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FLUORINATED ALCOHOLS AND THEIR METAL COMPLEXES

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CONTENTS

ABBREVIATIONS

R_f	fluorinated alkyl group, $C_nF_{(2n+1)}$
HFA	hexafluoroacetone, $(CF_3)_2C{=}O$
H_2PFP	perfluoropinacol, $HOC(CF_3)_2C(CF_3)_2OH$
PFP^{2-}	perfluoropinacol dianion, $[^-OC(CF_3)_2C(CF_3)_2O^-]$
H_2TFC	tetrafluorocatechol, *ortho*-$HO{-}C_6F_4{-}OH$
TFC	tetrafluorocatechol dianion, *ortho*-$[^-O{-}C_6F_4{-}O^-]$
TMED	*N,N,N′,N′*-tetramethylethylenediamine
bipy	α,α'-bipyridyl
diphos	1,2-bis(diphenylphosphino)ethane
diars	*o*-bis(dimethylarsino)benzene
cp	cyclopentadienyl
$[TAS^+]$	tris(dimethylamino)sulphonium cation
FAE	gaseous fluoride ion attachment enthalpy

Molecular dimensions are given in ängstroms, with uncertainties in the last figure(s), where available, in parentheses.

All thermochemical quantities are quoted in kilojoules per mole (kJ mol^{-1}).

A. INTRODUCTION: SCOPE OF THE REVIEW

One of the largest and most important groups of ligands is that in which coordination to the metallic ion occurs through oxygen. If that oxygen atom is bonded to carbon, the resulting complexes may be divided into two classes. In the first class are those complexes such as the metal carboxylates, carbonates, acetylacetonates etc. which are stable to hydrolysis and may be studied by conventional solution chemistry. In the second class are the metal alkoxides whose generally low hydrolytic stability requires the use of careful technique for study and restricts the range of complexes which may be prepared. For recent reviews, see ref. 1.

In recent years, it has been found that highly fluorinated alcohols are capable of giving metal complexes which, although formally alkoxides, have properties closer to the first of the above classes. The high acidity of the parent alcohol or diol often stabilizes the metal derivative to the point where it resembles a carboxylate rather than an alkoxide. However, the fluorinated alkoxide anion usually acts as a unidentate ligand, with less tendency to bridge between metal ions than either the carboxylate or the unfluorinated alkoxide. These features, combined with their chemical stability and resistance to oxidation, make the fluorinated alkoxides valuable as a general means of attaching organic groups to a metal ion. By suitable design of the ligand molecule, various other donor sites may be incorporated, leading to a wide range of novel complexes of metals. To the present, derivatives of metals ranging from lithium to neptunium have been reported, and it may safely be claimed that, under the appropriate conditions, every metal can form stable fluorinated alkoxides.

In this review the current status of this field is set out. The ligands discussed are those where there is a high degree of fluorination adjacent to the hydroxyl group, i.e. CF_3CH_2OH, RCF_2OH, $RCF(CF_3)OH$, $RC(CF_3)_2OH$ and C_6F_5OH. In less highly fluorinated alcohols, the properties of the molecule are not significantly changed and metal complexes are more "typical" alkoxides.

In Section B, an introduction to the synthesis and properties of highly fluorinated alcohols is given. Their coordination complexes are then discussed in Section C. Derivatives of monofunctional alcohols are discussed first, followed by those of diols and phenols. In Section D, derivatives of multifunctional ligands are discussed according to the second donor site present. Within each type, complexes are discussed in the approximate order of first-row transition metals, followed by heavy transition metals, main-group metals and (briefly) non-metals.

In the final part of the review (Section E), some general properties of fluorinated alkoxides are discussed in terms of their chemical, spectroscopic and structural characteristics and their possible applications.

B. PROPERTIES OF FLUORINATED ALCOHOLS

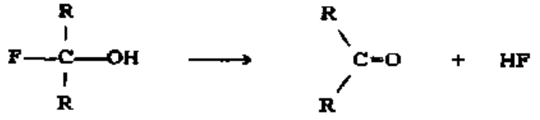
Brief general reviews on fluorinated alcohols appeared in 1970 and 1973 [2].

(i) Stability

In 1970 the claim was made that "by and large, an instructor can now substitute a perfluoro analogue for a conventional organic compound with the assurance that he is talking about a real compound rather than a hypothetical one" [3]. However, the fluorinated alcohols will always remain an exception to this generalization. All primary fully fluorinated alcohols,

R_f–OH, and most secondary alcohols, $(R_f)_2CF(OH)$, will be unstable. Only in the case of tertiary alcohols, $(R_f)_3C$–OH, is stability possible.

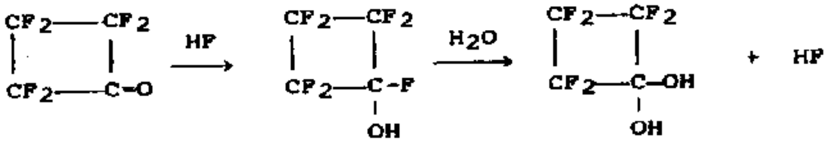
The reason for this problem is the ready elimination of HF from any alcohol where the same carbon atom carries fluorine and hydroxide, i.e. a ketone fluorohydrin:



(1)

Using normal bond-energy values, ΔH for the forward reaction is calculated to be about -60 kJ mol^{-1}. In the specific case of trifluoromethanol, Batt and Walsh calculated a value of -893 kJ mol^{-1} for ΔH_f° using group additivity bond energies [4]; this corresponds to a slightly exothermic decomposition ($\Delta H = -18$ kJ mol^{-1}) into COF_2 and HF. This is consistent with the experimental evidence of Klöter and Seppelt who prepared CF_3OH by the reaction of CF_3OCl with HCl at -120 °C; it melts sharply at -82 °C but decomposes at higher temperatures [5].

One of the very few isolable compounds of this type is octafluorocyclobutanol, **2**, boiling point 58 °C, for which the corresponding cyclic ketone **1** is destabilized by strain in the four-membered ring [6]. However, this alcohol reacts immediately with water to eliminate HF and form the corresponding *gem* diol **3**:



1 **2** **3**

(2)

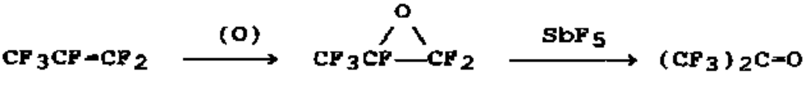
A fluorinated alcohol of surprising stability is pentafluoro-1-propen-2-ol, $CF_2{=}C(CF_3)OH$. Although elimination of HF cannot occur in this case, the alcohol is the enol isomer of pentafluoroacetone $CF_2HC(O)CF_3$. The ketone is the more stable compound, but the metastable propenol does not readily isomerize when pure [7].

With tertiary fully fluorinated alcohols $(R_f)_3COH$, elimination of HF is not possible. Similarly, highly fluorinated secondary alcohols $(R_f)_2CHOH$, of which hexafluoro-2-propanol is the most familiar example, are very stable.

(ii) Synthesis

The aim of this section will be to show important synthetic routes to fluorinated alcohols; no attempt is made to list all known compounds.

The usual synthetic route to a fluorinated alcohol is the reaction of a nucleophile with a fluorinated carbonyl compound. Hexafluoroacetone (HFA) is by far the most important fluorinated ketone, and its chemistry has been reviewed by Krespan and Middleton [8] and, more recently, by Witt et al. [9]. HFA may be prepared in a number of ways [8], of which two routes suitable for commercial production are the fluorination of hexachloroacetone using HF and Cr^{3+} catalyst, and the isomerization of hexafluoropropene oxide **4**:



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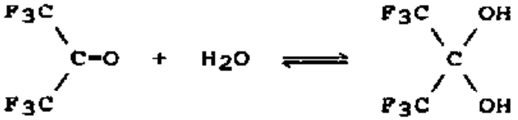
(3)

Addition of water to HFA gives "hexafluoroacetone hydrate" [10], i.e. hexafluoropropane-2,2-diol, **5**:



5

(4)

As with **3**, the presence of the electronegative substituents stabilizes the *gem* diol, and **5** is a solid of melting point 49 °C. Aliphatic alcohols react similarly with HFA to give hemiketals $ROC(CF_3)_2OH$ [11,12]. Hydrogenation of HFA gives hexafluoro-2-propanol, $(CF_3)_2CHOH$ [10], and other products of the addition of active hydrogen to HFA have been reviewed [8,9].

While the product of reaction of X–H with $(CF_3)_2C{=}O$ is generally $XC(CF_3)_2{-}OH$, the addition is in the opposite direction when X is a more electropositive element such as silicon [13,14], germanium, tin [15], cobalt or ruthenium [16], giving a direct route to hexafluoro-isopropoxides of such elements:

$$R_3SiH + (CF_3)_2C{=}O \rightarrow R_3SiOC(CF_3)_2H \quad (R = Cl \text{ or } CH_3) \tag{5}$$

The strongly electrophilic nature of HFA makes it subject to attack by the nucleophile $HC(CF_3)_2O^-$, giving "head-to-tail" dimerization of the ketone. Termination with a non-protonic electrophile then leads to stable derivatives such as **6** [14]:

$$\begin{array}{l} H^- + (CF_3)_2C{=}O \rightarrow HC(CF_3)_2C{-}O^- \xrightarrow{HFA} HC(CF_3)_2OC(CF_3)_2C{-}O^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow Me_3SiCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad HC(CF_3)_2OC(CF_3)_2OSiMe_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{6} \end{array} \tag{6}$$

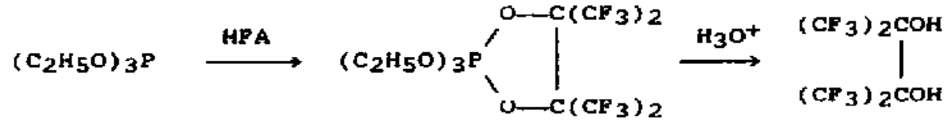
Tertiary alcohols derived from HFA are particularly relevant to the present review. They may be divided into two classes: fully fluorinated $R_fC(CF_3)_2OH$ and partially fluorinated $RC(CF_3)_2OH$. Fully fluorinated organolithium reagents such as $CF_2{=}CF{-}Li$ [17,18] or $C_6F_5{-}Li$ [17,19] may be used in synthesis. However, a more general synthetic route came from the key realization by Miller et al. [20] that addition of F^- to fluorinated alkenes would generate fluorinated carbanions [21] (for reviews see ref. 22):

$$CF_2{=}CF_2 \xrightarrow{CsF/diglyme} [CF_2{-}CF_3]^- \xrightarrow{(1)\ HFA\ (2)\ H_3O^+} CF_3CF_2C(CF_3)_2OH \qquad (7)$$

Perfluoro-*t*-butanol, $(CF_3)_3COH$, is not available by either of the above routes. It was first prepared via $(CF_3)_3CNO$ [23], and other routes have been developed involving the intermediate $CCl_3C(CF_3)_2OH$ [24,25] and by the reaction of HFA at 150 °C with CsF in "wet" diglyme [26]:

$$CsF + 2(CF_3)_2C{=}O \rightarrow CF_3C(O)F + Cs^+[(CF_3)_3CO^-] \qquad (8)$$

The most important fluorinated diol is perfluoropinacol (H_2PFP), $(CF_3)_2C(OH)C(CF_3)_2OH$. It has been prepared from HFA using the photo-initiated reduction with 2-propanol [10], by the reduction of HFA with sodium [27] or lithium [28] in a donor solvent, or by use of triethyl phosphite [29,30]:



(9)

Partially fluorinated tertiary alcohols $RC(CF_3)_2OH$ may be made by reaction of Grignard [12,31] or organolithium [32] reagents with HFA. Despite the electrophilic nature of the ketone, steric hindrance can sometimes inhibit the reaction; for example, HFA is less reactive toward phenyl magnesium bromide than is acetone [31].

