its structure has been confirmed unambiguously by reaction with dimethyl sulfate (*190*), whereby both isomers **101c** and **101e** are formed. The X-ray structure of **101a** is in agreement with these observations (*237*). The neutral compounds **101d** and **101f** are strong acids.

HFA has been found to insert into one of the acidic C—H bonds of malodinitrile (*186*).

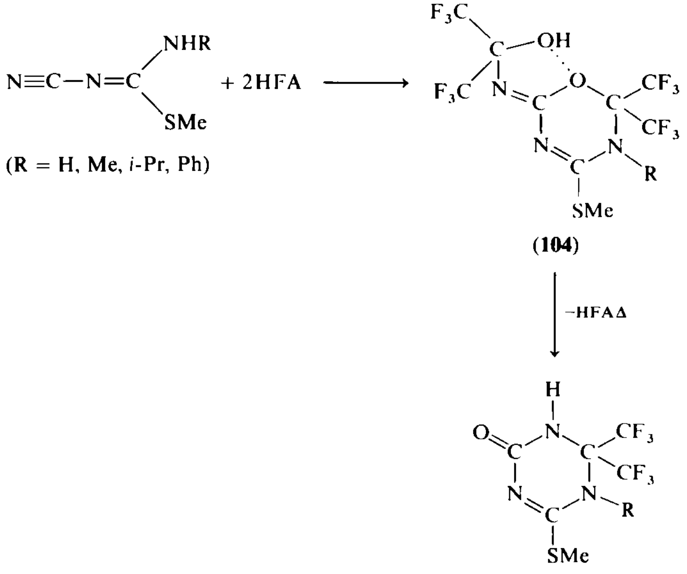
HFA forms an adduct **102** with hydrogen cyanate that decomposes above 0°C. Storage over a long period produces oxadiazinedione **103** and loss of one molecule of HFA (*143*).



(102) (103)

(87)

Mercaptodicyanamides react with two molecules of HFA to form six-membered heterocycles **104b–d**. Derivative **d**, a recrystallizable solid, has been isolated. Pyrolysis yields triazinones **105b–d** via Chapman rearrangement with evolution of HFA. The unsubstituted six-membered ring **105a** is also available, but no indication of intermediate **104a** has been found (*147, 291*).

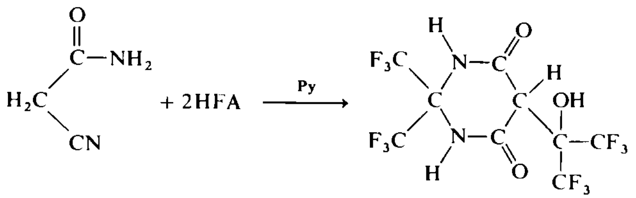


(104)

(105)

(88)

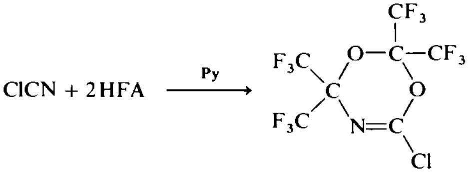
A substituted diazinedione **106** has been synthesized from HFA and cyanoacetamide (*146, 147*) in the presence of pyridine.



(106)

(89)

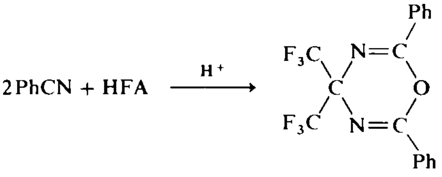
The pyridine-catalyzed reaction of cyanogen chloride with HFA yields the perhalogenated dioxazine **107** (*270*).



(107)

(90)

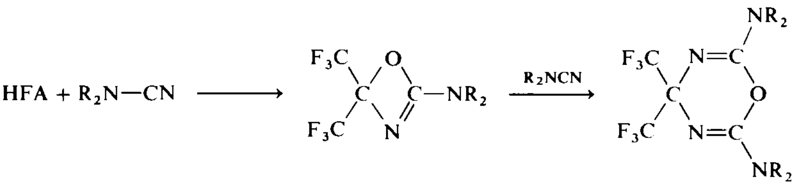
The acid-catalyzed reaction of benzonitrile proceeds with formation of 1,3,5-oxadiazine **108a** (*256*).



(91)

(108a)

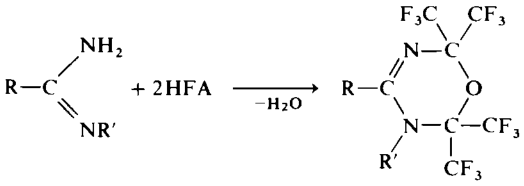
Amino-substituted derivatives **108b–d** are formed via 1,3-oxazetines **109b–d** from substituted cyanoamides and HFA (*53*, *53a*, *140*).



(92)

[R = Me, Et, $(CH_2)_{5/2}$] **(109)** **(108b-d)**

Amidines (*51*, *52*), guanidine (*79*), and biguanidine (*80*) react with HFA with elimination of water and formation of oxadiazines **110**.

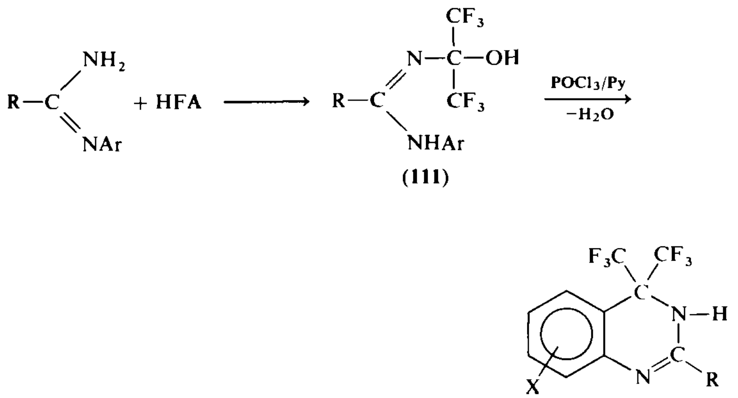


(93)

(110)

a	**b**	**c**	**d**	**e**
R = NH_2	$(NH)_{1/2}$	Ar	Al	Ar
R′ = H	H	Ar, Al, H	Ar	Ar

The dehydrating agent in the case of the guanidines is HFA itself; phosphorus oxychloride has to be used to effect ring closure in the case of the amidines (*52*). An intermediate 1:1 adduct **111** can be isolated, which, in addition to the formation of **110d** and **110e**, on dehydration reacts with the aromatic system to yield 3,4-dihydrochinazolines **112** (*52*).



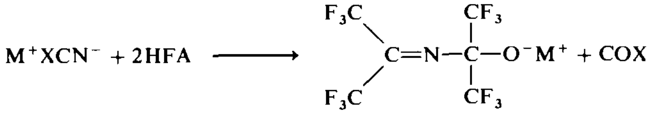
(111)

(112)

(94)

Thermal elimination of CO_2 and formation of a perfluorinated ketimine have been found when pentafluorophenyl isocyanate was treated with HFA at 150°C in dimethylformamide (*82*), in analogy to the reaction with imino sulfoxides (*296*) mentioned earlier.

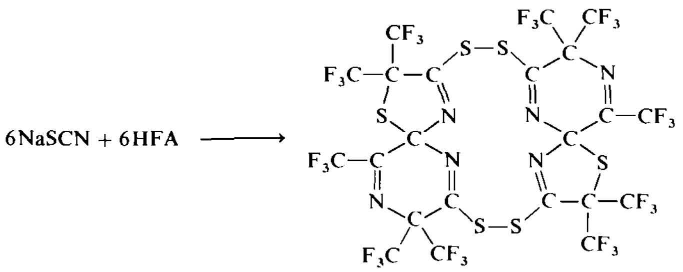
With evolution of CO_2 or COS, respectively, cyanate and thiocyanate anions react with HFA to form an ionic hexafluoropropaneimine **113**, whose crystal structure shows the anion to be dimeric in the solid state (*237*).



$$M^+XCN^- + 2HFA \longrightarrow (F_3C)_2C{=}N{-}C(CF_3)_2{-}O^-M^+ + COX \qquad (95)$$

(X = O, S; M = K, Na) (113)

A by-product (**114**, 7% yield) has been found in the HFA/NaSCN reaction. The X-ray structure shows the elimination of all oxygen atoms and cleavage of some C—C bonds (*238*).

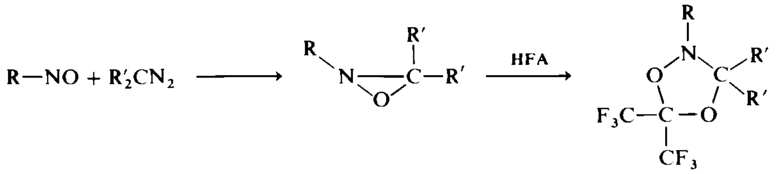


(114)

(96)

3. *Cyclizations Not Involving Pseudohalides*

The reaction of perfluorinated nitrosoalkanes with substituted diazomethanes has been found to produce oxaziridines (*81, 243*). Insertion of HFA into the O—N bond yields 1,3,4-dioxazolidines **115a** and **115b** (*81, 273, 274*).

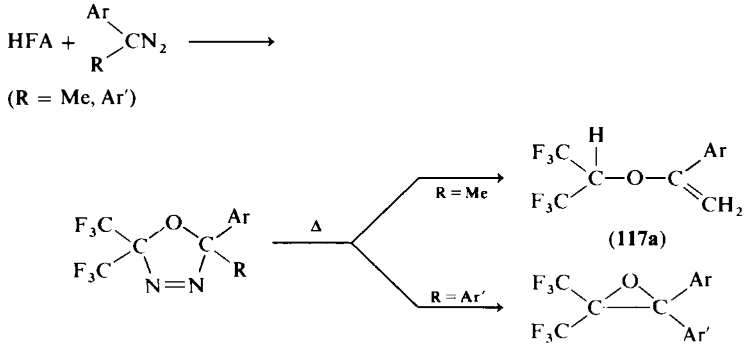


(97)

[**a**: R = t-C_4F_9, R' = Ph (*81*); **b**: R = R' = CF_3 (*273, 274*)]

(115)

Stable Δ^3-1,3,4-oxadiazolines **116** have been synthesized from HFA and disubstituted diazomethanes (*252*). Thermal elimination of N_2 yields oxiranes **117b** if both substituents are aryl, and vinyl ethers **117a** in the case of methyl-substituted diazomethanes (*252*).



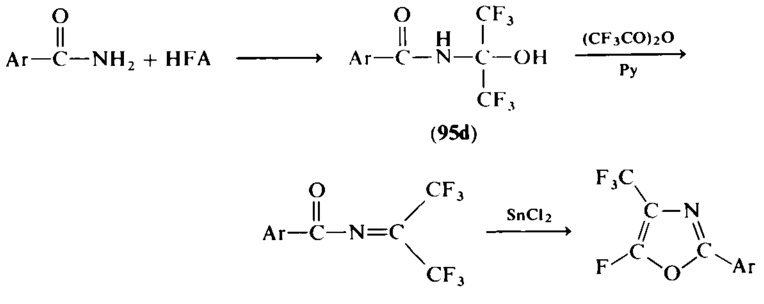
(R = Me, Ar')

(117a)

(98)

(116) **(117b)**

The condensation products of benzoylamides with HFA have been reductively cyclized with anhydrous tin dichloride to yield oxazoles **118** (*50a*).