A useful intermediate is the keto alcohol $CH_3C(O)CH_2C(CF_3)_2OH$, prepared by the reaction of HFA with acetone at 135 °C [33].

Pentafluoropropen-2-ol, 7, is prepared from chloropentafluoroacetone by the following sequence [7]:

$$CF_2ClC(O)CF_3 \xrightarrow{P(OMe)_3} CF_2{=}C(CF_3)OP(O)(OMe)_2 \xrightarrow[(conc)]{H_2SO_4} \underset{7}{CF_2{=}C(CF_3)OH} \qquad (10)$$

Synthetic routes using fully fluorinated ketones other than HFA are restricted by their limited availability. Photodimerization of octafluoroacetophenone gives the chiral diol $[CF_3(C_6F_5)C(OH){-}]_2$, one of the first fully fluorinated compounds to be optically resolved [17,34], and the partially fluorinated benzopinacol $[C_6F_5(C_6H_5)C(OH)-]_2$ is similarly prepared from the ketone $C_6F_5C(O)C_6H_5$ [35].

Pentafluorophenol, C_6F_5OH, is prepared by the reaction of hexafluorobenzene with KOH in *t*-butanol [36].

(iii) Structures

There is little experimental data available on the structures of fluorinated alcohols, but the simple nature of trifluoromethanol has led to numerous theoretical treatments. An early INDO calculation was done by Gordon and Pople [37], and more recent ab initio calculations have been reported by Olsen and Howell [38], by Francisco [39] and by Grein [40]. A staggered conformation is found, and structural data are given in Table 1. Francisco finds excellent agreement between calculated and experimental [5] values of the vibrational spectrum of CF_3OH. Ab initio calculations on both CF_3OH and CF_3NH_2 have been reported by Heaton and Mills [41], who find the O–H bond to be weakened by about 20% on fluorination, and suggest that this contributes to the increased acidity. In contrast, Batt and Walsh find the O–H bond to be 5% stronger in CF_3OH than in CH_3OH [4].

These calculated dimensions form a useful starting point for consideration of bond lengths, particularly r(C–O), in fluorinated alkoxides. The presence of fluorine lowers the energy of antibonding orbitals on the carbon atom, and donation of electron density from non-bonding pairs on oxygen leads to partial π bonding in the C–O bond. As a result, the C–OH bond length is less than its normal value of 1.43 ± 0.01 Å [42].

This effect should be reduced when the substituents on the carbinol are CF_3 or other groups, less electron-withdrawing than fluorine, and the few experimental results available on unionized alcohols are consistent with this. Electron diffraction [43] on $(CF_3)_3COH$ gives a C–O bond length of 1.414 ± 0.022 Å, while an X-ray structure determination [44] on P-coordinated $Ph_2PCH_2C(CF_3)_2OH$ gives $r(C–O) = 1.388 \pm 0.007$ Å.

TABLE 1

Calculated bond lengths (Å) in CF_3OH

	r(C–O)	r(C–F^1) [a]	r(C–F^2)	r(O–H)
Gordon and Pople (1968) [37]	1.36	1.34		1.04
Olsen and Howell (1978) [38]	1.346	1.347		0.947
Francisco (1984) [39]	1.343	1.328	1.344	0.966
Grein (1985) [40]	1.338	1.357	1.346	0.954

[a] Where two C–F bond lengths are given, F^1 is the fluorine atom *anti* to the proton; F^2 atoms are *gauche* to the proton.

(iv) Chemical properties

Fluorinated tertiary alcohols are stable, relatively unreactive compounds which do not have the central position in synthetic chemistry occupied by their unfluorinated analogues. This difference may be attributed to the increased strength of the C–O bond associated with the presence of electron-withdrawing CF_3 groups.

(a) Acidity

For potential use as ligands, the most important property of the fluorinated alcohols is their increased acidity. The first observations were made by Swarts [45], and many subsequent studies have appeared [10,17,23,24,46]. The general trend may be illustrated by quoting some changes in pK_a values (aqueous solution) when methyl groups are replaced by trifluoromethyl:

CH_3CH_2OH,	15.9;	CF_3CH_2OH,	12.8		
$(CH_3)_2CHOH$,	17.1;	$(CF_3)_2CHOH$,	9.3		
$(CH_3)_3COH$,	19.2;	$(CF_3)_2C(CH_3)OH$,	9.6;	$(CF_3)_3COH$,	5.4

Complete fluorination of a tertiary alcohol produces an acidity comparable to that of a carboxylic acid, while partial fluorination, to give $R{-}C(CF_3)_2{-}OH$, produces an acidity which, while weaker, is still stronger than that of an unfluorinated alcohol by 6–9 pK_a units.

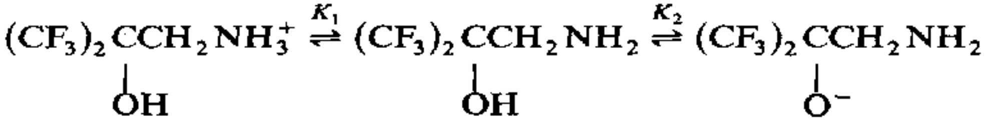
The simplest fluorinated diols, hexafluoro-2,2-propanediol("hexafluoroacetone hydrate"), and perfluoropinacol, H_2PFP, have respective pK_a values of 6.58 and 5.95 [10]. Although no second end point can be detected in the titration of H_2PFP, the dianion may be isolated as Na_2PFP in a non-aqueous medium [27], and metal complexes of $[PFP]^{2-}$ are readily prepared (Section C(vi)).

Pentafluorophenol has a pK_a of 5.52 [36], a decrease on complete fluorination of only 4.4 units (cf. the change of nearly 14 units on fluorination of *t*-butanol) and is less acidic than C_6Cl_5OH (pK_a 5.23). The mixed alcohols $C_6F_5C(CF_3)_2OH$ and $CF_3C(C_6F_5)_2OH$ are much weaker than $(CF_3)_3COH$, with pK_a values of 7.9 and 9.2 respectively, while no end point could be seen in a titration of $(C_6F_5)_3COH$ [17]. The surprisingly low electronegativity of the pentafluorophenyl group has been explained by Chambers in terms of destabilization of negative charge on the fluorinated aromatic ring by interaction with non-bonding *p*-electron density on fluorine atoms [47].

The analogous trifluorovinyl-substituted alcohols, $CF_2{=}CFC(CF_3)_2OH$ and $CF_3C(CF_2{=}CF)_2OH$, have pK_a values of 6.8 and 7.7 respectively [17], showing the trifluorovinyl substituent to be more electron withdrawing than pentafluorophenyl. A study of pK_a values in 60% dimethylsulphoxide (DMSO) solution shows the same general trends [48]. The pK_a figures are the following: C_6F_5OH, 6.0; CH_3COOH, 6.3; $(CF_3)_3COH$, 6.7; $(CF_3)_2C(OH)_2$, 8.7; $(CF_3)_2CHOH$, 11.2; C_6H_5OH, 11.8; CF_3CH_2OH, 14.5; H_2O, 18.3.

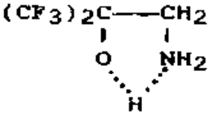
Measurement of the ionization enthalpies, ΔH_i, of alcohols in DMSO shows a clear difference accompanying fluorination [49]. Whereas water and unfluorinated alcohols have ΔH_i in the range 150–162 kJ mol^{-1}, the values for fluorinated alcohols are as follows: CF_3CH_2OH, 127 kJ mol^{-1}; $(CF_3)_2CHOH$, 89 kJ mol^{-1}; $(CF_3)_3COH$, 59 kJ mol^{-1}.

The acidity of amino-substituted fluoro alcohols is of interest because of their resemblance to amino acids and the possibility of zwitterionic behaviour [50]:



$$(CF_3)_2\underset{\mathrm{OH}}{\underset{|}{C}}CH_2NH_3^+ \overset{K_1}{\rightleftharpoons} (CF_3)_2\underset{\mathrm{OH}}{\underset{|}{C}}CH_2NH_2 \overset{K_2}{\rightleftharpoons} (CF_3)_2\underset{\mathrm{O^-}}{\underset{|}{C}}CH_2NH_2 \qquad (11)$$

Values of pK_1 and pK_2 are 5.35 and 8.63 respectively, giving an isoelectric point of 6.99; the comparable figures for glycine are 2.34, 9.60 and 5.97. From IR spectra, the solid state structures of this alcohol and $(CF_3)_2C(OH)CH_2NHCH_3$ are believed to be hydrogen bonded:



but with a longer chain, a complete charge separation is found in $(CF_3)_2C(O^-)CH_2CH_2NH_3^+$ [50].

(b) Gaseous electron and proton affinities

Using ion cyclotron resonance, Clair and McMahon have studied fluorinated alcohols in the gas phase. For the reaction

$$(CF_3)_3CO^-(g) + H^+(g) \rightarrow (CF_3)_3COH(g) \qquad (12)$$

ΔH is -1376 kJ mol^{-1} [51], intermediate between the proton affinities of Cl^- and Br^-. A related quantity of considerable interest is the electron affinity of the alkoxy radical. For the reaction

$$(CF_3)_3CO^{\cdot}(g) + e^-(g) \rightarrow (CF_3)_3CO^-(g) \qquad (13)$$

ΔH is -368 kJ, greater than the electron affinity of any halogen atom, and among the highest known for an organic radical.

The gaseous fluoride ion affinities of alcohols correlate with acidities over a wide range [52]. For fluorinated alcohols, the dissociation of an adduct of this type follows the course

$$[R{-}O\cdot\cdot H\cdot\cdot F]^-(g) \rightarrow R{-}O^-(g) + H{-}F(g) \qquad (14)$$

TABLE 2

Comparison of boiling points of fluorinated and unfluorinated alcohols

Fluorinated alcohol	Boiling point (°C)	Unfluorinated alcohol	Boiling point (°C)	Difference (°C)
CF_3OH	−20 (estimated)	CH_3OH	65	~85
$(CF_3)_3COH$	45	$(CH_3)_3COH$	82	37
$C_6F_5C(CF_3)_2OH$	162	$C_6H_5C(CH_3)_2OH$	202	40
$(CF_3)_2C(OH)C(CF_3)_2OH$	130	$(CH_3)_2C(OH)C(CH_3)_2OH$	172	42
C_6F_5OH	143	C_6H_5OH	182	39

and ΔH values reflect the stability of the alkoxide anions: $(CF_3)_3COH$, 74 kJ mol^{-1}; $(CF_3)_2CHOH$, 105 kJ mol^{-1}; CF_3CH_2OH, 134 kJ mol^{-1}.

(c) Hydrogen bonding

It would be out of place in this review to describe the very extensive studies which have been reported on hydrogen bonding in fluorinated alcohols, and details may be found in refs. 54–60 and citations therein.

The presence of electron-withdrawing groups adjacent to the hydroxyl function makes the oxygen a weaker donor, while the proton is a stronger acceptor. As a result, there is weaker intermolecular hydrogen bonding between fluorinated alcohols, but stronger interaction between the alcohol and a donor molecule (in particular, an ether) than is the case in the absence of fluorination.

A high degree of fluorination always lowers the boiling point of an alcohol. Typical boiling point values are given in Table 2.

However, a similar difference is commonly found when the boiling points of small polar molecules containing no possibility of hydrogen bonding are compared with those of their fluorinated analogues. With the possible exception of CF_3OH, the lower boiling points of fluorinated alcohols may equally well be interpreted in terms of the weakness of interactions between fluorocarbon molecules [53], rather than in terms of a specific decrease in hydrogen bonding.

Filler and Shure [24] used the shift in the IR O–H frequency of the alcohol between CCl_4 and THF solutions, $\Delta\nu$, as a measure of the strength of hydrogen-bonding, and later work has extended the range of alcohols studied [17]. Purcell and coworkers measured the enthalpy of interaction between fluorinated alcohols and ethers and found a linear correlation with O–H spectral shifts [54,55]. Using precise calorimetry, Guidry and Drago

TABLE 3

Correlation between enthalpy change and pK_a with degree of fluorination of alcohols

	C_2H_5-OH	$CHFCH_2$-OH	CHF_2CH_2-OH	CF_3CH_2-OH	$(CF_3)_2CH$-OH	$(CF_3)_3C$-OH
pK_a	15.9	14.5	13.3	12.4	9.3	5.4
$\Delta H°$ (kJ)	−8.3	−11.8	−15.1	−18.2	−27.4	−36.9

found evidence for intramolecular hydrogen-bonding from CF_3 groups to −OH [56].

Very detailed IR spectroscopic work has been reported by Murto and coworkers [57,58]. Luck and coworkers have extended these studies to the argon matrix phase [59,60]. They have measured $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the interaction of alcohols with $(CH_3)_2O$ in CCl_4 solution, finding trends consistent with earlier studies. The enthalpy change correlates with the pK_a as the degree of fluorination is increased [60] (see Table 3).

For comparison, the enthalpy of interaction of phenol with $(C_2H_5)_2O$ is -24 kJ mol^{-1} [61], while HF has ΔH values of -43 kJ mol^{-1} and -30 kJ mol^{-1} for hydrogen-bonding to $(CH_3)_2O$ and $(C_2H_5)_2O$ respectively [62].

Schriver and Burneau, in an IR study on $(CF_3)_3COH$ in matrices, have shown the existence of dimers and interaction between the alcohol and chlorinated solvents [63].

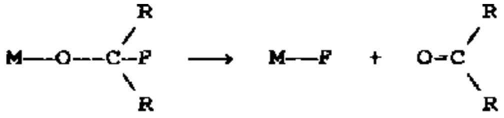
In contrast to the well-defined reaction with ethers, fluorinated alcohols do not generally form stable hydrates. An exception is found with the *gem* diols $(R_f)_2C(OH)_2$, where the presence of two hydroxyl groups leads to stronger interaction with water and hydrate formation [8,10]. Although reaction with a stronger base might be expected to produce ionization of a fluorinated alcohol, the low temperature NMR spectra of mixtures of $(C_2H_5)_3N$ with $(CF_3)_2CHOH$ and C_6F_5OH have been interpreted in terms of hydrogen-bonded molecular adducts, rather than proton-transferred ion pairs [64].

C. METAL DERIVATIVES OF FLUORINATED ALCOHOL, DIOLS and PHENOLS

The emphasis in this review is on the properties of fluorinated alcohols as ligands towards metal ions and of the complexes so formed. There is in addition a considerable body of work on the derivatives of fluorinated alcohols formed by important non-metallic elements including silicon, nitrogen, phosphorus, oxygen, sulphur and the halogens. For convenience, leading references to this work have been included for the alcohols in this section, but no extended discussion has been attempted.

(i) Stability

The stability of covalent alkoxides towards fluoride elimination will be limited in the same way as that of the fluorinated alcohols themselves. For the reaction



$$\mathrm{M{-}O{-}C(R)_2{-}F} \longrightarrow \mathrm{M{-}F} + \mathrm{O{=}C(R)_2} \qquad (15)$$

a crude estimate of ΔH may be obtained from bond dissociation energies. Calculating the value of ΔH for the decomposition in this way for various elements M gives the results shown in Table 4

For M = F, direct measurements have been made on the dissociation of trifluoromethyl hypofluorite

$$CF_3{-}O{-}F \rightleftharpoons COF_2 + F_2 \qquad (16)$$

for which $\Delta H = +113$ kJ [65]. The variance between this result and the previous calculation is to be expected, given the obvious danger of using conventional bond energies in highly fluorinated systems, but the general trend is clear; the $M{-}O{-}CF_3$ structure will be more stable when M is a small highly electronegative atom.

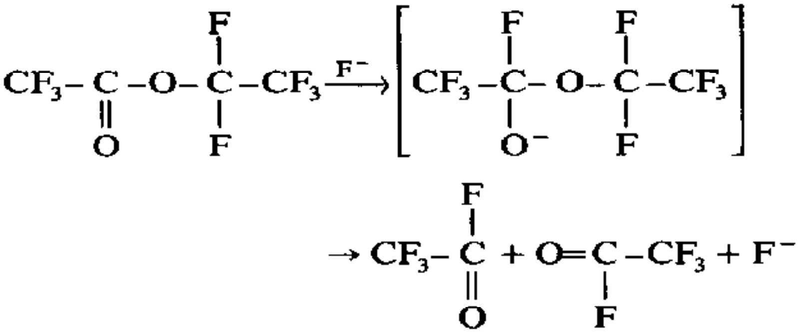
Where M is carbon, the value of ΔH for eqn. (15) simply represents the difference in energy between two C–O single bonds and one C=O double bond. In hydrocarbon derivatives, these depend on the molecular geometry and ΔH can vary accordingly. Thus the process $CH_3C(O)OCH_2CH_3 \rightarrow 2CH_3CH{=}O$ is unfavourable ($\Delta H = +110$ kJ) because of the instability of the $-CH{=}O$ group. The difference produced by fluorination is elegantly demonstrated by the work of Shreeve and coworkers on perfluoroesters [66]. They find that perfluoro(ethyl acetate) or other esters derived from primary alcohols may be synthesized at very low temperatures (optimally −105 °C) by fluoride-catalysed dimerization of perfluoroacyl fluorides. The esters appear to be stable at room temperature when pure, but immediately revert

TABLE 4

Calculated ΔH values for the decomposition of alkoxides for various elements M

M =	C	Si	N	O	F	Cl	Br
ΔH (kJ mol^{-1})	−83	−69	−38	−4	+79	+13	−4

to acyl fluorides in the presence of small amounts of alkali metal fluorides, showing that their apparent stability must be kinetic in origin:



$$CF_3-\underset{\underset{O}{\|}}{C}-O-\overset{F}{\underset{F}{C}}-CF_3 \xrightarrow{F^-} \left[CF_3-\overset{F}{\underset{O^-}{C}}-O-\overset{F}{\underset{F}{C}}-CF_3\right]$$

$$\rightarrow CF_3-\overset{F}{\underset{\underset{O}{\|}}{C}} + O{=}\underset{F}{C}-CF_3 + F^- \qquad (17)$$

For M = Si, where intramolecular transfer of fluorine from carbon to silicon may easily occur, elimination of COF_2 will be rapid, and attempts to synthesize derivatives of the type $R_3Si-O-CF_3$ lead instead to R_3SiF [67,68].

A second factor affecting the stability to hydrolysis of fluorinated alkoxides of metals will be the acidity of the parent alcohol. Clearly, in a potential hydrolysis sequence

$$M(OR)_n \overset{H_2O}{\rightleftharpoons} M^{n+}(aq) + nRO^- \overset{H_2O}{\rightleftharpoons} M(OH)_n + nROH \qquad (19)$$

the position of the equilibrium will be affected by several factors, but one important influence will be the base strength of the ion RO^-. The stabilization of each alkoxide linkage relative to the hydrolysis products from this cause alone will be directly proportional to the difference in pK_a values between the parent alcohols: $\Delta G_1 - \Delta G_2 = 2.303RT(pK_1 - pK_2)$ and this will increase with the degree of fluorination as shown in Table 5.

Simplistic as the above arguments are, they do provide a rough guide to the relative stabilities which may be expected among fluorinated alkoxides. Synthetic work on covalent compounds of both metals and non-metals has therefore been concentrated on the very stable derivatives of such potential ligands as CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_3COH$, C_6F_5OH, $HOC(CF_3)_2$-$C(CF_3)_2OH$ and the wide variety of tertiary alcohols $RC(CF_3)_2OH$.

(ii) Synthesis

Important general methods of synthesis for fluorinated alkoxides are described in this section; examples and references are given in the following sections under specific compounds. The synthetic approaches may be divided into two classes: those which start from the parent alcohol, and those where the alkoxide is synthesized directly without use of the alcohol. In

TABLE 5

Stabilization of alkoxide linkage in relation to pK_a difference between fluorinated and unfluorinated alcohols

Unfluorinated alcohol	pK_a	Fluorinated alcohol	pK_a	per M–O link at 298 K (kJ mol^{-1})
CH_3CH_2OH	15.9	CF_3CH_2OH	12.8	18
$(CH_3)_2CHOH$	17.1	$(CF_3)_2CHOH$	9.3	44
$(CH_3)COH$	19.2	$(CF_3)_3COH$	5.4	78

many cases, the parent alcohol is not capable of independent existence, and direct synthesis of the alkoxide is essential.

The acidic nature of fluorinated alcohols makes it easy to prepare group I metal derivatives, which may then be used to attach the alkoxide function to other elements. This reaction, which is usually carried out under anhydrous conditions, is the most generally useful synthetic route where the alcohol is available:

$$R(R_f)_2COH \xrightarrow{BuLi} R(R_f)_2COLi \xrightarrow{MCl_n} [R(R_f)_2CO]_nM \qquad (20)$$

where R = H, alkyl, CF_3 etc.

Alternatively, the alcohol and the metal halide may be reacted directly in the presence of a suitable proton acceptor:

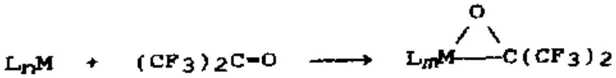
$$MCl_n + n(R_f)_2RCOH + nB \rightarrow [(R_f)_2RCO]_nM + n[BH]^+Cl^- \qquad (21)$$

The base B may be a tertiary amine, the reaction being carried out in inert solvent, or OH^- (if the product is stable to water) with reaction carried out in ethanol etc. The latter method is particularly useful for the preparation of derivatives of PFP^{2-} or the hybrid ligands discussed in Section D.

A useful direct synthetic route to derivatives of hexafluoro-2-propanol, mentioned in Section B(ii), is the reaction of a metal hydride with HFA (eqn. (5)).

Where the parent alcohol is not available, the metal derivatives may be prepared by two general routes: oxidative addition or template synthesis.