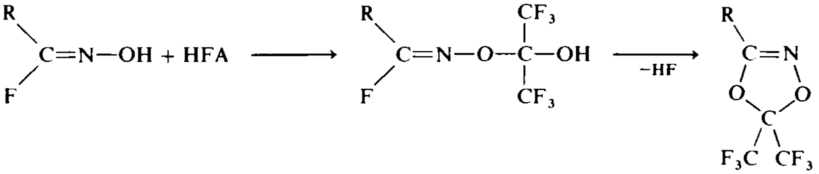


(95d)

(98a)

(96d) **(118)**

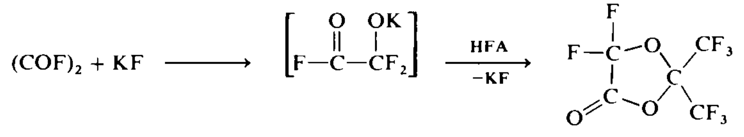
1,3,4-Dioxazolines **119** are available from fluorinated oximes via insertion of HFA into the O—H bond and subsequent thermal elimination of hydrogen fluoride with triethylamine or potassium fluoride (*275, 276*)


(99)

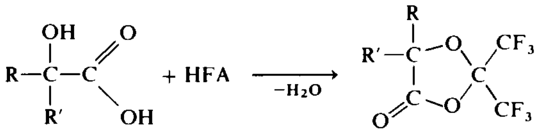
(R = CH_2CF_3, $CH(CF_3)_2$, $CHFCF_3$)

(119)

Dioxolanones are accessible from the reactions of oxalyl fluoride (*71*) and α-hydroxy acids (*285*) with HFA.

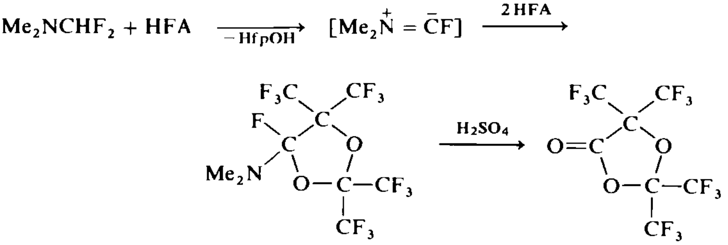

(100)

(120a)


(101)

(120b)

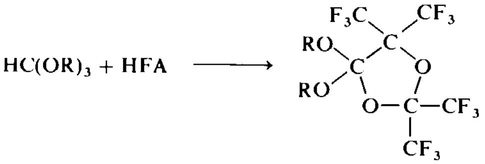
Oxazolidinones containing the hexafluoroisopropylidene group have been synthesized from α-amino acids and HFA (*253, 286*). Elimination of hydrogen fluoride from difluoromethyldimethylamine with HFA, and addition of HFA, yield dioxolane **121a**, which can be converted with sulfuric acid into the fully fluorinated dioxolanone **120c**. The reaction has been described as proceeding via an aminofluoronitrene (*164*).


$$Me_2NCHF_2 + HFA \xrightarrow[-HfpOH]{} [Me_2\overset{+}{N}=\overset{-}{C}F] \xrightarrow{2HFA}$$

(102)

(121a) **(120c)**

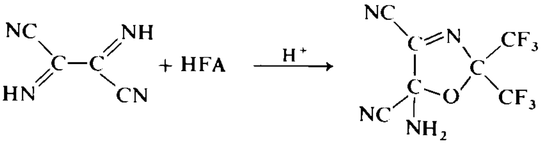
Alkoxy-substituted dioxolanes are available from orthoformic esters and HFA (*36*).



(121b)

(103)

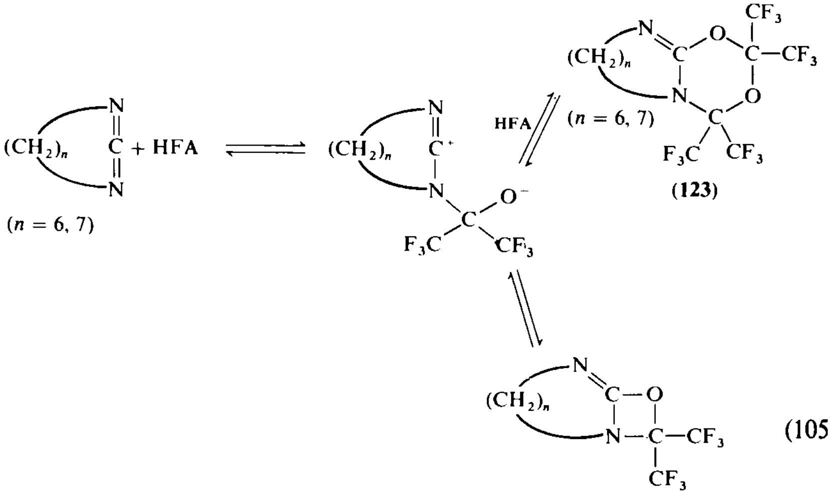
A Δ^3-Oxazolines (**122**) has been obtained from the acid-catalyzed reaction of diiminosuccinonitrile with HFA (*20*).



(122)

(104)

Cyclic carbodiimides react with HFA to form six- and four-membered rings **123** and **124**, which have been investigated spectroscopically. Isolation was successful only in the case of the 10-membered ring **123b**; the other two compounds are in equilibrium with their precursors (*225*).



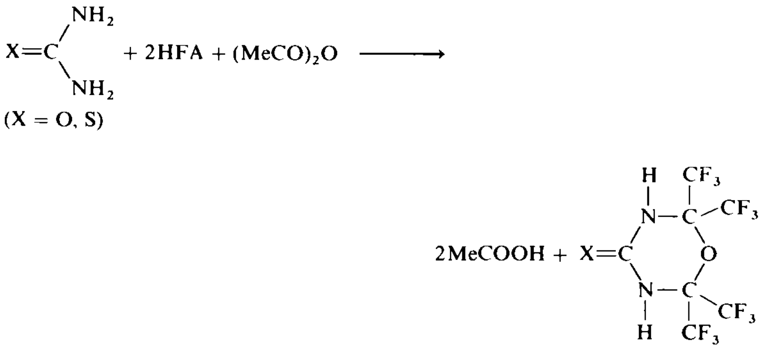
(123)

(*n* = 6) **(124)**

(105)

Interestingly only the C-C double bond of ketenes (*111*) and ketimines (*284*) is attacked by HFA.

Carboxamides form rather unstable 1:1 adducts with HFA insertion into one N—H bond occurring as with urea (*202*). Addition of another molecule of HFA can only be effected by salt formation with pyridine. The addition is reversible. A stable product **125a** is obtained from urea in the presence of acetic acid anhydride (*257*). Thiourea forms the corresponding oxadiazinthione **125b** with HFA (*257*).



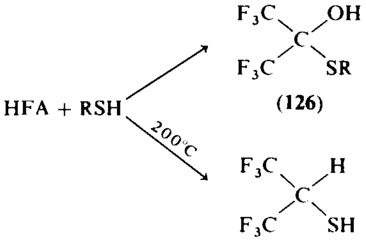
(106)

(125)

B. SULFUR

1. Insertion Reactions

The reaction of HFA with hydrogen sulfide (*136*) and mercaptans (*103*, *150*) yields hemimercaptals **126** at moderate temperatures in analogy to Eqs. (79), (81), and (84)-(87). Monothioacetic (*206*), trifluoroacetic (*218*), and benzoic (*206*) acids react similarly.



(126)

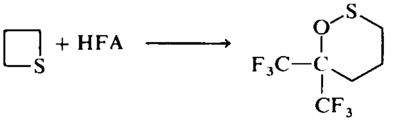
(127)

(107)

(R = H, Me, *n*-Pr, *i*-Pr, *t*-Bu, Ph, C_6F_5, MeCO, CF_3CO, PhCO)

Pyrolytic conditions favor the formation of the thiol **127** (*168*). Attempted dehydration of **126a** (R = H) with diethylamine and subsequent acidification yield hexafluoropropanol (*150*).

Carbon-sulfur bonds show a remarkable inertness toward attack of HFA. For example, thiirane, bis(trifluoromethyl) disulfide, and tetrafluoro-1,3-dithietane are not affected. However, thietane forms 1,2-oxathiane **128** (*195*).

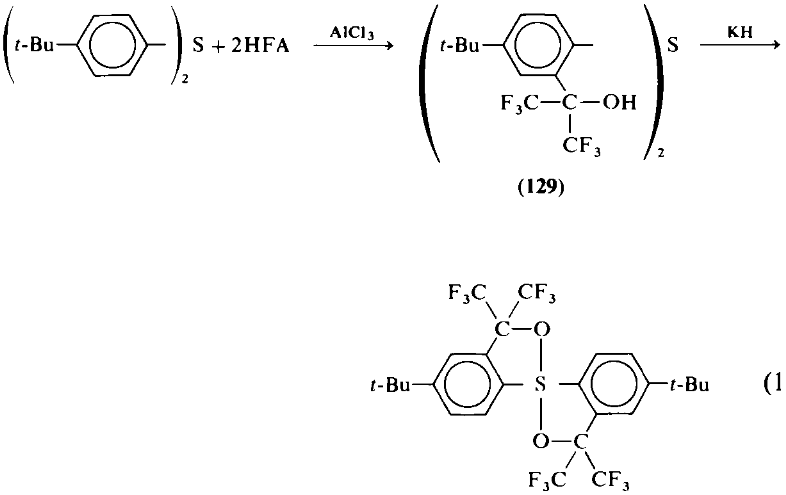


(**128**)

(108)

Sulfides with α hydrogen atoms like dimethyl sulfide, dimethyl disulfide, and tetrahydrothiophene form diols under UV irradiation (*195*). In the tetrahydrothiophene-2HFA$_2$ adduct the hydroxyhexafluoropropyl groups are in trans positions and the trifluoromethyl groups show nonequivalence (*195*). Aromatic thio compounds like thiophenols (*17*), diaryl sulfides (*179, 180, 207*), and thiophene (*95*) add HFA in an ortho position, as does furan (*95*).

Reduction of the adduct **129** of HFA and a para-substituted diarylsulfane with potassium hydride yields a spirocyclic sulfur(IV) compound **130** (*180*).

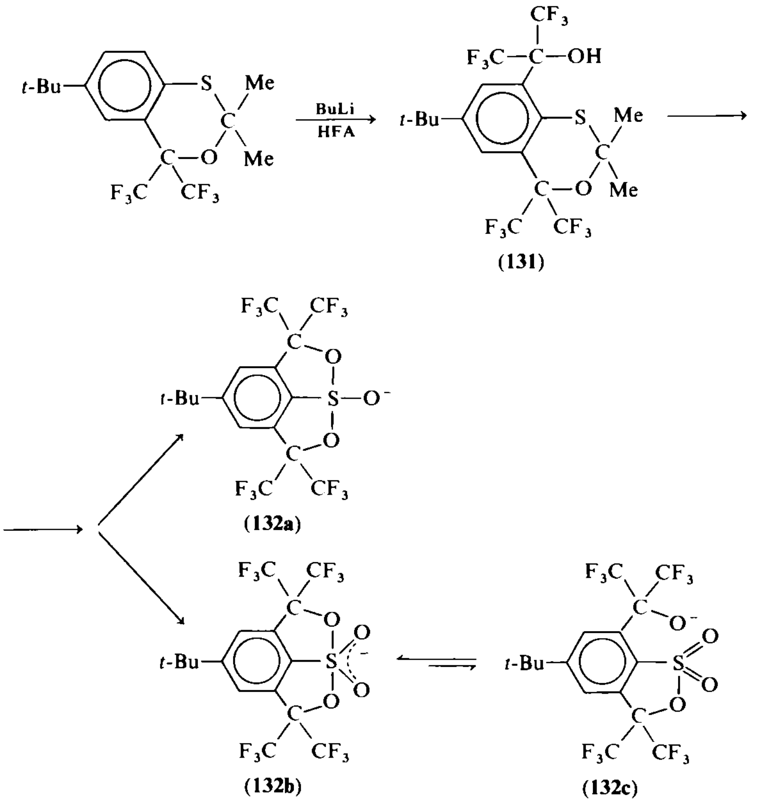


(**129**)

(**130**)

(109)

Multistep synthesis according to Eq. (110) affords sulfur anions **132a** and **132b** with unusual coordination via alcohol **131** (*207*). The spirocyclic anion **132b** has been estimated to be ~13 kJ/mol more stable than its open-chain isomer **132c**.