Oxidative addition is particularly useful in the preparation of organometallic alkoxides (Section D(ii)) where a metal in a low valency state reacts with a ketone, usually HFA, simultaneously forming a metal–oxygen and a metal–carbon bond in structure **8**:



(22)

8

An ingenious application of a redox process to form an alkoxide uses the reactive perfluoroalkyl hypochlorites, which are capable of oxidizing covalent halides:

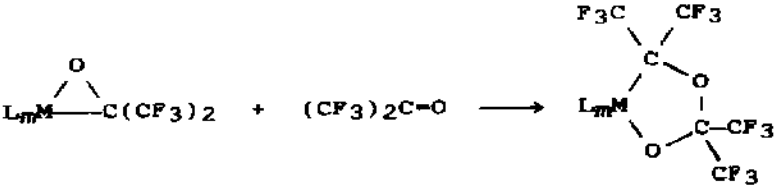
$$\mathrm{MCl}_n + n\mathrm{R_fOCl} \rightarrow (\mathrm{R_fO})_n\mathrm{M} + n\mathrm{Cl_2} \qquad (23)$$

The phrase "template synthesis" is used to describe a condensation reaction that only occurs in the presence of the metal substrate, which then becomes incorporated into an alkoxide complex. Usually, the parent alcohol ligand is incapable of existence in isolation. Addition of fluoride ion to a fluorinated acid fluoride or ketone, which requires the presence of a large metallic counter-ion, may be placed in this category:

$$\mathrm{R_fC(O)R'_f} + \mathrm{M^+F^-} \xrightarrow[\text{solution/suspension}]{\mathrm{CH_3CN}} \mathrm{M^+[R_fR'_fCFO^-]} \qquad (24)$$

where $\mathrm{R_f}$ and $\mathrm{R'_f} = \mathrm{F, CF_3, C_2F_5}$ etc. Another important example is the reaction of a second molecule of HFA with a three-membered organometallic ring, **8**, leading to "head-to-tail" dimerization of the ketone and ring expansion in the product **9**:

(25)



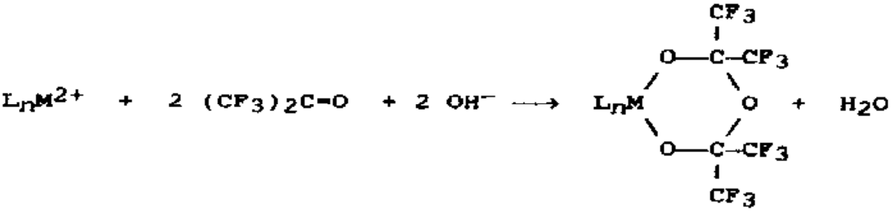
8

9

This may be contrasted with the dimerization of HFA on phosphorus(III), (eqn. (9)) which leads to formation of a C–C bond between the two ketone residues.

A six-membered ring, **10**, is produced when two molecules of HFA condense "head-to-tail" in the presence of a metal ion and base (Section B(vi)(b)). The parent diol, $\mathrm{HOC(CF_3)_2{-}O{-}C(CF_3)_2OH}$, is unstable with respect to HFA and $\mathrm{(CF_3)_2C(OH)_2}$ and cannot be isolated:

(26)

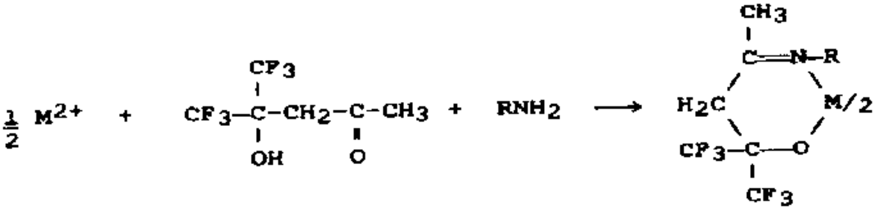


(L = phosphine or amine co-ligand)

10

Template synthesis is very useful in the preparation of alkoxy-imino complexes such as **11** (Section D(iii)) using a fluorinated keto alcohol:

(27)



11

Two special synthetic routes for CF_3–O derivatives, applicable only where the desired product is stable and highly resistant to further oxidation, may be briefly mentioned. Direct fluorination is used in the preparation of trifluoromethyl hypofluorite from carbonyl fluoride [69]:

$$COF_2 + F_2 \xrightarrow[\text{catalyst}]{\text{CsF}} CF_3\text{–O–F} \tag{28}$$

The only reported example of the direct fluorination of a methoxy substituent is the conversion of dimethyl sulphate to its fluorinated analogue $(CF_3O)_2SO_2$; even here, some breakdown occurs [70].

The second special synthetic route is the insertion of oxygen into CF_3–M bonds in a reactive molecule, a reaction which is successful for phosphorus [71]:

$$(CF_3)_3P + 2O_2 \rightarrow (CF_3O)_3P{=}O \tag{29}$$

(iii) Derivatives of primary alcohols

(a) Trifluoromethanol

The reaction of carbonyl fluoride with fluorides of the heavier group I metals, giving ionic trifluoromethoxides $M^+[CF_3O^-]$, was reported in 1965 [72]. It was later extended to the preparation of other primary fully fluorinated alkoxides $M^+[R_fCF_2O^-]$ by the use of perfluoroacyl fluorides (eqn. (24)) [67]. The stabilities of the methoxides are considerably greater than those of longer-chain alkoxides, and variation of cation shows the expected decrease in stability with decreasing size in the order $Cs^+ > Rb^+ > K^+$. Derivatives of Li^+, Na^+, Tl^+ or Ba^{2+} could not be prepared under the experimental conditions used. A forecast that large complex cations would be very suitable for the stabilization of CF_3O^- was later confirmed by the isolation of the tris(dimethylamino)sulphonium salt, $[TAS^+][CF_3O^-]$ by Farnham et al. [73].

The value of ΔH for the reaction

$$MF(s) + COF_2(g) \rightarrow M^+[OCF_3^-](s) \tag{30}$$

may be found from

$$\Delta H = U_0(MF) - U_0(MOCF_3) + FAE(COF_2) \tag{31}$$

where U_0 is the lattice energy of each solid and FAE is the fluoride attachment enthalpy of COF_2, i.e. ΔH for the process

$$COF_2(g) + F^-(g) \rightarrow OCF_3^-(g) \tag{32}$$

(The term FAE is used rather than "fluoride affinity" because of ambiguity of sign convention in the latter.) The FAE value of COF_2 has been found by ion cyclotron resonance to be -178 ± 4 kJ mol^{-1} [74]. Unfortunately, there is no structural or thermochemical data on the group I trifluoromethoxides, so their lattice energies cannot be obtained accurately. A first approximation is to use the lattice energies of the corresponding fluoroborates, with which the trifluoromethoxides are roughly isostructural [72]. On this basis, the ΔH values for eqn. (29) shown in Table 6 may be obtained.

Clearly, no great accuracy can be claimed for these figures, but the trend toward greater stability of the trifluoromethoxides of the larger cations is apparent. Using a different approach, Lawlor and Passmore calculated a value of 540 kJ mol^{-1} for $U_0(\mathrm{CsOCF_3})$ [77]. Combining this with an earlier value of -147 kJ mol^{-1} for FAE($\mathrm{COF_2}$) [78] led them to conclude that ΔH for $\mathrm{Cs^+[OCF_3^-]}$ is slightly endothermic ($+12$ kJ mol^{-1}), but revision of FAE($\mathrm{COF_2}$) leads to $\Delta H = -3$ kJ mol^{-1}, in good agreement with the value in Table 6.

Other work on trifluoromethoxides has been concerned with ab initio MO calculations and the correlation of the resulting structures with the observed vibrational spectra. Christe et al. analysed the IR spectrum of $\mathrm{Cs^+[OCF_3^-]}$, compared it with that of the isoelectronic neutral molecule $\mathrm{F_3NO}$, and concluded that there is considerable double-bond character in both the C–O and N–O bonds [79]. A refinement of IR data through the matrix isolation technique was introduced by Ault [80], who suggested that the loss of degeneracy in certain vibrations was associated with removal of the C_{3v} symmetry of the $\mathrm{CF_3O^-}$ anion by interaction with $\mathrm{Cs^+}$.

This conclusion is supported by a detailed theoretical treatment by Francisco and Williams [81]. They find that both $\mathrm{Li^+[OCF_3^-]}$ and $\mathrm{Na^+[OCF_3^-]}$ should be stable as gaseous ion pairs, the failure to prepare them in the solid state being attributable to the high lattice energies of the respective fluorides. They postulate a bidentate mode of coordination of the

TABLE 6

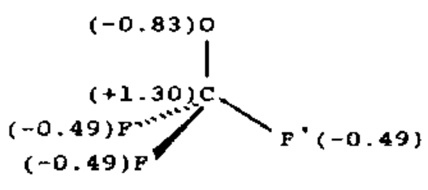
Enthalpy of formation of $\mathrm{M^+[OCF_3^-]}$ salts

Salt	$U_0(\mathrm{MF})$ [a] (kJ mol^{-1})	$U_0(\mathrm{MBF_4})$ [b] (kJ mol^{-1})	ΔH (kJ mol^{-1})
$\mathrm{Li^+[OCF_3^-]}$	1009	692	139
$\mathrm{Na^+[OCF_3^-]}$	904	635	91
$\mathrm{K^+[OCF_3^-]}$	801	597	26
$\mathrm{Rb^+[OCF_3^-]}$	768	580	10
$\mathrm{Cs^+[OCF_3^-]}$	715	557	−20

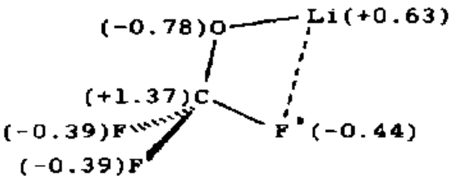
[a] Born–Haber cycle values from Waddington [75].

[b] Values from Kaganyuk [76].

CF_3O^- anion to Li^+ or Na^+ in these molecules, leading to distortion of the C_{3v} anion, and the following charge distribution:



Free Anion



$[CF_3O^-]Li^+$ ion pair

Closely agreeing calculated dimensions for free CF_3O^- have been reported by Farnham et al. [73]. Data are given in Table 7.

The changes in C–O and C–F bond lengths and electron density distribution on coordination of the free ion to Li^+ or to Na^+ are attributed to changes in fluorine hyperconjugative delocalization of oxygen lone pair electron density into C–F antibonding orbitals.

A crystallographic determination of the C–O bond length in $[TAS^+][CF_3O^-]$, where cation–anion interactions are minimal, gives 1.227 Å, in excellent agreement with the above figure for free trifluoromethoxide [73]. The experimental data, also included in Table 7, show the slight departure of the ion from C_{3v} symmetry, caused by the orientation of one fluorine atom (F′) toward the complex cation.

Both theory and experiment show the CF_3O^- ion to contain one of the shortest nominally single C–O bond lengths known, little more than the

TABLE 7

Bond lengths (Å) and angles (°) in trifluoromethoxides

	Free CF_3O^- [a]	Free CF_3O^- [b]	CF_3OLi [a]	CF_3ONa [a]	$[TAS^+]$ $[CF_3O^-]$ [c]
r(C–O)	1.230	1.214	1.269	1.258	1.227 (4)
r(C–F)	1.405	1.394	1.344	1.355	1.390 (3)
r(C–F′)			1.484	1.465	1.397 (4) [d]
r(M–O)			1.763	2.073	
r(M–F′)			1.860	2.167	
∠(OCF)	117.0	116.8	118.3	117.9	116.5
∠(OCF′)			105.3	108.5	115.8
∠(FCF′)	101.0	101.3	107.1	106.0	101.7

[a] Calculated values from ref. 81.
[b] Calculated values from ref. 73.
[c] Experimental values from ref. 73.
[d] F′ is oriented toward the TAS^+ cation.

normal C=O double-bond length of 1.20 Å. Comparison with the calculated C–O bond length in CF_3OH of 1.34 Å, which is already short, shows a decrease of approximately 8% on ionization as more electron density is removed from oxygen, and contributing structures may be drawn:

$$F-\overset{F}{\underset{F}{C}}-O^- \longleftrightarrow F-\overset{F^-}{\underset{F}{C}}=O \longleftrightarrow F^- \quad \overset{F}{\underset{F}{C}}=O \longleftrightarrow F-\overset{F}{\underset{F^-}{C}}=O \tag{33}$$

The trifluoromethoxide ion is, of course, the extreme case of such behaviour. Similar calculations on the ions $[CF_3CF_2O^-]$ and $[(CF_3)_2CFO^-]$ give slightly longer C–O bond lengths of 1.222 Å and 1.245 Å respectively [73], but no experimental results are available. These structural data on fully fluorinated ionic alkoxides may be compared with those found in partially fluorinated systems discussed in Section E(iii).

Covalent derivatives of trifluoromethanol are largely limited to non-metals, and are therefore largely outside the scope of this review, but they will be briefly discussed because of their importance in establishing the general characteristics of the group. The stability of trifluoromethyl hypofluorite, CF_3OF, has already been mentioned (eqn. (16)) and the extensive chemistry of this important compound, a key intermediate in the preparation of many trifluoromethoxy derivatives, has been fully reviewed by Shreeve [69].

The tendency of the trifluoromethoxy group to form stable bonds to electronegative elements leads to remarkable stability in the $CF_3{-}O{-}O{-}X$ system, and an extensive chemistry of compounds such as $CF_3{-}O{-}O{-}F$, $CF_3{-}O{-}O{-}Cl$, $CF_3{-}O{-}O{-}H$, $CF_3{-}O{-}O{-}NO_2$, $CF_3{-}O{-}O{-}CF_3$ and even $CF_3{-}O{-}O{-}O{-}CF_3$, has been developed by Cady, by Shreeve, and by DesMarteau and their coworkers. Although reactive and strongly oxidizing, these peroxides are much more stable than their hydrocarbon analogues; the trioxides $R_fO_3R_f$ are the only isolable examples of catenated trioxides. Bis(trifluoromethyl)peroxide is made by the reaction [82]

$$CF_3OF + COF_2 \xrightarrow[\text{catalyst}]{AgF} CF_3{-}O{-}O{-}CF_3 \tag{34}$$

The reaction fails in the presence of CsF, and it is suggested that $Ag(OCF_3)_2$ may be an intermediate. The O–O bond is stable to reaction with fluorine which yields $CF_3{-}O{-}O{-}F$ [83].

The peroxynitrate CF_3OONO_2 is prepared by the reaction of CF_3OOH with N_2O_5, or CF_3OOF with N_2O_4 [84], while the trioxide CF_3OOOCF_3 is made by the reaction of OF_2 with COF_2/CsF [85], or of $CF_2(OF)_2$ with $CsOCF_3$ [86].

The structures of compounds $CF_3{-}O{-}X$ or $CF_3{-}O{-}O{-}X$, where X is an electronegative atom or group, are interesting for comparison with those of fluorinated alkoxides. Some bond lengths are given in Table 8

TABLE 8

Bond lengths (Å) in compounds CF_3OX and CF_3OOX

Compound	C–F	C–O	O–O	O–X	Ref.
CF_3–O–F	1.319 (3)	1.395 (6)		1.421 (6)	87
CF_3–O–Cl	1.325 (3)	1.365 (7)		1.679 (3)	88
CF_3–O–CF_3	1.327 (2)	1.369 (4)			89
CF_3–O–O–H	1.324 (4)	1.376 (10)	1.447 (8)	0.974 (42)	90
CF_3–O–O–F	1.322 (9)	1.419 (24)	1.366 (33)	1.449 (15)	90
CF_3–O–O–Cl	1.323 (7)	1.372 (22)	1.447 (15)	1.699 (6)	90
CF_3–O–O–CF_3	1.320 (3)	1.399 (9)	1.419 (20)		91

Comparing these data with those for CF_3–O–H (Table 1) and ionic CF_3O^- (Table 7), it is clear that the C–O bond is considerably lengthened and the C–F bond shortened when an electronegative substituent is bonded to the trifluoromethoxy group, reflecting a decrease in fluorine hyperconjugation and less double-bond character to the C–O bond. The C–O bond lengths of fluorinated alkoxides, discussed later in this review, generally fall in between these two extremes, according to the degree of polarization of the metal–oxygen bond.

The O–O bond lengths of these peroxy compounds are less than that in H_2O_2 (1.475 Å), consistent with the idea that the presence of electron-withdrawing groups decreases repulsion between non-bonding pairs on oxygen, but they do not approach the extreme value of 1.217 Å found in O_2F_2. Calculations on structures and bond energies in trifluoromethyl peroxy compounds have been carried out by Olsen [92] and by Glidewell [93].

Apart from Harmon and Lagow's synthesis of bis(trifluoromethyl) sulphate, mentioned above [70], most of the reports on trifluoromethoxy derivatives of sulphur involve oxidative addition of CF_3OCl or CF_3OF, going either from S(II) to S(IV) or from S(IV) to S(VI). The following reactions are typical:

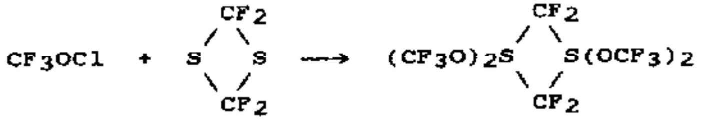
$$CF_3OF + SF_4 \longrightarrow CF_3OSF_5 \text{ and } \underline{cis}\text{-}(CF_3O)_2SF_4 \quad [94] \tag{35}$$

$$CF_3OOOCF_3 + SF_4 \longrightarrow (CF_3O)_2SF_4 \text{ and } CF_3OSF_4OOCF_3 \quad [95] \tag{36}$$

$$CF_3OOOCF_3 + SO_2 \longrightarrow (CF_3O)_2SO_2 \quad [95] \tag{37}$$

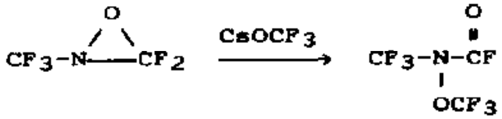
$$CF_3OCl + CF_3SCF_3 \longrightarrow (CF_3)_2S(OCF_3)_2 \quad [96] \tag{38}$$

$$CF_3OCl + CF_3S(O)CF_3 \longrightarrow (CF_3)_2S(O)(OCF_3)_2 \quad [96] \tag{39}$$



[96] (40)

There has been relatively little work reported on trifluoromethoxy derivatives of nitrogen, possibly because of the difficulty of finding substrates for oxidative addition reactions. CF_3ONF_2 is made by the reaction of N_2F_4 with CF_3OF [97,98] or with CF_3OOOCF_3 [95]. Nucleophilic attack by CF_3O^- results in a ring-opening addition reaction [99]:



(41)

With phosphorus, which has a very extensive chemistry of derivatives of tertiary fluorinated alcohols, there are hardly any stable trifluoromethoxy complexes. The phosphate $(CF_3O)_3P{=}O$ is of limited stability, decomposing quantitatively to COF_2 and POF_3 in 3 days at 60 °C [71]. The same compound is identified in a mixture of products when PCl_5 reacts with CF_3OCl, but no pure product can be characterized [100].

The reaction of CF_3OCl with BCl_3 gives the trifluoromethoxy borane $(CF_3O)_3B$; this decomposes rapidly at 25 °C giving BF_3 [101]. This behaviour is reminiscent of the instability of perfluoroalkyl derivatives of three-coordinate boron, which was resolved by the preparation of the ion $[CF_3BF_3]^-$, the only stable trifluoromethyl derivative of boron [102]. A similar approach to the stabilization of fluorinated alkoxides of boron as $[(CF_3O)_3BF]^-$ or $[(CF_3O)_4B]^-$ is clearly possible.

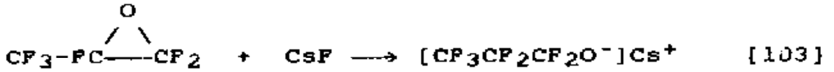
(b) Other fully fluorinated primary alcohols

Ionic derivatives of higher fully fluorinated primary alcohols are readily prepared by the reaction of group I fluorides with perfluoroacyl fluorides [67]:

$$R_fCF_2COF + MF \xrightarrow{CH_3CN} M^+[R_fCF_2O^-] \qquad (R_f = CF_3,\ C_2F_5 \text{ or } C_3F_7;\ M = K,\ Rb \text{ or } Cs) \tag{42}$$

As with the trifluoromethoxides, Cs^+ gives the most stable salts. In general, the higher fluorinated alkoxides have a much lower thermal stability than trifluoromethoxides and much greater solubility in acetonitrile, such that it is difficult to remove the solvent without decomposition after synthesis.

An alternative route to some primary fluorinated alkoxides is through fluorinated epoxides, which are reported to be more reactive towards CsF than are acyl fluorides [103]:



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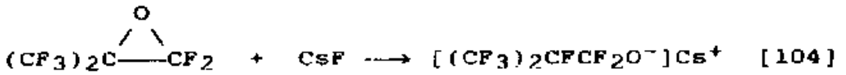


(44)

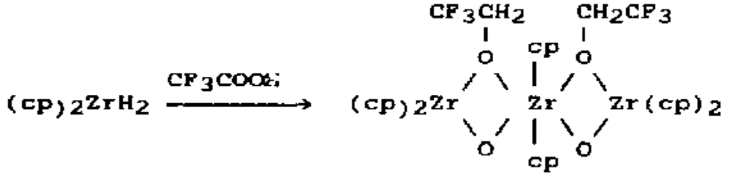
The R_fO^- ion is a relatively weak nucleophile, but it will react with a reactive alkyl halide, such as $CH_2{=}CHBr$, to yield the ether $R_f{-}O{-}CH_2{-}CH{=}CH_2$ [67]. The preparation of fully fluorinated esters by the CsF-catalysed dimerization of perfluoroacyl fluorides was mentioned above [66]. Oxidation of ionic fluorinated alkoxides R_fO^- with F_2 or ClF gives the hypofluorites $R_f{-}O{-}F$ or hypochlorites $R_f{-}O{-}Cl$ respectively [69], and through the use of these compounds, a series of derivatives similar to the trifluoromethoxy derivatives described in the previous section could be prepared. Some work in this area has appeared [69], but the greater interest is found when R_f is the perfluoro-*t*-butoxy group, described in Section B(v)(a), rather than primary alkoxy groups.

(c) Trifluoroethanol

Because of its stability and ready availability (from the reduction of various derivatives of trifluoroacetic acid), trifluoroethanol has been one of the most studied of fluorinated alcohols. As mentioned in the introduction, the degree of fluorination is not sufficient to bring about major changes in behaviour, and its derivatives are similar to those of unfluorinated alcohols. In the references cited here, CF_3CH_2OH is often one of a number of alcohols whose similar derivatives are being studied; differences which may be associated with the presence of the electron-withdrawing CF_3 group, such as a lower degree of alkoxy bridging, are generally small.

Homoleptic trifluoroethoxides of germanium and the early transition metals, $(CF_3CH_2O)_4M$ (M = Ge, Ti, Zr) and $(CF_3CH_2O)_5M$ (M = Nb, Ta), may be prepared by reaction of the appropriate metal chloride with CF_3CH_2OH in benzene in the presence of ammonia; they are viscous liquids or low melting solids, clearly associated [105]. The mixed complex $(acac)_2Ti(OCH_2CF_3)_2$ may be prepared by alcohol exchange; the alkoxide groups are mutually *cis* [106]. $TiCl_2(OCH_2CF_3)_2$ is dimeric, with alkoxy bridges which may be cleaved by reaction with nitrogen donors [107] or Ph_3AsO [108]. In $TiCl_3(OCH_2CF_3)$, the metal is four-coordinate and one additional monodentate ligand may be added [109]. Reaction of $(iPrO)_3TiNR_2$ with CF_3CH_2OH gives $(iPrO)_3Ti(OCH_2CF_3)$ [110], while reaction of $cpTiCl_3$ with $LiOCH_2CF_3$ gives both $cpTi(OCH_2CF_3)_3$ and $cpTiCl(OCH_2CF_3)_2$; the latter may be methylated to give $cpTi(Me)(OCH_2CF_3)_2$, an efficient polymerization catalyst [111].