(131)

(132a)

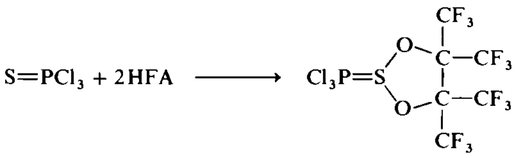
(132b)

(132c)

(110)

2. Dioxathiolanes

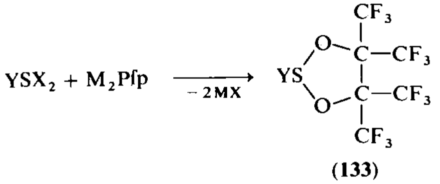
A λ^4-1,3,2-dioxathiolane **133a** is formed in the reaction of HFA with trichlorothiophosphorane (*195*).



(111)

(133a)

The reaction of sulfur chlorides (*7*, *64*) and iminosulfur difluorides (*64*) with dialkali salts of perfluoropinacol is another synthetic route to 1,3,2-dioxathiolanes **133b**–**e**.


(133)

(112)

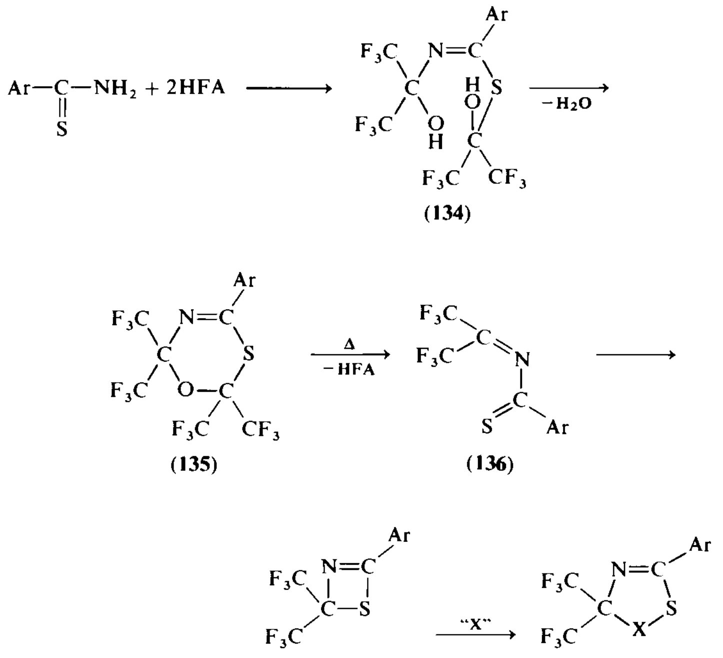
133	**b**	**c**	**d**	**e**
Y	O	O_2	CF_3N	C_2F_5N
X	Cl	Cl	F	F
M	Li, Na	Li, Na	Li	Li
Ref.	*7, 64*	*7, 64*	*64*	*64*

In analogy with the disproportionation in the reaction of dichlorosulfane and sodium fluoride to yield sulfur tetrafluoride, sulfur dichloride reacts with two molecules of perfluoro pinacolate to yield a spirocyclic λ^4-bisthiadioxolane **133f** with elimination of elemental sulfur (*64*). Compound **133f** has also been obtained from the reaction of perfluoropinacol with dichlorosulfane in the presence of pyridine (*18*).

3. Reactions with X=S Double Bonds and Pseudohalides

Carbon disulfide has been found to be inert toward attack of HFA even at elevated temperatures (*195*). Thiocarboxamides react with two molecules of HFA. The intermediates with the likely structure **134** can be dehydrated with phosphorus oxychloride, pyridine (*44*), or trifluoroacetic acid anhydride (*49*) to yield Δ^4-1,3,5-oxathiazines **135**. A retro Diels–Alder reaction takes place with evolution of HFA when **135** is heated to 140°C (*44*, *45*). The heterobutadienes **136** are in equilibrium with the thiazetes **137**, which are more stable at ambient temperature (*45*).

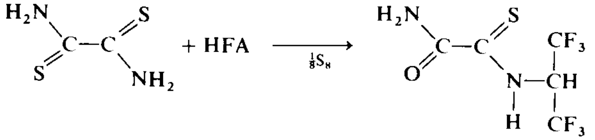
The stability of the strained four-membered ring is due to the trifluoromethyl groups. Compounds like P_4S_{10} (*49*), P_4Se_{10}, Sb_4Te_6, In_2Te_3, and elemental Te (*50*) cause ring expansion. Six-membered heterocycles have also been reported (*49*).



(134) (135) (136)

(X = S, Se, Te) (137) (138) (113)

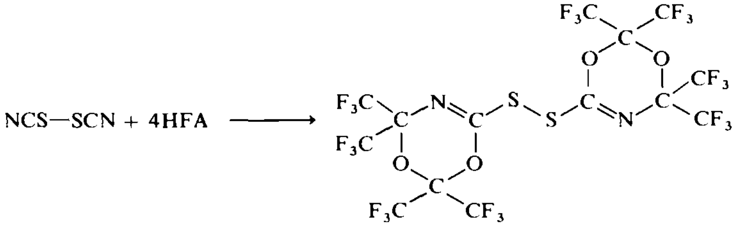
HFA inserts into an N—H bond of dithiooxamide with elimination of sulfur to yield monothiooxamide **139** (*234*). The X-ray structure of **139** shows the six atoms of the thiooxamide skeleton to be almost planar.



(114)

(139)

HFA has been reacted with a series of dicyanosulfanes NCS_nCN (*n* = 1–4) under the catalytic action of triethylamine. The monosulfane produces a red oil which shows extensive decomposition during attempts of purification (*176*). Spectral data suggest formation of a Δ^4-1,3,5-dioxazine ring system as has been found in the reactions of the homologous dicyanoselenane [Eq. (116)] and thiocyanogen with HFA, which results in compound **140**. The X-ray structure has been reported. A remarkable feature is the stability of the sulfur-sulfur bond, which is not affected by HFA similarly to the reaction of dialkyl disulfides with HFA (*195*). Cleavage has been achieved with elemental chlorine (*235*).



(115)

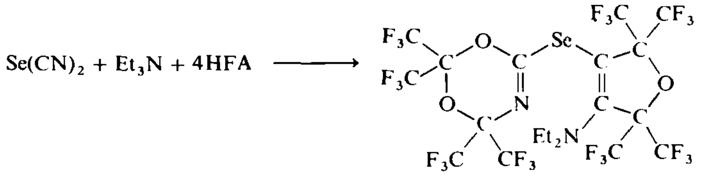
(140)

The same product **140** is formed when the $Hg(SCN)_2$-HFA adduct **192** (Section V,F) is treated with elemental bromine (*241*).

The higher sulfanes ($n = 3, 4$) react in a similar manner; the products obtained are rather unstable and form **140** with elimination of sulfur (*142*).

C. SELENIUM AND TELLURIUM

Involvement of the catalyst has been observed in the reaction of excess HFA with dicyanoselenane. A bicyclic compound is formed with one dioxazine ring attached to selenium, the other ring being generated by complete dehydrogenation of an ethyl group (*240*). The X-ray structure of **141** has been reported.



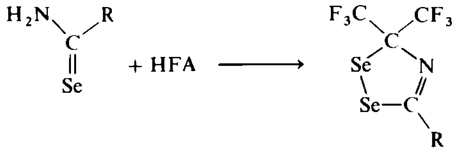
(116)

(141)

A striking difference to the reactions with cyanate and thiocyanate [Eq. (95)] has been found with potassium selenocyanate. Elemental selenium is precipitated and cyanide ion is the reactive species in accordance with Eq. (86) (*237*).

Diselenazolines **142** are formed from selenourea or selenocarboxamides and HFA (*48*).

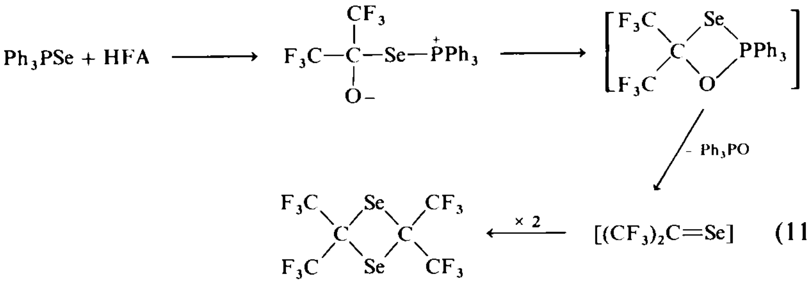
Compound **142** is a useful synthon for the synthesis of other selenium-containing heterocycles (*48*, *49*).



(R = NMe$_2$, Ar) **(142)**

(117)

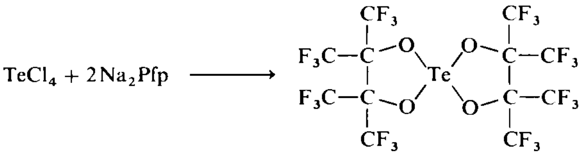
A mechanism [Eq. (118)] has been proposed for the generation of diselenetane **143** from HFA and triphenylselenophosphorane at elevated temperatures (*214*).



(143)

(118)

Tellurium tetrachloride reacts with disodium perfluoropinacolate to yield the spirocycle **144**, a homologue of the sulfur spirocycle **133f** (*7*).



(144)

(119)

V. Metal Complexes of HFA

Green, Stone, and co-workers have done considerable work on HFA metal complexes. Most of their publications, of which the earlier ones were reviewed by Stone in 1972 (*261*), deal with low-valent group VIIIB elements. Two kinds of reactions are generally observed.

1. Insertion into C—H bonds of the ligands as well as formation of metallacycles (i.e., metallaoxiranes and 1,2,4-metalladioxolanes) according to Eqs. (2)-(4), depending on the coordination sphere and reaction conditions. All metallaoxiranes and 1,2,4-metalladioxolanes are listed in Tables VII and VIII. Three-membered rings have been synthesized by reaction of metal

TABLE VII

3-BIS(TRIFLUOROMETHYL)METALLAOXIRANES

Compound	M	L[a]	*n*	L′[a]	*m*	Method	Reference
145	Fe	C_4Me_4 CO	1 2	CO	1	a	*31*
158a	Ni	*t*-BuNC	2	L	2	a	*124, 135*
b		PhNC	2	L	2	a	*135*
c		COD	1	L	1	a	*38, 40*
d		PEt_3	2	L	2	a	*39*
e		$PMePh_2$	2	L	2	a	*39*
f		PPh_3	2	C_2H_4	1	a	*15*
a, d–l		L″	2	COD	1	b	*38, 39, 41, 124, 135*
163a	Ru	$PMePh_2$, CO	2 2	CO	1	a	*54*
163b		$P(OCH_2)_3CEt$ CO	2 2	CO	1	a	*65*
164	Os	PMe_2Ph, CO	2 2	CO	1	a	*125*
167a	Rh	$PMePh_2$, acac	2 1	CO		a	*200*
b		PPh_3 $NCH(CF_3)_2$ Cl	2 1 1			a	*184*

171a		PPh_3	1	PPh_3	2	a	*63*
		NO	1				
b		$PMePh_2$	2				
		CO	1			a	*61*
		Cl	1				
c		PPh_3	2				
		CO	1			a	*61*
		Cl	1				
173a	Pd	PEt_3	2	L	2	a	*199*
b		$(PPh_2CH_2)_2$	1	$P(OPh)_3$	2	b	*94*
c		$PMePh_2$	2	L	2	a	*94, 199*
d		PPh_3	2	$(CF_3)_2CNH$	1	b	*94*
e		$P(OPh)_3$	2	L	2	a	*94*
179a	Pt	COD	1	L	1	a	*128, 129*
		COD	1	C_2H_4	3	b	*129*
b		PEt_3	2	L	1	a	*138*
c		$P(i\text{-}Pr)_3$	2	L	1	a	*138*
d		$PMePh_2$	2		2	a	*61*
			2	PPh_3	2	b	*40*
e		$(PPh_2CH_2)_2$	1	PPh_3	2	b	*40*
f		PPh_3	2	L	2	a	*61, 134*
			2	COD	1	b	*128, 129*
			2	DBA	1	a	*58, 59*
			2	CF_3CN	1	b	*29*
g		$P(OPh_3)$	2	L	2	a	*40*

[a] L″, *t*-BuNC, PEt_3, $PMePh_2$, PPh_3, $P(OPh)_3$, $P(OCH_2)_3CEt$, $\frac{1}{2}(PPhCH_2)_2$, $\frac{1}{2}(C_5H_4N)_2$, $\frac{1}{2}(o\text{-}AsMe_2)_2C_6H_4$; acac, acetylacetonate; DBA, dibenzalacetone.

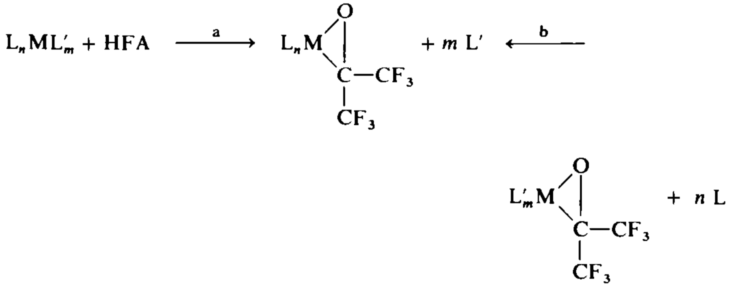
TABLE VIII

3,3,5,5-TETRAKIS(TRIFLUOROMETHYL)-1,2,4-METALLADIOXOLANES

Compound	M	L	*n*	L′	*m*	Method	Reference
160a	Ni	*t*-BuNC	2	L	2	a, b	*124, 135*
b		*o*-(AsMe$_2$)$_2$C$_6$H$_4$	1			b	*41*
166	Rh	PPh$_3$ acac	1	PPh$_3$	1	a	*200*
174a	Pd	*t*-BuNC[a]	2			a	*77, 93*
b		*c*-C$_6$H$_{11}$NC[a]	2			a	*77*
c		PEt$_3$	2	L	2	a	*199*
d		(PPh$_2$CH$_2$)$_2$	1			b	*94*
e		PMePh$_2$	2	L	2	a, b	*94, 199*
f		P(OMe)$_2$Ph	2	L	2	a	*94*
g		P(OMe)$_3$	2	L	2	a	*94*
h		AsMe$_2$(CH$_2$Ph)	2	L	2	a	*94*
180a	Pt	*t*-BuNC[a]	2			a	*105, 131*
b		COD	1	L	1	a	*128, 129*
			1	*i*-Pr	2	a	*40*
c		PMePh$_2$	2			b	*40*
d		(PPh$_2$CH$_2$)$_2$	1			b	*40*
e		P(OMe)$_3$	2	L	2	a	*40*

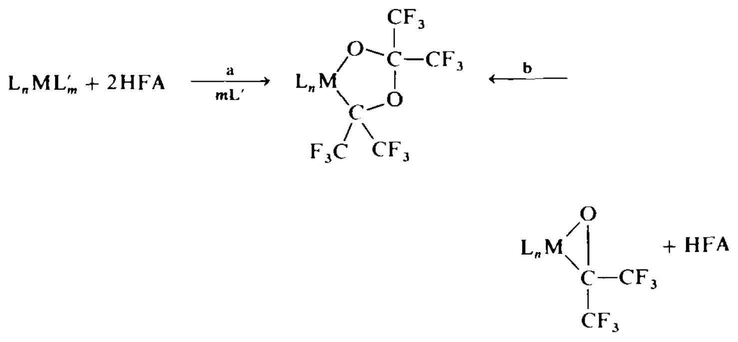
[a] Trimer M$_3$(RNC)$_6$.

complexes containing labile ligands with HFA (method a) and by ligand displacement, with the heterocycle remaining intact (method b) according to Eq. (120).



(120)

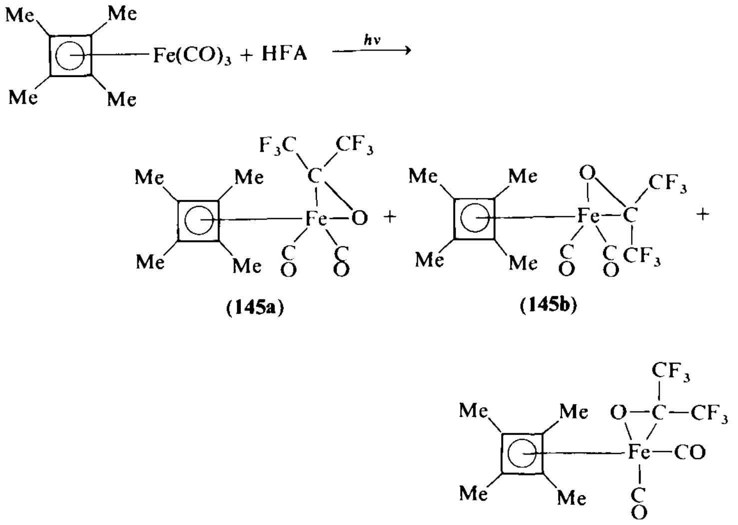
2. Similarly, five-membered rings can be synthesized by either addition of excess HFA to the complexes with exchange of ligands (method a) or by ring expansion of the corresponding metallaoxiranes (method b) [Eq. (121)].



(121)

A. IRON, COBALT, AND NICKEL

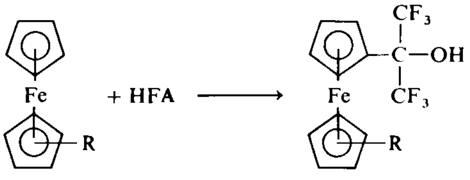
The photochemical reaction of tetramethylcyclobutadieneiron tricarbonyl with HFA leads to the formation of three isomers of the complex **145**. The stereochemistry of these isomers has been investigated by NMR spectroscopy (*31*).



(**145a**) (**145b**) (**145c**)

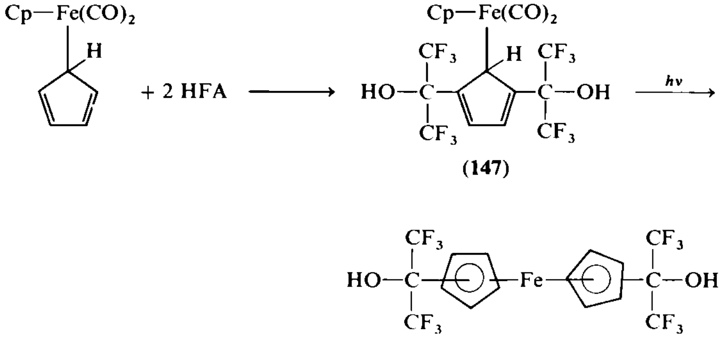
(122)

Ferrocenes react directly (180°C/15 days) or in the presence of $AlCl_3$ as catalyst (20°C/24 hours) to yield fluorinated 2-ferrocenylpropanols **146a–c** (*42*).



(R = H, COMe, COPh) (**146a-c**) (123)

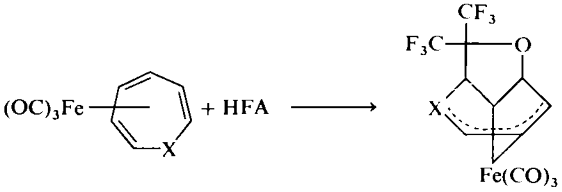
In η^5,η^1-bis(cyclopentadienyl)iron dicarbonyl the σ-bonded ligand is easily attacked by HFA with conservation of the σ bond. Photochemical treatment of **147** affords **146d**, in which both cyclopentadienyl rings become π bonded (*76*).



(**147**)

(**146d**) (124)

High stereospecifity has been found in the reaction of HFA with tricarbonyl (η^4-cycloheptadiene)iron complexes (*126*, *127*).



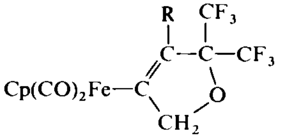
(X = CH$_2$, CO, NCO$_2$Me) (**148a-c**) (125)

Mainly oxo addition products **148a**–**c** are formed.

Iron complexes with hydrated furane ligands are available from appropriate alkynyl- and alkenyl-substituted iron compounds as precursors (*174*).

$Cp(CO)_2Fe{-}CH_2{-}C{\equiv}C{-}R + HFA \longrightarrow$

(R = Me, Ph)

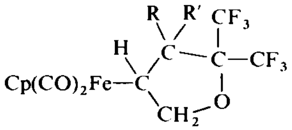


(149)

(126)

$Cp(CO)_2Fe{-}CH_2{-}CH{=}CRR' + HFA \longrightarrow$

(R = Me, H; R′ = Me, H, Me, Ph, Cl)



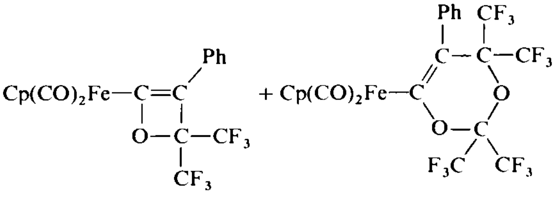
(150)

(127)

Photochemical decarbonylation of **149b** in the presence of PPh_3 affords a chiral metal center as reflected in the nonequivalence of the two CF_3 groups (*174*).

A σ-phenylethinyliron complex reacts with either one or two molecules of HFA to yield four- and six-membered rings **151** and **152**, respectively (*78*).

$Cp(CO)_2Fe{-}C{\equiv}CPh + HFA \longrightarrow$

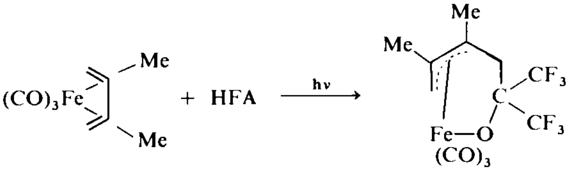


(151) **(152)**

(128)

Exchange of one CO group in the starting material by PPh_3 only leads to the formation of the oxetane (*78*). Once formed, the four-membered rings **151** do not undergo ring expansion.

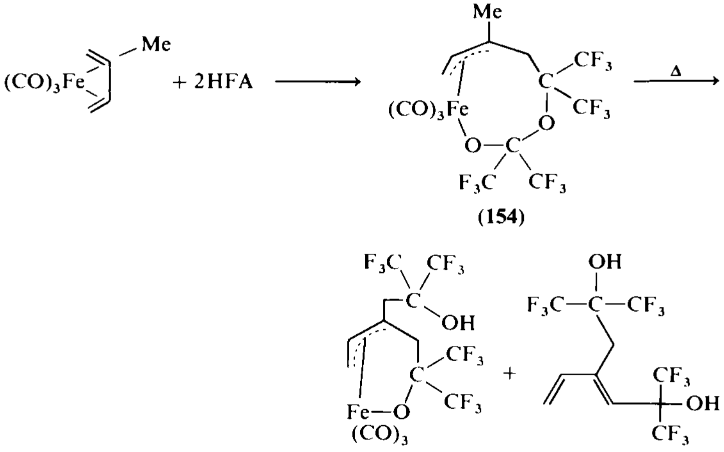
Addition of HFA to substituted butadieneiron complexes includes the metal atom (*132*, *133*).