A zirconium complex of $CF_3CH_2O^-$ is formed directly by hydride reduction of CF_3COOH; a trinuclear alkoxy-bridged structure **12** is suggested [112]:



12

(45)

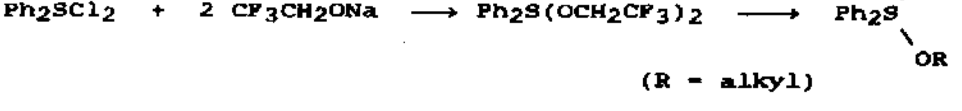
The vanadium(III) derivative $V(OCH_2CF_3)_3$ is alkoxy bridged and the nitrogen-base adducts $L_2V(OCH_2CF_3)_3$ remain bridged [113]. Choukron and coworkers [114,115] have prepared a number of vanadyl complexes $(iPrO)_nV(O)(OCH_2CF_3)_3)_{(3-n)}$ ($n = 1$–3); $V(O)(OCH_2CF_3)_3$ is monomeric. With niobium, the complex $[Nb(O)(OCH_2CF_3)_3 \cdot CH_3CN]_2$ remains dimeric in non-polar solvent, with both μ-alkoxy and μ-oxo bridges, but becomes monomeric in CH_3CN solution; in the last point it differs from the unfluorinated ethoxy analogue, which remains dimeric [116].

The iron(III) complex $Fe(OCH_2CF_3)_3$ is dimeric [117], whereas the rhodium(I) complex $(Me_3P)_3RhOCH_2CF_3$ has been shown by a complete structure determination to be monomeric [118]. Handy and coworkers have prepared complexes of molybdenum(VI), $MoF_n(OCH_2CF_3)_{(6-n)}$, where $n =$ 1–6 [119a], and tungsten(VI), $WF_5(OR_f)$, where $R_f = CF_3CH_2$, $C_2F_5CH_2$ and $(CF_3)_2CH$ [119b]. Using ^{19}F NMR shifts, they show that the degree of electron withdrawal through the metal–oxygen bond increases with the degree of fluorination of the alkoxide. A high oxidation state is also found in the chromium(VI) derivatives, $CrO_2(OCH_2CF_3)_2$, associated through alkoxy bridges [120]. The uranium(V) derivative $U(OCH_2CF_3)_5$ was one of the first fluorinated alkoxides to be characterized [121].

Mehrota and coworkers have studied a number of "double" alkoxides, i.e. compounds in which two different metals are present in conjunction with alkoxide groups. For a review, see ref. 122. Where the latter is $[CF_3CH_2O^-]$, one metal is commonly aluminium(III), and complexes are known with stoichiometries $Cr[Al(OCH_2CF_3)_4]_3$ [123], $Sn[Al(OCH_2CF_3)_4]_2$ [124], $Cu[Al(OCH_2CF_3)_4]_2$ [125], $Co[Al(OCH_2CF_3)_4]_2$ [126a], or $Ni[Al(OCH_2CF_3)_4]_2$ [126b]. The absorption spectra generally indicate a high coordination number for the metal ions, presumably associated with bridging alkoxide groups, but unfortunately there is little structural data available on this interesting group of compounds.

Among main-group element derivatives of trifluoroethanol, $Al(OCH_2CF_3)_3$ is a stronger Lewis acid than unfluorinated alkoxides of aluminium and, as such, a better polymerization catalyst [127]. The tin complex $SnCl_3(OCH_2CF_3)(CF_3CH_2OH)$ is monomeric in benzene solution, in contrast to dimeric $SnCl_3(OEt)_3$ [128]. Direct reaction of the alcohol with TlOH gives $TlOCH_2CF_3$, which is volatile (melting point 134 °C; sublimation at 50 °C) [129].

Kitazume and Ishikawa have used the trifluoroethoxy group in sulphur(IV) chemistry in the sequence



$$Ph_2SCl_2 + 2\ CF_3CH_2ONa \longrightarrow Ph_2S(OCH_2CF_3)_2 \xrightarrow{ROH} Ph_2S\begin{matrix} \diagup OCH_2CF_3 \\ \diagdown OR \end{matrix} \quad (R = \text{alkyl}) \tag{46}$$

Because of the acidity of the CF_3CH_2O- substituent, the unfluorinated R group is relatively positive, and the compounds are useful alkylating agents [130]. The sulphites $(R_fO)_2S{=}O$ ($R = CF_3CH_2$, $(CF_3)_2CH$, $(CF_3)_2(CH_3)C$ or $(CF_3)_3C$) are more stable than their unfluorinated analogues [131]; they may be converted into fluorosulphonates and bis(fluoroalkyl) sulphates [132,133]:

$$(R_fO)_2S{=}O \xrightarrow{ClF} R_fOSO_2F \xrightarrow{R_fOH} (R_fO)_2SO_2 \qquad (47)$$

Both selenium(IV) and selenium(VI) derivatives are known [134], and NMR study of $Se(OCH_2CF_3)_4$ shows equivalent CF_3 groups at 25 °C, resolving at −80 °C, consistent with a non-rigid trigonal bipyramid (TBP) geometry; it reacts with $K^+[CF_3CH_2O^-]$ to give $[Se(OCH_2CF_3)_5]^-$. Tellurium similarly gives $Te(OCH_2CF_3)_4$ [134], while reaction of TeF_6 with CF_3CH_2OH gives *mer*- and *fac*-$TeF_3(OCH_2CF_3)_3$ and *cis*- and *trans*-$TeF_2(OCH_2CF_3)_4$ [135]. Phosphorus gives $P(OCH_2CF_3)_3$, $Ph_2P(OCH_2CF_3)_3$ and six-coordinate complexes [136], while the antimony(V) derivative $SbCl_4(OCH_2CF_3)$ is monomeric [128].

(iv) Secondary alcohols

The chemistry of secondary fluorinated alkoxides is dominated by derivatives of two compounds: heptafluoro-2-propanol, $(CF_3)_2CFOH$, and hexafluoro-2-propanol, $(CF_3)_2CHOH$, and these will be considered separately.

(a) Heptafluoro-2-propanol

The observation that CsF dissolves rapidly in acetonitrile when HFA is added was initially interpreted in terms of formation of the ion $[(CF_3)_2CFO^-]$ [72], and subsequent work is consistent with this. In fact, the gaseous fluoride attachment enthalpy of HFA is more favourable than those of COF_2 or fluorinated acyl fluorides [74] (see Table 9).

This difference is presumably due to greater stabilization of the anion, through fluorine hyperconjugation, as the degree of substitution on the α-carbon atom increases. A very similar result has been obtained from solution studies, which show that exchange of fluoride ion is very rapid in the system

$$(CF_3)_2C{=}O + [CF_3O^-] \rightleftharpoons [(CF_3)_2CFO^-] + COF_2 \qquad (48)$$

and that ΔG is -30 kJ mol^{-1} in the forward direction [137].

TABLE 9

Gaseous fluoride attachment enthalpy of COF_2 and fluorinated acyl fluorides

FAE	COF_2	CF_3COF	CF_3CF_2COF	$(CF_3)_2C{=}O$
(kJ mol^{-1})	−178	−191	−197	−208

This slightly increased stability is reflected in the derivatives of $(CF_3)_2CFOH$, but fluoride elimination is still the limiting factor and stable covalent alkoxides of electropositive elements are not formed. The perfluoro ester $CF_3C(O)OCF(CF_3)_2$ is unstable in the presence of alkali metal fluorides [66], whereas the partially fluorinated esters $RC(O)OCF(CF_3)_2$ decrease in stability in the order $R = CH_2{=}C(CH_3) > CH_2{=}CH_2 > CH_2CH_3$; it was noted that the acyl fluoride is produced more rapidly by the reaction of KF/CH_3CN with the ester than with the acid chloride [138]. The borane $B[OCF(CF_3)_2]_3$ decomposes to HFA and BF_3 at 25 °C, but more slowly than $B(OCF_3)_3$; it may be stabilized as the Me_3N adduct [101]. It is interesting to contrast this with the ready reaction of HFA with BX_3 to give $B[OCX(CF_3)_2]_3$ ($X = Cl$, Br); not surprisingly, this reaction fails with BF_3 [139].

As with $[CF_3O^-]$ (eqn. (41)), the ion $[(CF_3)_2CFO^-]$ attacks the strained N–O bond in a three-membered ring to give $(CF_3)_2CFO{-}N(CF_3){-}C(O)F$ [99]. Similarly, Russian workers have studied the reaction of $Cs[OCF(CF_3)_2]$ with hexafluoropropylene oxide to produce fluorinated telomers containing ether linkages [103,140]. In its organic reactions, the ion $[(CF_3)_2CFO^-]$ has been characterized as a weak nucleophile but as a strong base [141]. Because of the ease with which it eliminates F^-, it may also be used as a convenient source of "soluble" fluoride in halide exchange reactions.

(b) 1,1,1,3,3,3-Hexafluoro-2-propanol

The stable readily available $(CF_3)_2CHOH$ is one of the most important fluorinated alcohols. In contrast to the fully fluorinated alcohols, fluoride elimination is not a problem, and derivatives of many elements have been reported, including alkoxides of metals ranging from lithium to neptunium. Except in a few cases where HFA is reacted with a hydride (eqn. (5)), they are generally made from the alcohol by standard routes. The lithium and sodium derivatives are useful intermediates in the preparation of covalent derivatives of $(CF_3)_2CHOH$. They are stable, easily prepared and surprisingly volatile, subliming at 50 °C and 70 °C respectively at 0.05 mm [142], contrary to earlier reports that $(CF_3)_2CHONa$ decomposes explosively on heating [143].

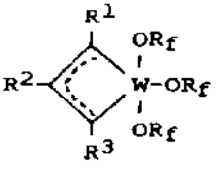
Two early papers by Kapoor et al. [144] and by Mazdiyasni et al. [145] reported the synthesis of $Al[OCH(CF_3)_2]_3$, $M[OCH(CF_3)_2]_4$ ($M = Si$, Ge, Ti, Zr or Hf) or $M[OCH(CF_3)_2]_5$ ($M = Nb$ or Ta), by the reaction of the appropriate chloride either with $(CF_3)_2CHOH$ and NH_3 in benzene [144] or with $(CF_3)_2CHONa$ [145]. Except for the silicon and germanium derivatives, which have boiling points of 158 °C and 145 °C respectively, these alkoxides are involatile liquids or low melting solids, clearly associated. When the alcohol/ammonia synthetic route is applied to Y^{3+} and lanthanide ions, the products are either the involatile solids $M[(OCH(CF_3)_2]_3$ [146] or stable ammoniates $M[OCH(CF_3)_2]_3(NH_3)_2$ distilling at 120–140 °C/0.08 mm; the volatility of the latter increases as the ionic radius decreases, presumably because of reduced bridging interactions [147].

Stone and coworkers reacted the dichlorides $(cp)_2TiCl_2$, $(PEt_2)_2NiCl_2$ and *cis*-$(PPh_3)_2PtCl_2$ with $(CF_3)_2CHONa$ to obtain the corresponding di-alkoxides [148]. The titanocene complex is the most stable of the three; it is volatile (sublimes at 70 °C/0.1 mm) and appears to be monomeric.

From ^{19}F NMR measurements on $(CF_3)_2CHOWF_5$, the electron-withdrawing effect of the $(CF_3)_2CHO$ group is shown to be greater than that of CF_3CH_2O or $C_2F_5CH_2O$ [119]. When UCl_4 reacts with $NaOCH(CF_3)_2$ in tetrahydrofuran (THF), the product is the six-coordinate complex $U[OCH(CF_3)_2]_4(THF)_2$; the solvent is displaced by TMED to give $U(OCH(CF_3)_2](TMED)$ [149]. Eller and Vergamini [150] find that the six-coordinate uranium(IV) complexes $U(OR_f)_4(OEt)(EtOH)$ are not associated when $R_f = (CF_3)_2CH$ or $(CF_3)_3C$, whereas oligomerization is found in $U(OEt)_5$; they attribute this difference to the steric bulk of the fluorinated groups, although reduced basicity at oxygen may also be a factor. The neptunium(IV) complex $(cp)_3NpOCH(CF_3)_2$ has been studied by Mössbauer spectroscopy, which shows the withdrawal of electron density on Np to increase in the order $Cl < OCH(CF_3)_2 < C_4H_9$ [151].