(153)

(129)

While the unsubstituted butadiene complex does not react, the isoprene complex yields a 2:1 addition product **154** when trace amounts of $Fe(CO)_5$ are present (*132*, *133*).



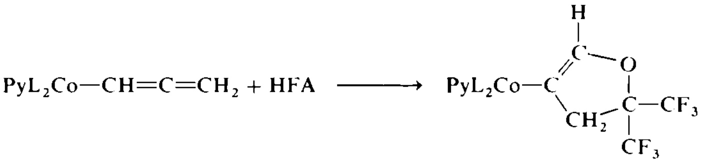
(154)

(155) (156)

(130)

Heating **154** in hexane in a sealed tube affords the isomer **155** by insertion of one molecule of HFA into a C—H bond of the methyl group, and the diene **156** by cleavage of the metal bonds and migration of a hydrogen atom (*132*, *133*).

Only two reports deal with the reactions of cobalt complexes with HFA. Insertion into the cobalt–hydrogen bond of a hydride complex affords a cobalt hexafluoroisopropylate (*136a*). An oxolene(2) is formed from an alkylcobalt compound and HFA (*66*). For mechanistic reasons the authors favor the depicted structure **157** over the isomeric oxolene (3) ring reported for the analogous iron complex **149** (*174*).



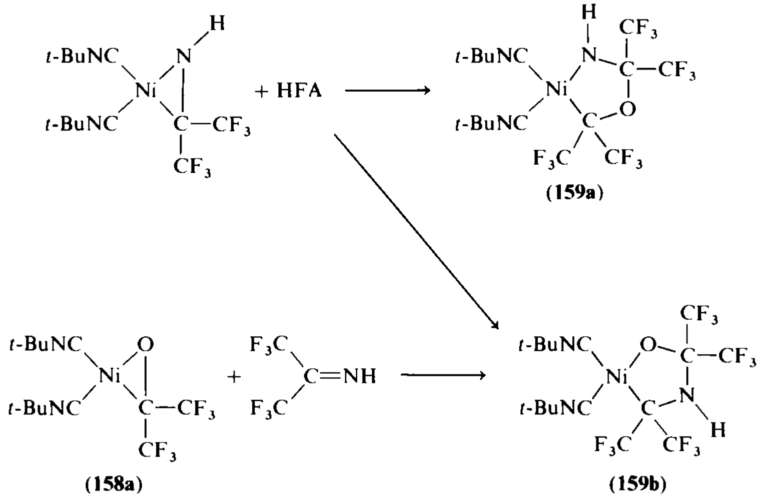
(157)

(131)

Potassium tetrafluorocobaltate(III), a mild fluorinating agent, leads to the formation of molecules like CF_4, COF_2, and CF_3COF (*21*).

Starting from $Ni(COD)_2$, a series of three-membered rings **158a**, **d**-**l** has been synthesized (see Table VIII) (*38*, *39*, *41*, *124*, *135*). Single-crystal X-ray diffraction studies of **158a,f** reveal that the complex is nearly planar, the nickel atom being equidistant from carbon and oxygen (*68*, *69*).

While ring expansion of bis(*t*-butylisocyanide)hexafluoroisopropylideneiminenickel with HFA affords two isomers **159a,b** in a 1:4 ratio, the inverse reaction of the HFA complex **158a** with the imine yields only **159b** (*135*), the structure of which has been determined (*69*).

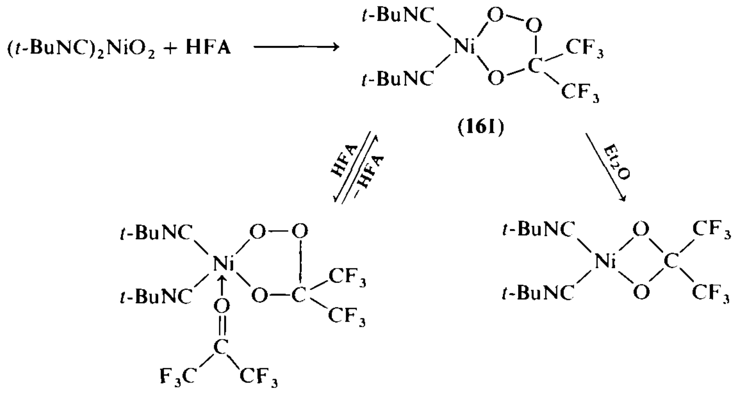


(132)

Only little evidence has been found for ring expansion of the analogous phenylisocyanide complex **158b** with HFA. The observation is in contrast to the reaction with hexafluoroisopropylideneimine (*135*). Compound **158a** reacts with tetrafluoroethane eliminating HFA and forming a perfluorinated niccolacyclopentane (*135*).

The five-membered nickel ring **160a** can be obtained in both ways [Eq. (121)] (*124*, *135*); the diarsano-*o*-phenylene complex **160b** has been synthesized via ring expansion (*41*) (see Table VII).

At $-50°C$ peroxobis(*t*-butylisonitrile)nickel forms an explosive 1:1 adduct with HFA **161**, which has been assigned a five-membered ring structure by analogy with the complexes of peroxoplatinum compounds with CO_2 and CS_2. Excess HFA yields a labile 2:1 complex with no fluorine coupling in the ^{19}F NMR spectrum. Thus, structure **161a** has been proposed for this complex. Peroxide **161** easily transfers one oxygen atom to diethyl ether with ring contraction to form a niccoladioxetane **162** (*124*, *135*).



(161)

(161a)

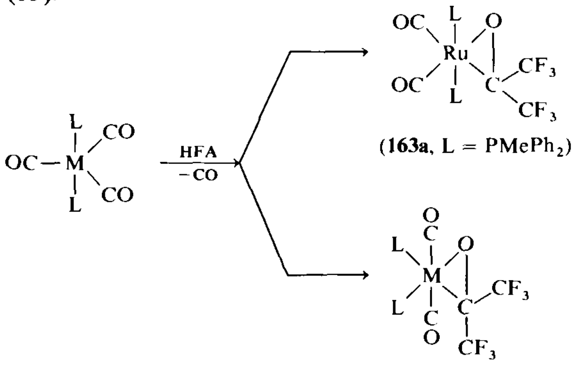
(162)

(133)

Similarly, dioxobis(triphenylphosphane)platinum reacts with HFA. Ring contraction has been achieved with triphenylphosphane. An unstable bis adduct which is believed to be a seven-membered ring has also been reported (*137*).

B. RUTHENIUM AND OSMIUM

Only a few examples are known in which ruthenium and osmium compounds undergo addition reactions with HFA. While *trans*-$(PPh_3)_2Ru(CO)_3$ does not yield stable products (*65*), *trans*-$(PMePh_2)_2Ru(CO)_3$ forms a complex in which the phosphane ligands are still in trans positions (*54*). The analogous osmium complex **164** (*125*) and the phosphite ruthenium complex **163b** show isomerization; the CO ligands are in trans positions. In the case of **163b**, the rearrangement has been proved by ^1H NMR spectroscopy (*65*).

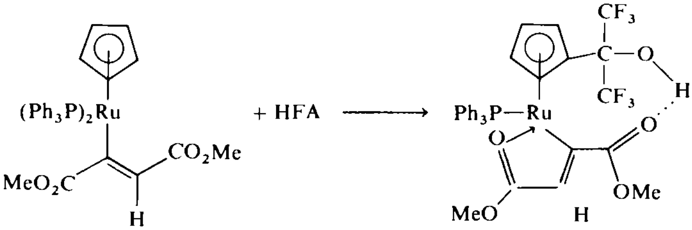


(**163a**, L = $PMePh_2$)

(134)

[L = $P(OCH_2)_3CEt$, M = Ru; **163b**,]
[L = PMe_2Ph, M = Os; **164**]

In analogy to ferrocenes [Eq. (123)], the cyclopentadienyl ring is attacked by HFA according to Eq. (135) (*27*).



(165)

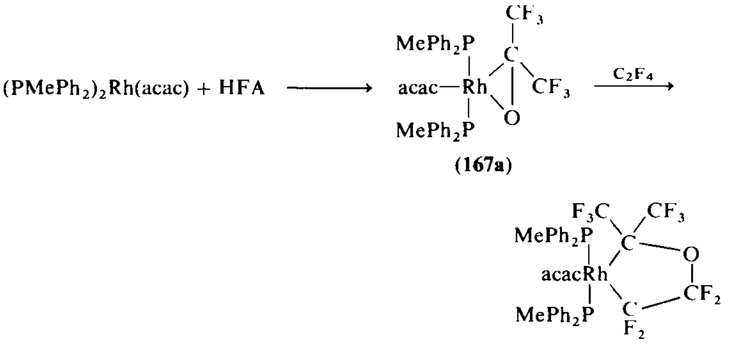
(135)

The loss of one molecule of PPh$_3$ in **165** is compensated by coordination to one carbonyl oxygen atom. The other one forms a hydrogen bond, as seen in the X-ray crystal structure of **165** (*28*, *215*).

In analogy to the homologous iron complex **148c** [Eq. (125)], (η^4-*N*-methoxycarbonyl-^{1}H-azepine)ruthenium tricarbonyl reacts with HFA (*127*).

C. Rhodium and Iridium

Probably due to steric effects, an interesting contrast in reactivity depending on the ligands has been found in the reaction of excess HFA with bisphosphanorhodium(+I) acetylacetonates. The bis(triphenylphosphane)-substituted complex yields a metalladioxolane **166** by losing one ligand. With methyldiphenylphosphane a metallaoxirane **167a** is formed (*200*). The ^{19}F NMR chemical shift of **167a** with trans configuration of the phosphane ligands shows a signal shifted 10 ppm to higher field in comparison to the related group VIIIA complexes **158**, **163**, **173**, and **179** (*200*).



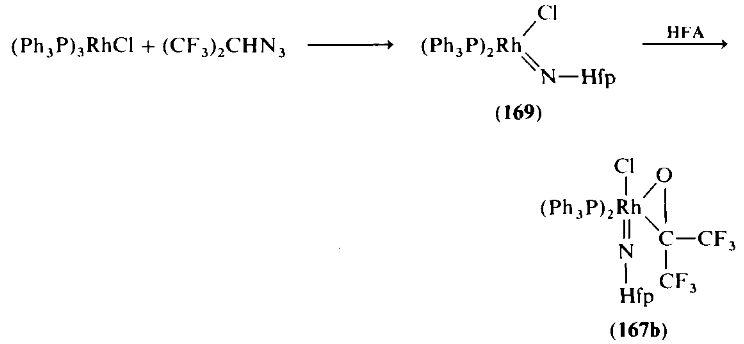
(167a)

(168)

(136)

Addition of tetrafluoroethylene to **167a** affords the 1,3-metallaoxolane **168** (*200*) in contrast to the corresponding reaction of the nickel complex **158a**, in which HFA is exchanged (*135*).

A similar extension of the coordination sphere at the rhodium atom has been found in the reaction of the nitrene complex **169** with HFA (*184*).