Considerable recent activity on fluorinated alkoxides of molybdenum and tungsten has been stimulated by their application as catalysts for olefin and acetylene metathesis by Schrock and coworkers. They point out that "...the key requirement of a practical metathesis catalyst is a crowded alkoxide coordination sphere... the metal centre must be reasonably electrophilic" [152]. A suitable fluorinated group can satisfy both of these requirements, and several alkylidyne and metallo-cyclobutadiene complexes have been prepared with bulky fluorinated alkoxides as co-ligands on the metal. The complex $(CH_3)_3CCW[OCH(CF_3)_2]_3(dme)$ catalyses the metathesis of 3-heptyne in ether [153].

Several other complexes containing hexafluoro-isopropoxide and hexafluoro-*t*-butoxide groups have been prepared, and the complex **13** was structurally characterized [153]:



13 $R_f = CH(CF_3)_2$; $R^1 = R^2 = R^3 = Et$

14 $R_f = C(CF_3)_2(CH_3)$; $R^1 = R^2 = R^3 = Et$

15 $R_f = CH(CF_3)_2$; $R^1 = R^3 = {}^tBu$; $R^2 = H$

16 $R_f = CH(CF_3)_2$; $R^1 = {}^tBu$; $R^2 = H$; $R^3 = Ph$

The five-coordinate tungsten atom is in approximately TBP geometry in **13** and in the similar complex **15** [154]; both **15** and **16** may be deprotonated at the R^2 site [152]. Both of the tungstenacycles **13** and **14** are catalysts for the metathesis of disubstituted acetylenes by an associative mechanism in non-coordinating solvents [153].

The molybdenum complex $Me_3CCMo[OCH(CF_3)_2]_3(dme)$ shows a similar catalytic activity; it reacts with $Me_3C \equiv CH$ in pyridine to give the complex $(CF_3)_2CHO\overline{MoC(CMe_3)CHC}(CMe_3)(pyr)_2$ and other organometallic products whose structures have been determined [155,156].

Catalytic activity of a different kind has been demonstrated by Yamamoto and coworkers who have prepared a number of hexafluoroisopropoxides by insertion of HFA into metal–hydrogen bonds [16]:

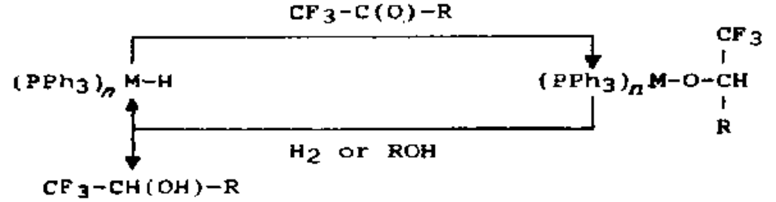
$$(PPh_3)_3CoH(N_2) + CF_3C(O)R \rightarrow (PPh_3)_3Co[OCHR(CF_3)] \quad \mathbf{(17)} \qquad (49)$$

$$(PPh_3)_4RuH_2 + CF_3C(O)R \rightarrow (PPh_3)_3Ru[OCHR(CF_3)] \quad \mathbf{(18)} \qquad (50)$$

$$(PPh_3)_4RhH + CF_3C(O)R \rightarrow (PPh_3)_3Rh[OCHR(CF_3)] \quad \mathbf{(19)} \qquad (51)$$

$$(R = CF_3 \text{ or } Ph)$$

The ruthenium complex **18** (R = Ph) reacts with H_2 or with ethanol or 2-propanol at 25 °C liberating $CF_3CH(OH)Ph$; the rhodium complex **19** reacts with H_2 but not with alcohols, whereas the cobalt complex **17** is unreactive. These alkoxides therefore serve as isolated intermediates in the catalytic hydrogenation of ketones:



(52)

In main-group chemistry the borane $B[OCH(CF_3)_2]_3$ may be made either by the reaction of BH_4^- with HFA [143] or by the reaction of $SCl[OCH(CF_3)_2]_3$ with BCl_3 [157]. The analogous aluminium derivative $Al[OCH(CF_3)_2]_3$ is readily prepared [144,145]; it is a stable but moisture-sensitive solid of melting point 185 °C. Laussac and coworkers have made a detailed study of its adducts with Lewis bases, showing by NMR that potentially bidentate diphosphine donors form only 1 : 1 adducts in which the metal is four-coordinate; in contrast, less sterically hindered $AlCl_3$ forms both 1 : 1 and 2 : 1 adducts [158]. Ethylenediamine is also monodentate, and $Al[OCH(CF_3)_2]_3$ gives both a 1 : 1 adduct (tetra-coordinate Al; O_3N donor set) and a 2 : 1 adduct (penta-coordinate Al; O_3N_2 donor set) [159]. Partial hydrolysis of this complex gives the hydroxy-bridged dinuclear complex

$[(CF_3)_2CHO]_2(en)Al(\mu\text{-}OH)_2Al(en)[OCH(CF_3)_2]_2$ in which the reduced steric demands of OH^- have allowed Al to become six-coordinate. The thallium(I) alkoxide $TlOCH(CF_3)_2$, like the analogous trifluoroethoxide, is quite volatile (sublimes at 50 °C) [129].

The silicon and germanium derivatives of $(CF_3)_2CHOH$ were mentioned above [144,145]. There has been considerable work on phosphorus derivatives, largely by Roeschenthaler and coworkers, and compounds in both the trivalent and pentavalent states are known [100,160]:

$$PCl_3 \xrightarrow{LiOR_f} P(OR_f)_3 \xrightarrow{Cl_2} Cl_2P(OR_f)_3 \xrightarrow{LiOR_f} P(OR_f)_5 \tag{53}$$

$$RPCl_2 \xrightarrow{LiOR_f} RP(OR_f)_2 \xrightarrow{Cl_2} Cl_2PR(OR_f)_2 \xrightarrow{LiOR_f} RP(OR_f)_4 \tag{54}$$

$$Ph_3PBr_2 \xrightarrow{NaOR_f} Ph_3P(OR_f)_2 \quad [161] \tag{55}$$

where $R_f = CH(CF_3)_2$ and $R = Me$ or Ph.

$P[OCH(CF_3)_2]_5$ is stereochemically non-rigid, showing only one ^{19}F NMR signal down to −95 °C, whereas $PhSP[OCH(CF_3)_2]_4$ shows inequivalent fluorine signals below −26 °C [162]. A number of dialkylphosphino derivatives $R_2POCH(CF_3)_2$ are known; they may be methylated to stable cationic species $[MeR_2POCH(CF_3)_2]^+$ [163]. A crystallographic structure determination on the cyclic complex $(CF_3)_2\overline{C{-}NH{-}P}[OCH(CF_3)_2]_3$ shows the phosphorus atom to be in a distorted TBP arrangement [164]. It is interesting that HFA adds across P–H bonds to form P–C rather than P–O bonds; with silicon, the converse is found (eqn. (5)). Phosphine gives $H_2PC(CF_3)_2OH$ [165] whereas Ph_2PH gives $Ph_2PC(CF_3)_2OH$ [166]; the latter rearranges to $Ph_2POC(CF_3)_2H$ in the presence of PR_3 [167a].

The sulphite $[(CF_3)_2CHO]_2S{=}O$ is known [131], as are derivatives of sulphur(II) and sulphur(IV) [167b]:

$$SCl_2 \xrightarrow{LiOCH(CF_3)_2} S[OCH(CF_3)_2]_2 \xrightarrow{Cl_2} ClS[OCH(CF_3)_2]_3 \tag{56}$$

The selenium derivative $Se[OCH(CF_3)_2]_4$ is only stable below −50 °C; NMR shows that it has a TBP structure [134]. The tellurium analogue may be isolated as a stable THF adduct [134].

(v) Tertiary alcohols

(a) Perfluoro-t-butanol

As the most acidic of the isolable fluorinated alcohols, $(CF_3)_3COH$ is important in alkoxide chemistry. Its great stability (in particular, its resistance to fluoride elimination) is shown by the striking observation of Dear et al. that its lithium and sodium salts melt at 142–143 °C and may be distilled at atmospheric pressure without decomposition at temperatures of 218° C and 232° C respectively [142]. The potassium salt may be sublimed at 140° C/0.2 mm but it decomposes above 220° C without melting. This trend in stabilities is, of course, the reverse of that found with fluorinated primary and secondary alkoxides, where the lithium derivative is the least stable.

In view of the acidity of the parent alcohol, it would be unrealistic to describe the alkali metal derivatives as covalent. However, it is clear that ionic interactions are weakened by the large size of the $(CF_3)_3CO^-$ anion, to the point where the lattice can break down into ion pairs either on heating or in solution (the salts are very soluble in ether, and even in non-polar solvents they have sufficient solubility for recrystallization from benzene.) There appears to be some association of $(CF_3)_3COLi$ and $(CF_3)_3CONa$ in the vapour, but their solid state structures are not known.

In addition to the use of $(CF_3)_3COH$ and its alkali metal salts, an alternative route to the synthesis of derivatives is through the hypochlorite, $(CF_3)_3COCl$ [69]. Canich et al. find that, through oxidative addition or displacement reactions, this reagent can be used to attach the $(CF_3)_3CO$ group to a variety of elements, both metallic and non-metallic [168]. In many cases, the hypochlorite will lead to products unavailable through the use of the alcohol, but the reagent is so strongly oxidizing that they invariably have the central atom in a high oxidation state.

Metallic alkoxides of titanium(IV), vanadium(V), chromium(VI), lead(II), bismuth(III) and tellurium(IV) were prepared by the following reactions at 0° C [168]:

$$4(CF_3)_3COCl + TiCl_4 \rightarrow Ti[OC(CF_3)_3]_4 + 4Cl_2 \quad (57)$$

$$3(CF_3)_3COCl + VOCl_3 \rightarrow VO[OC(CF_3)_3]_3 + 3Cl_2 \quad (58)$$

$$2(CF_3)_3COCl + CrO_2Cl_2 \rightarrow CrO_2[OC(CF_3)_3]_2 + Cl_2 \quad (59)$$

$$2(CF_3)_3COCl + Pb \rightarrow Pb[OC(CF_3)_3]_2 + Cl_2 \quad (60)$$

$$3(CF_3)_3COCl + Bi \rightarrow Bi[OC(CF_3)_3]_3 + 3/2Cl_2 \quad (61)$$

$$4(CF_3)_3COCl + Te \rightarrow Te[OC(CF_3)_3]_4 + 2Cl_2 \quad (62)$$

Other chlorides including UCl_4, $SnCl_4$, $SiCl_4$ and CuCl do not react with $(CF_3)_3COCl$, probably because the rather unstable reagent decomposes (into HFA and CF_3Cl) faster than the alkoxide is formed.

The titanium alkoxide, melting point 126° C, may be sublimed at 50° C in vacuo and appears to be monomeric. Like the chromium and vanadium complexes, it is extremely moisture sensitive, suggesting that the steric shielding of 12 CF_3 groups is not sufficient to give even short-lived kinetic stability against nucleophilic attack on the electropositive central atom. For the same reason, attempts to synthesize Ti[OC$(CF_3)_3]_4$ from the alcohol and $TiCl_4$ were not successful [168].