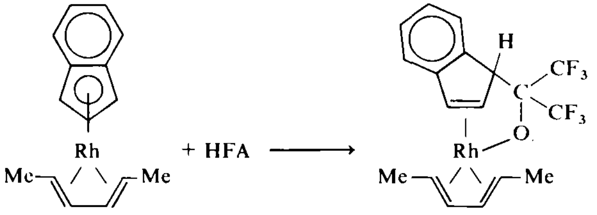


(169)

(167b)

(137)

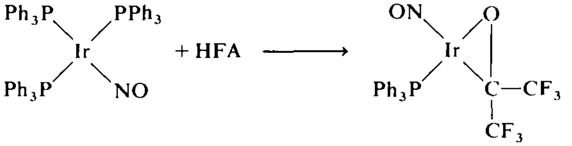
Cyclopentadienylrhodium(+I) complexes with substituted butadiene ligands react thermally with HFA with oxidation of the metal atom and addition to the diene in analogy to Eq. (129). Two isomers are found with isoprene (*132*, *133*). 1,3-Pentadienecyclopentadienylrhodium forms only one complex with HFA (*133*) and the dimethylbutadiene complex, in addition to oxidation, undergoes insertion of a HFA molecule into a C—H bond of the cyclopentadienyl ring (*132*, *133*). Whereas higher temperatures are required to effect addition of HFA to the cyclopentadienyl complexes, the corresponding indenylbutadienerhodium complexes undergo insertion at room temperature (*56*). The 2,4-hexadiene complex undergoes addition at the indenyl system.



(170)

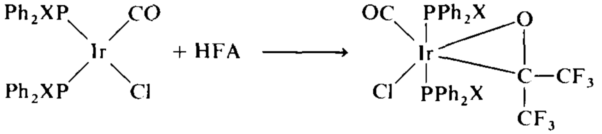
(138)

The X-ray structure of **170** has been reported (*56*). Generally only unsubstituted sp^2-hybridized carbon atoms of butadiene ligands are attacked by HFA (*133*). Different behavior has been found in the reactions of iridium complexes with HFA. With tris(triphenylphosphane)nitrosyliridium the geometry is retained [Eq. (139)] (*63*). However, the Vaska complexes lead to octahedral environments of the metal atom [Eq. (140)] (*61*). IR and NMR spectra suggest that the phosphane ligands are in trans positions and the chlorine atom is trans to oxygen (*61*).



(171a)

(139)

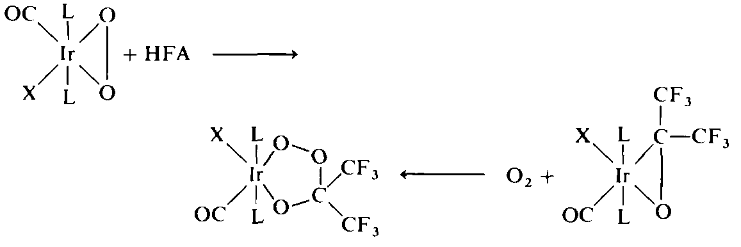


(X = Me, Ph)

(171b, c)

(140)

Mechanistic and kinetic studies have been carried out on some oxygenated Vaska-type complexes. Using ^{18}O-labeled complexes shows that insertion occurs into the Ir—O rather than into the O—O bond (*23*).



(172) **(171)**

(141)

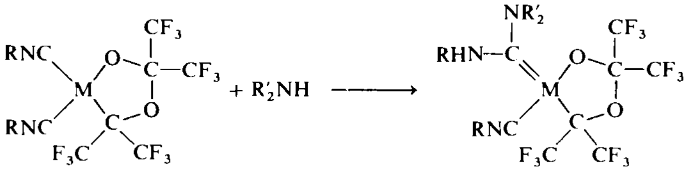
[L = PPh_3, X = Cl, Br, I; L = $PMePh_2$, $P(C_6H_4\text{-}p\text{-}Me)_3$, $P(C_6H_4\text{-}p\text{-}OMe)_3$, $AsPh_3$, X = Cl]

The reaction of the oxygen complexes with HFA proceeds at a rate two orders of magnitude faster than the addition of O_2 to the metallaoxirane (*23*).

D. PALLADIUM AND PLATINUM

While three-membered ring formation prevails in the iron and cobalt triad and with nickel complexes, more metalladioxolanes than metallaoxiranes are known with palladium and platinum (see Tables VII and VIII). Formation of the three- or five-membered rings is strongly dependent on stoichiometry, reaction conditions, and steric requirements of the ligands. While the bis(diphenylphosphano)ethane-substituted metallaoxirane **173b** undergoes ring expansion with excess HFA to yield **174d** and the corresponding imine, the bis(triphenylphosphane)-substituted palladaaziridine reacts with HFA with exchange and retention of the three-membered ring (**173d**). Interestingly, attempted exchange of the phosphite ligand in **173e** with methyldiphenylphosphane results in the loss of HFA (*94*).

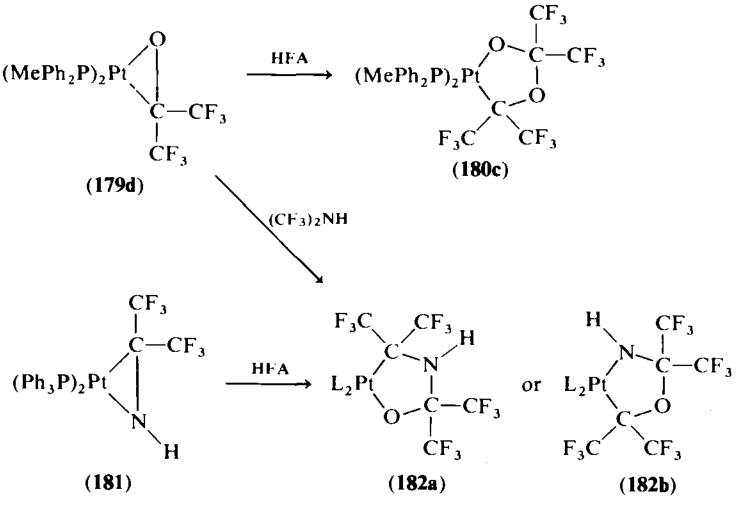
An interesting addition reaction has been found with the isocyanide complexes of the nickel triad and dialkylamines [Eq. (142)]. The metal atom is oxidized, with formation of diaminocarbenes (*77*). The ligand cis to the metal-bonded oxygen is attacked. This is shown in the X-ray structure of **177b** (*197*).


(142)

M	R	Compound
Ni	*t*-Bu, *i*-Pr	**160a,c**
Pd	*t*-Bu, *c*-C_6H_{11}	**174a,b**
Pt	*t*-Bu	**180**

M	R	R′	Compound
Ni	*t*-Bu, *i*-Pr	Et	**176a,b**
Pd	*t*-Bu, *c*-C_6H_{11}	Me, Et	**177a**
Pt	*t*-Bu	Me, Et	**178a,b**

Whereas bis(triphenylphosphane)platinaaziridine **181** reacts readily with HFA, the corresponding oxirane is inert toward ring expansion. This may be explained in terms of stronger π acceptor and weaker σ donor capacity of

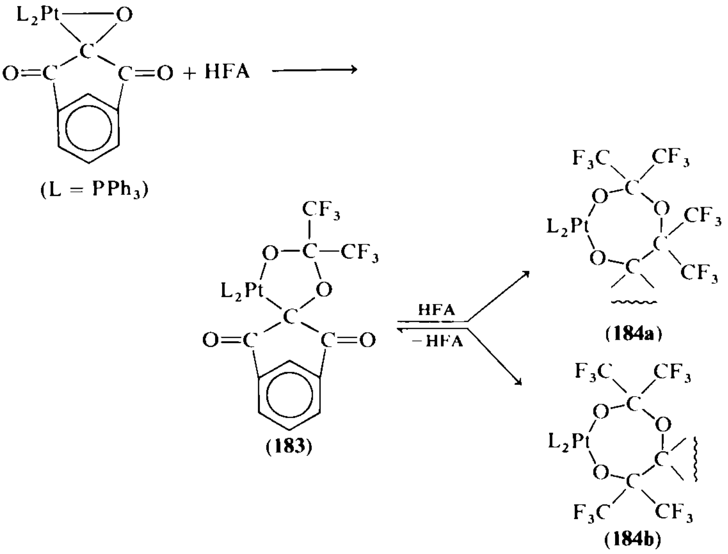

(143)

(179d) **(180c)** **(181)** **(182a)** **(182b)**

HFA than of the imine. Attack on the metal atom of one molecule of HFA and imine is a prerequisite for the formation of five-membered rings. The lack of electron density in the HFA adduct inhibits ring expansion. According to these observations the displacement of triphenylphosphane by the more nucleophilic methyldiphenylphosphane promotes dioxolane formation (*40*). Platinaoxazolidines are available in both ways. No structural assignment has been given for the mixed compounds **182a, b** (*16*).

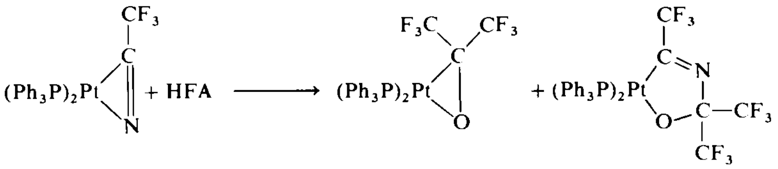
Together with the formation of platinaoxirane **179b**, dioxaphospholane **57b** (R = Et) has been isolated (*138*). In contrast to the reaction of bis(triphenylphosphane)dibenzalacetoneplatinum in which platinaoxirane **179f** is formed, the analogous reaction of the bis(triethylphosphane)dibenzalacetone complex with HFA yields a product, which from spectroscopic data is assumed to arise from attack of HFA at the dienone ligand (*59*). The ^{195}Pt NMR spectrum of **179b** has been reported (*123*).

Like HFA, indanetrione reacts with tetrakis(triphenylphosphane)platinum to form a platinaoxirane, which readily adds one molecule of HFA to yield **183**. Further action of HFA affords a rather unstable seven-membered ring compound (**184**), which thermally loses either indanetrione or HFA to reform a platinadioxolane. Whether isomer **a** or **b** is formed cannot be deduced from ^{19}F NMR spectroscopy (*145*).



(144)

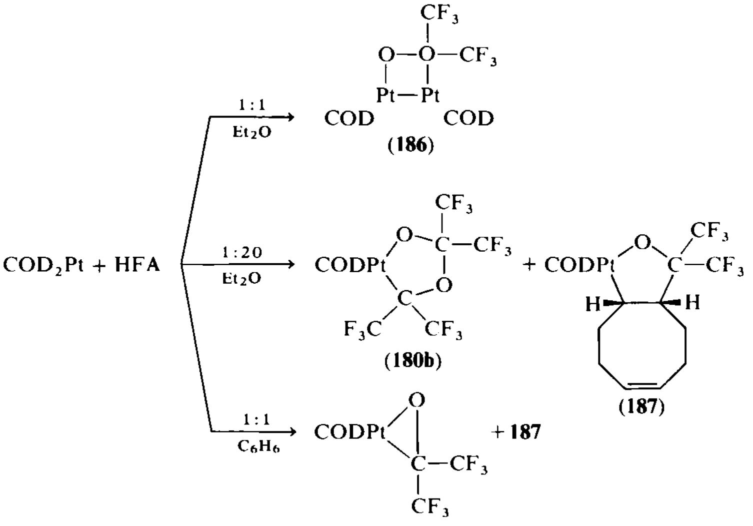
Displacement of the labile trifluoroacetonitrile ligand by HFA leads to the formation of **179f**. A minor product **185** is obtained by cycloaddition of HFA (*29*).



(179f) **(185)**

(145)

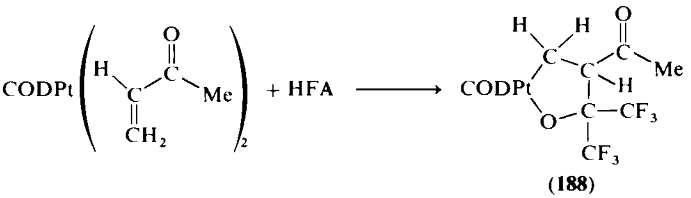
Some novel structures have been found in the reaction between bis(cyclooctadiene)platinum(0) and HFA, depending on the reaction conditions (*128*, *129*).



(186) **(180b)** **(187)** **(179a)**

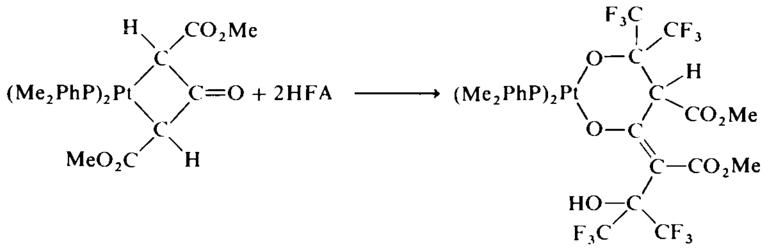
(146)

Whereas ligand exchange in **187** with triphenylphosphane and *o*-bis(dimethylarsano)phenylene proceeds with retention of conformation, ring contraction occurs with triphenylphosphane and **163** to form **179a**, which is also formed in the reaction between HFA and tris(ethylene)platinum in the presence of COD (*129*). The X-ray structures of **186** (*128*, *129*) and **180b** have been reported (*129*).



(188)

(147)



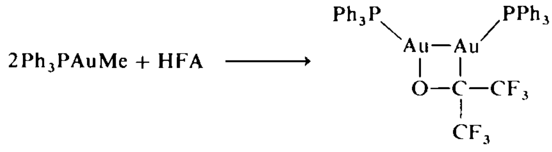
(189)

(148)

Insertion into Pt—C bonds occurs with a π-bis(1-buten-3-one)platinum(0) complex with oxidation [Eq. (147)] (*130*) and a σ-bonded platina(II)cyclobutanone with total change of the coordination sphere at the metal atom [Eq. (148)] (*62*). The structure of **189** has been characterized by X-ray analysis (*62*).

E. Gold

Only one reaction is known in which a gold compound reacts with HFA. (Triphenylphosphane)methylgold(I) forms a four-membered ring **190**, which is assigned a structure related to the diplatinum compound **186** (*196*).



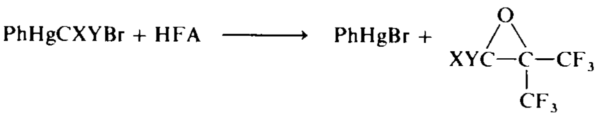
(190)

(149)

The analogous reaction with hexafluoroisopropylideneimine is not successful; the nitrogen ring can be synthesized by exchange of HFA in **190** (*196*).

F. Mercury

HFA reacts with trihalogenomethylphenylmercury compounds to form oxiranes **191**, probably via dihalocarbene intermediates (*248*).

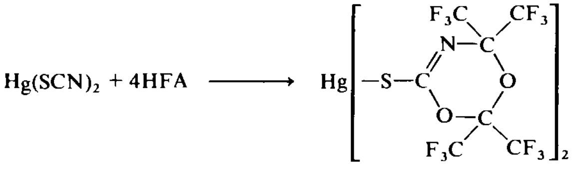


(150)

(X, Y = Cl, Br)

(191)

Mercury dithiocyanate reacts with HFA to form six-membered rings, in analogy to phosphorus, arsenic, and sulfur compounds (*vide supra*) (*241*).

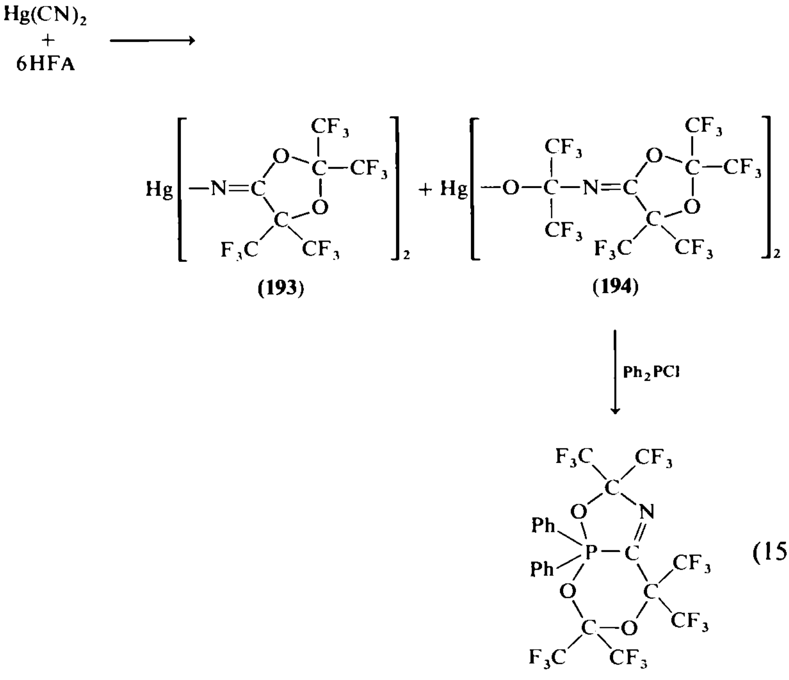


(192)

(151)

Compound **192** is a useful precursor for the transfer of the ligand with halogen-containing molecules by precipitation of HgX_2 (*241*).

The reaction of mercury dicyanide with HFA yields a mixture of **193** and **194** [Eq. (152)]. Subsequent reaction of this mixture with diphenylchlorophosphane affords the bicyclic compound **80a**. This bicycle is structurally related to the product **80** from the reaction of HFA with phenyldicyanophosphane [Eq. (68)], which is also accessible from the cyanotrimethylsilane–HFA system [Eq. (12)] (*210*) (*vide supra*).



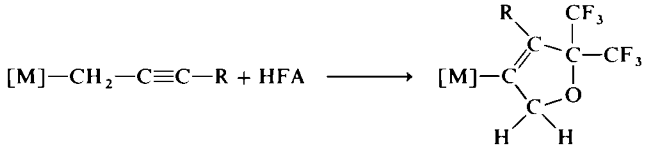
(193) **(194)**

(80a)

(152)

G. Group VI and VII Elements

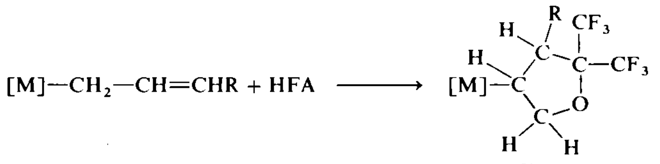
Complexes of manganese, molybdenum, and tungsten containing dihydro- and tetrahydrofuranate ligands are obtained in analogy to the iron complexes **149** and **150** (Section V,A) (*174*).



(153)

(195), **(196)**

[**195**: [M] = $CpMo(CO)_3$, R = Ph; **196**: [M] = $Mn(CO)_5$, R = Me, Ph]

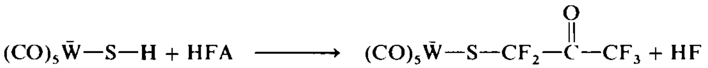


(154)

(197)-**(199)**

[M]	R	
$CpMo(CO)_3$	Ph	**197**
$CpW(CO)_3$	Ph	**198**
$Mn(CO)_5$	H, Me	**199**

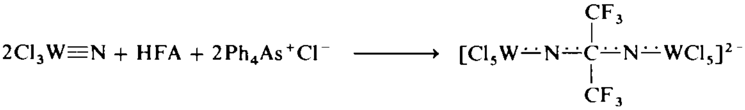
The pentacarbonyltungstenhydrogen sulfide anion has been reacted with excess HFA in acetone at ambient temperature. Equation (155) is one of the rare examples where fluorine abstraction, rather than insertion, occurs (*13*).



$$(CO)_5\overset{-}{W}-S-H + HFA \longrightarrow (CO)_5\overset{-}{W}-S-CF_2-\overset{\overset{\displaystyle O}{\|}}{C}-CF_3 + HF \qquad (155)$$

(200)

The reaction of HFA and nitridotungsten trichloride followed by addition of tetraphenylarsonium chloride yields **201**. Single-crystal X-ray structure analysis proves the formation of this surprising compound (*236*).



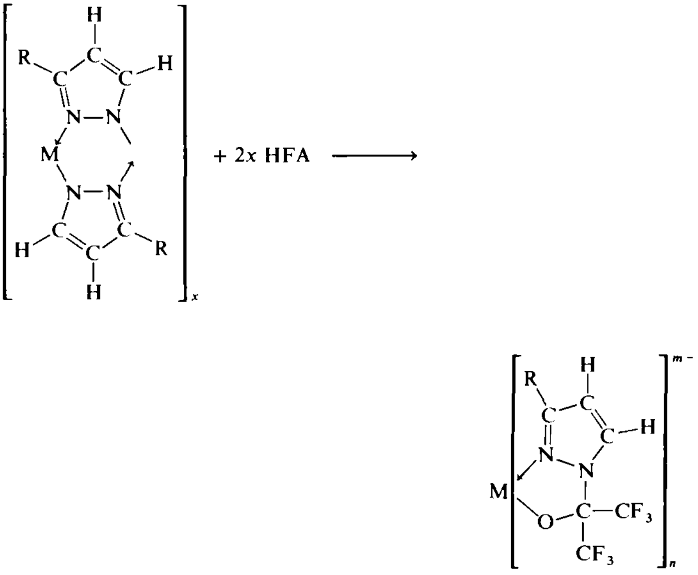
$$2Cl_3W\equiv N + HFA + 2Ph_4As^+Cl^- \longrightarrow [Cl_5W\overset{\cdots}{-}N\overset{\cdots}{-}\underset{\displaystyle CF_3}{\overset{\displaystyle CF_3}{\overset{|}{\underset{|}{C}}}}\overset{\cdots}{-}N\overset{\cdots}{-}WCl_5]^{2-} \qquad (156)$$

(201) $2Ph_4As^+$

The W—N bond of 174.3(15) pm is a little longer than that in $[Cl_5WNC_2Cl_5]^-$, which was considered to be a triple bond. Since the geometry at nitrogen is almost linear [176.9(14)°], a triple-bonded resonance extreme with a positive formal charge on nitrogen may make a significant contribution.

H. REACTIONS WITH POLYMERIC PYRAZOLE COMPLEXES

Several *d* and *f* transition metals have been found to yield polymeric complexes with pyrazoles (*14*, *178*). Reactions of these polymers with HFA produce monomeric species, HFA adding to the free nitrogen atom and the metal. Substitution of one carbon atom adjacent to nitrogen also results in degradation of the polymers. However, no reaction has been found when both α carbon atoms are sterically hindered (*14*).



(157)

(202)–(213)

Most pyrazole complexes are inert to moist air, with only the silver and gold compounds **206** and **207** showing limited stability (*178*). The X-ray structures of the unsubstituted thorium and uranium derivatives **209a** and **210a**, which are isostructural, have been reported (*280*). The hexafluoroacetonylpyrazole complexes are listed in Table IX.

TABLE IX

HEXAFLUOROACETONYLPYRAZOLE COMPLEXES

Compound	M	*n*	R	*m*	Reference
202	Fe	3	H	0	*178*
203	Ni	3	H	1	*178*
204	Cu	2, 3	H	0	*178*
205	Zn	3	H	1	*178*
206	Ag	1	H	0	*178*
207	Au	1	H	0	*178*
208	Eu	4	H	1	*178*
209	Th	4	H, Me	0	*14*, *178*
210	U	4	H, Me	0	*14*
211	UO_2	2	H	0	*178*
212	Np	4	H, Me	0	*14*
213	Pu	4	H, Me	0	*14*

VI. Miscellaneous

A. REACTIONS WITH METALS AND METAL HALIDES

The reductive coupling of HFA with alkali metals to yield perfluoropinacolate (*7*, *64*) has already been mentioned in earlier sections, together with metathetical reactions with a variety of dihalides. Similarly, free perfluoropinacol reacts with a series of metal halides in aqueous solution to yield anionic and neutral complexes of transition metals listed in Table X.

The moisture-sensitive complexes **215** and **217c** have been prepared from dilithium perfluoropinacolate and the appropriate dihalide in tetrahydrofuran. One molecule of THF is also coordinated to the metal (*64*).

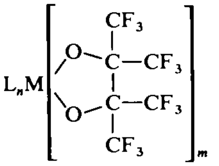
Several "organic" reactions of HFA are catalyzed by Lewis acids (e.g., $AlCl_3$) (*168*, *185*, and references cited therein).

Starting from the aldol condensation product of HFA with acetone (*255*), a series of nickel and copper di- and triamide complexes have been synthesized, which can undergo intramolecular condensation with elimination of water (*181*).

HFA forms 1:1 adducts with metal fluorides. The stability of the perfluoroisopropoxides **226** increases with the size of the cation (*224*). The salts are the

TABLE X

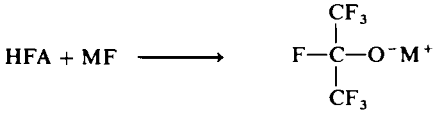
ANIONIC AND NEUTRAL PERFLUOROPINACOLMETAL COMPLEXES



Compound	M	*m*	L	*n*	Reference
214	Al	3	K	3	*8*
215	Ti	1	Cl	2	*64*
216	VO	2	K	2	*287*
217a	CrO	2	K	1	*287*
217b	CrO	2	Cs	1	*287*
217c	Cr	1	O	2	*64*
218	Mn	2	K	2	*8*
219	Fe	3	K	3	*8*
220	$Co \cdot 2H_2O$	2	K	2	*288*
221a	Ni	2	K	2	*8, 289*
221b		1	L[a]		*289*
222a	Cu	2	K	2	*8*
222b, c		1	$(R_2NCH_2—)_2$[b]	1	*289*
223	Zn	2	K	2	*8*
224	Pd	1	PMe_2Ph	2	*289*
225	Pt	1	PMe_2Ph	2	*289*

[a] L = Various neutral N- and P-containing ligands.
[b] R = Me, Et.

reactive species, and a metal fluoride is necessary to promote reaction of HFA.

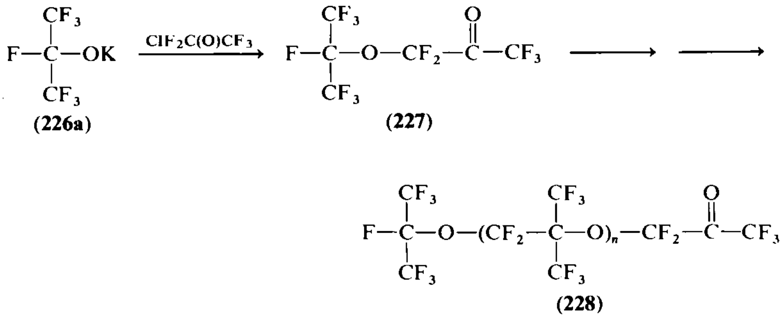


$$\text{HFA} + \text{MF} \longrightarrow \text{F—}\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{\text{C}}}\text{—}O^-M^+ \qquad (158)$$

(M = K, Rb, Cs, Ag, NEt_4) **(226)**

The lattice energy of the metal fluorides is the main factor in promoting the reaction. Though the lattice energy of NaF is smaller than that of AgF, no adduct formation has been observed. This is due to complex formation of AgF with the solvent acetonitrile prior to the reaction with HFA (*99*).

The potassium salt **226a** has been found to react with pentafluorochloroacetone. Subsequent treatment with KF and excess of pentafluorochloroacetone yields perfluorinated polyethers **228** (*167*).

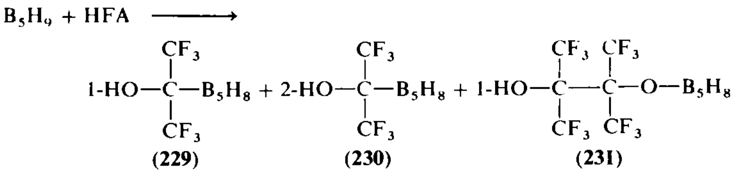


$$F\text{—}C(CF_3)_2\text{—}OK \xrightarrow{ClF_2C(O)CF_3} F\text{—}C(CF_3)_2\text{—}O\text{—}CF_2\text{—}C(O)\text{—}CF_3 \longrightarrow \longrightarrow F\text{—}C(CF_3)_2\text{—}O\text{—}(CF_2\text{—}C(CF_3)_2\text{—}O)_n\text{—}CF_2\text{—}C(O)\text{—}CF_3 \qquad (159)$$

(226a) **(227)** **(228)**

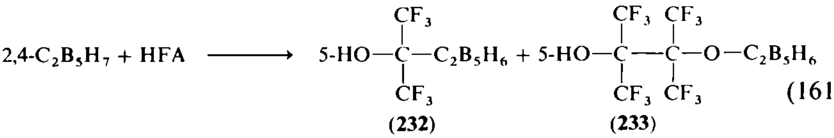
B. Boron

Only a few reports deal with the interaction of boron compounds with HFA. No addition products of HFA with monoborane have been detected in thermal (*101*) or in photochemical (*264*) reactions. However, co-photolysis of HFA with pentaborane(9) and 2,4-dicarbapentaborane(7) results in the insertion of HFA into B—H bonds (*16a*). Mechanisms are discussed in detail.



$$B_5H_9 + HFA \longrightarrow 1\text{-}HO\text{—}C(CF_3)_2\text{—}B_5H_8 + 2\text{-}HO\text{—}C(CF_3)_2\text{—}B_5H_8 + 1\text{-}HO\text{—}C(CF_3)_2\text{—}C(CF_3)_2\text{—}O\text{—}B_5H_8 \qquad (160)$$

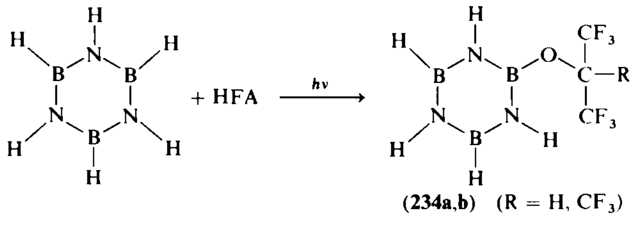
(229) **(230)** **(231)**



$$2{,}4\text{-}C_2B_5H_7 + HFA \longrightarrow 5\text{-}HO\text{—}C(CF_3)_2\text{—}C_2B_5H_6 + 5\text{-}HO\text{—}C(CF_3)_2\text{—}C(CF_3)_2\text{—}O\text{—}C_2B_5H_6 \qquad (161)$$

(232) **(233)**

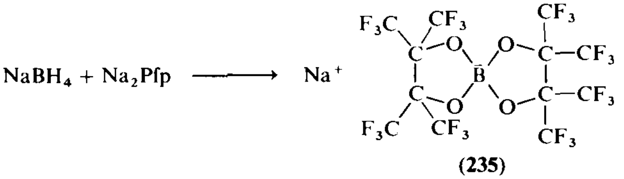
Photochemical insertion into a B—H bond occurs with borazine (*267*). The CF_3-substituted product **234b** arises from radical decomposition of the HFA molecule.



(162)

(234a,b) (R = H, CF_3)

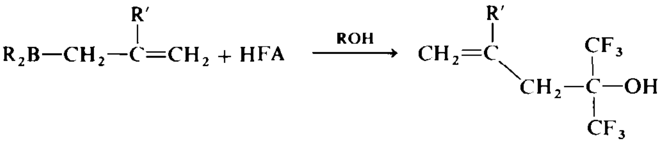
Phenyldichloroborane reacts with perfluoropinacolate to form a 1,3,2-dioxaborolane (*7*, *64*). A spirobicyclic boranate **235** is generated from sodium borohydride and disodium pinacolate (*7*).



(235)

(163)

Allylboranes react with HFA in the presence of alcohols like nonanol or triethanolamine to yield partially fluorinated, unsaturated alcohols **236** (*194*).



$$R_2B{-}CH_2{-}C(R'){=}CH_2 + HFA \xrightarrow{ROH} CH_2{=}C(R'){-}CH_2{-}C(CF_3)_2{-}OH \qquad (164)$$

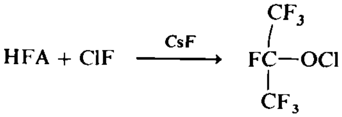
(R = Pr, Bu; R′ = H, Me) **(236)**

Migration of the double bond and rearrangement of the skeleton have been observed with 2-butenylboranes (*194*).

Pentacoordinated (10-B-5) and hexacoordinated (12-B-6) boron compounds are available from the reaction of BCl_3 with the dilithio salt of the bis addition product of HFA and pyridine (*265*). These hypervalent compounds show signals in the ^{11}B NMR spectrum at very high field (*173a*).

C. HALOGENATION REACTIONS

Chlorine monofluoride reacts with HFA under the catalytic influence of cesium fluoride to form perfluoroisopropoxy hypochlorite (**237**) (*292*).



$$HFA + ClF \xrightarrow{CsF} FC(CF_3)_2{-}OCl \qquad (165)$$

(237)

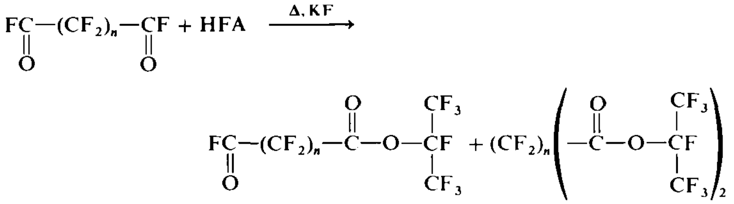
Fluorination of HFA with XeF_2 has not been observed (*114*).

Photochemical reaction of HFA with fluorine, also in the presence of oxygen, has been investigated by Aymonino (*19*). Depending on the stoichiometry, different product distributions have been observed.

$$HFA + F_2 \xrightarrow{h\nu} CF_3COF, COF_2, CF_3OF, CF_4 \qquad (166)$$

$$2HFA + O_2 + F_2 \xrightarrow{h\nu} CF_3COF, COF_2, CF_3OF, CF_3OOCF_3 \qquad (167)$$

Insertion of HFA into the C—F bonds of perfluorinated dicarboxylic acyl fluorides has been achieved thermally under the catalytic influence of potassium fluoride (*70*).



$$\underset{\underset{\displaystyle O}{\|}}{FC}-(CF_2)_n-\underset{\underset{\displaystyle O}{\|}}{C}F + HFA \xrightarrow{\Delta,\,KF} \underset{\underset{\displaystyle O}{\|}}{FC}-(CF_2)_n-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CF_3}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{C}}F + (CF_2)_n\left(-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CF_3}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{C}}F\right)_2 \qquad (168)$$

(238) **(239)**

A,ω-Diacyl-substituted perfluoro ethers react in a similar way (*70*).

VII. Summary

This article has summarized achievements in the synthesis of "inorganic" compounds using HFA as starting material.

Hexafluoroacetone has been found to be a very interesting synthon on the borderline between inorganic and organic chemistry, and has established its own chemistry with various nonmetallic and metallic substrates; only a few types of reactions resemble those of a regular ketone. The electron-withdrawing properties of the CF_3 groups are the stabilizing factor for structures that would otherwise be inaccessible. Only a few cases are known in which the electronic properties of HFA have inhibited any reaction.

Furthermore, the six fluorine atoms of HFA provide the chemist with a versatile tool for the investigation of dynamic processes by means of ^{19}F NMR spectroscopy.

Reactions of HFA with transition metals are known. Further studies in this direction will provide a better understanding of the chemistry of HFA.

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