The more traditional route of treating the metal chloride with the alcohol and ammonia in ether is successful for the synthesis of lanthanide derivatives M[OC$(CF_3)_3]_3(NH_3)_3$, where M = Yb, La, Gd or Y [169]. The beryllium complex Be[OC$(CF_3)_3]_2$, which appears to be dimeric, was made by the reaction of $BeEt_2$ with the alcohol [170]. However, most metallic derivatives have been prepared by reaction of a halide with the lithium or sodium alkoxide, e.g. for beryllium [170]

$$BeCl_2 \cdot 2Et_2O \xrightarrow{(CF_3)_3ONa} Be[OC(CF_3)_3]_2 \cdot 2Et_2O \xrightarrow{L} L_2Be[OC(CF_3)_3]_2 \quad (63)$$

where L = NH_3 or pyr.

Anderson has used this approach to prepare U[OC$(CF_3)_3]_4(THF)_2$ from UCl_4 [149], a reaction which fails with $(CF_3)_3COCl$, and to make the uranium(VI) complex $UO_2[OC(CF_3)_3]_2(THF)_2$ from the nitrate; it has each pair of identical ligands *trans* disposed [171]. Johnson et al. prepared the molybdenum(VI) complexes MoOCl[OC$(CF_3)_3]_3$ and MoO[OC$(CF_3)_3]_4$ [172]; the metal is in approximately TBP geometry in the latter [173].

As with the hexafluoroisopropoxides, the fully fluorinated alkoxides of molybdenum are active in acetylene metathesis. Schrock and coworkers have prepared $Me_3CCMo[OC(CF_3)_3]_3$, described as an excellent catalyst [155,174].

In non-metal chemistry, the reagent $(CF_3)_3COCl$ is again very useful [69]. An early reaction was with BCl_3, giving B[OC$(CF_3)_3]_4$ [101]. Unlike the borates with fluorine on the α-carbon atom, this compound is extremely stable. It gives a 1 : 1 adduct with ammonia, but steric hindrance prevents it from reacting with Me_3N as does the similar B[OCF$(CF_3)_2]_3$ [101].

Reaction of $(CF_3)_3COCl$ with iodine gives I[OC$(CF_3)_3]_3$ in excellent yield, but further oxidation to iodine(V) does not occur [168]. Similarly, reaction with CF_3I gives $CF_3I[OC(CF_3)_3]_2$ [175]. Sulphur(II) compounds are readily oxidized, giving a variety of products including S[OC$(CF_3)_3]_4$ [176,177]. On reaction of the hypochlorite with S_4N_4, the ring remains intact and alkoxide groups are attached to sulphur, giving $N_4S_4[OC(CF_3)_3]_4$ [178]. The sulphite $[(CF_3)_3CO]_2S{=}O$ is made from the alcohol [131].

The $(CF_3)_3C$ group is comparable to the CF_3 group in stabilizing peroxy linkages, and the peroxide $(CF_3)_3COOC(CF_3)_3$ is the unexpected product of the reaction of the alcohol with ClF_3 [179]; it may be distilled at 100 °C and is unreactive towards water. Other peroxy derivatives include $(CF_3)_3COOSO_2F$ [180] and $(CF_3)_3COOF$ [181].

The phosphorus(V) derivatives $(CF_3)_3COPF_4$ and $[(CF_3)_3CO]_2PF_3$ are made by reaction of $(CF_3)_3COCl$ with $PClF_4$ and PCl_2F_3 [182].

Even though several derivatives are known in which four $(CF_3)_3CO$ groups are attached to the same atom, the steric bulk of the group is obviously considerable. To some extent, this is compensated by the very strong metal–oxygen bonds formed. It should also be noted that the "bulk" of three CF_3 groups is on the carbon atom one bond removed from the oxygen actually bonded to the metal. Thus, the steric strain is somewhat remote from the immediate coordination sphere of the central atom, rather than adjacent to it, as is the case in a bulky R_3P ligand. However, it is significant that known complexes of $(CF_3)_3CO^-$ generally have either highly oxophilic central atoms such as Ti^{4+}, $[Mo{=}O]^{4+}$ or B^{3+}, or large species such as Pb^{2+} or U^{4+}. No simple derivative has been reported in which $(CF_3)_3CO^-$ acts as a pseudo-halogen such as $L_2M[OC(CF_3)_3]_2$ where M^{2+} is any transition metal ion and L a neutral co-ligand, or anionic complexes $[M\{OC(CF_3)_3\}_n]^{m-}$. In contrast, complexes of either type are easily prepared with perfluoropinacol (Section C(vi)(a)) which is chemically similar to perfluoro-*t*-butanol but less sterically demanding.

In summary, it appears that, despite its acidity and chemical stability, perfluoro-*t*-butoxide is not the ideal ligand. Greater general utility is found when the fluorinated tertiary alcohol function is combined with a second donor site in the ligand. In this way, chemical stability and a reasonable degree of acidity are combined with greatly reduced steric demands and the stabilizing chelate effect to produce a more widely applicable complexing agent.

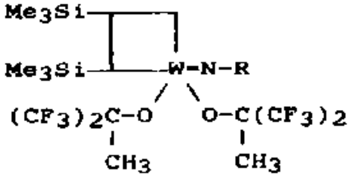
(b) Other fully fluorinated tertiary alcohols

As noted in Section B(ii), synthetic routes based on HFA are available to various fully fluorinated tertiary alcohols $R_f(CF_3)_2COH$, where $R_f = C_2F_5$, $CF_2{=}CF$, C_6F_5 etc. Little if any work has been reported on alkoxides derived from these molecules. They would seem to offer no advantage over $(CF_3)_3COH$, since they are generally less acidic and even more sterically demanding.

Some work has been reported on the vinylic alcohol $CF_2{=}C(CF_3)OH$ whose preparation and stability was noted above (eqn. (10)). It may be lithiated with butyllithium, then treated with Me_3MCl to give the derivatives $CF_2{=}C(CF_3)OMMe_3$ (M = Si or Ge) [183,184]. Clearly, this approach is capable of yielding a variety of complexes of this stable interesting system.

(c) Partially fluorinated tertiary alcohols

A wide variety of alcohols $R(CF_3)_2OH$ are available by the reaction of Grignard reagents etc. with HFA. The most common is hexafluoro-*t*-butanol, $CH_3(CF_3)_2COH$, $pK_a = 9.6$, which would be expected to have similar chemical properties to those of $(CF_3)_2CHOH$ ($pK_a = 9.3$) but to be more sterically demanding. The last point is vital in catalyst function, and Schaverein et al. have made use of this in designing the tungstenacycle **20**, described as "the first well-characterized, highly active, neutral, olefin metathesis catalyst" [185a]:



20 R = 2,6-diisopropylphenyl

The molybdenum alkylidyne complexes $Me_3CCMo[OC(CH_3)(CF_3)_2]_3$ [185a] and $Me_3CCMo[OC(CH_3)(CF_3)_2]_2(NAr)$ [185b], like the fully fluorinated analogue, are active in olefin and acetylene metathesis.

By analogy with the ready insertion of HFA into metal–hydrogen bonds, it might be expected that derivatives of $CH_3(CF_3)_2COH$ and related alcohols might be made by reaction of HFA with reactive metal alkyls. This was in fact demonstrated some years ago by Clark and Pickard, who prepared the compound $Me_2InOC(CF_3)_2CH_3$ from $InMe_3$ [186], but little further work on this type of reaction has been reported.

The sulphite $[CH_3(CF_3)_2CO]_2S{=}O$ was included in a number of similar compounds prepared and studied [131].

Derivatives of partially fluorinated alcohols $R(CF_3)_2COH$ where R contains a potential donor site are considered in Section D.

(vi) Fluorinated diols

(a) Perfluoropinacol

Perfluoropinacol dominates this class of fluorinated ligands because of its chemical stability, ease of preparation and the very wide range of derivatives which it forms. The diol has a pK_a of 5.95, very close to that of $(CF_3)_3COH$ (pK_a 5.4); the second dissociation cannot be detected in aqueous solution, but occurs sufficiently readily so that metal complexes of the di-ionized species $^-O{-}C(CF_3)_2C(CF_3)_2{-}O^-$ are readily prepared. Initial studies were carried out on methanolic or aqueous solution [187]:

$$M^{n+} + nH_2PFP + 2nOH^- \rightarrow [M(PFP)_n]^{n-} + 2nH_2O \qquad (64)$$

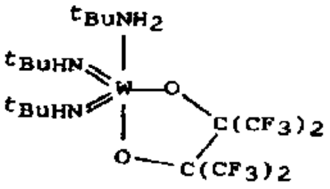
where M = Ni, Cu, Zn for $n = 2$ and M = Al, Fe for $n = 3$.

From the diamagnetic nature of the Ni^{2+} complex, it was assigned a square-planar configuration; this was subsequently confirmed by a full structure determination [188]. Through the use of a neutral co-ligand, the range of metal complexes may be considerably extended. With Ni^{2+}, nitrogen bases or phosphines may be used to prepare four-coordinate, square-planar, neutral complexes $L_2Ni(PFP)$ or the five-coordinate complex (DETA)Ni(PFP) (DETA = diethylenetriamine) [30]. The four-coordinate species are solvated in donor solvent to become five-, but not six-coordinate; this limit is presumably associated with the steric hindrance of the bulky PFP^{2-} ligand. However, even with a bulky diarsine as co-ligand to PFP^{2-}, the four-coordinate Ni^{2+} complex remains square planar rather than tetrahedral [189].

Use of bidentate nitrogen bases as co-ligands gives four-coordinate Cu^{2+} complexes such as (TMED)Cu(PFP) [30]. With softer transition metal ions, a phosphine or thioether co-ligand stabilizes the metal–alkoxide bond and complexes $(R_3P)_2M(PFP)$, where M = Pd [30,190] or Pt [30,191], and $(R_2S)_2Pt(PFP)$ [191] have been isolated.

Perfluoropinacol is very resistant to oxidation and can therefore be used to stabilize metals in high oxidation states. Reduction of CrO_4^{2-} in the presence of the diol leads to the chromium(V) complex $[O{=}Cr(PFP)_2]^-$ [192]; this is unusual in being formed in acidic solution, whereas the majority of formation reactions require basic conditions to ionize the diol. The isoelectronic vanadium(IV) complex $[O{=}V(PFP)_2]^{2-}$ has also been prepared [192], and the ESR spectra of both complexes have been studied [193]. Reaction of the vanadyl complex with thionyl halides gives the six-coordinate vanadium(IV) species $[VX_2(PFP)_2]^{2-}$; a trigonal prismatic geometry with *cis* halides is suggested on the basis of ESR spectra [194].

The tungsten(VI) complex **21**, a model for active sites in homogeneous propylene ammoxidation, has been prepared and structurally characterized [195]:

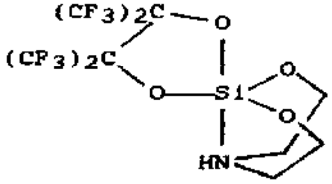


21

In non-aqueous donor solvent, the dianion PFP^{2-} can easily be prepared as the Li^+ or Na^+ salt, either by reacting the diol with a metal hydride or alkyl, or directly from HFA [27]:

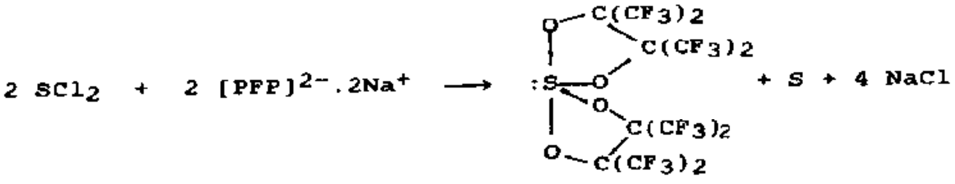
$$2(CF_3)_2C{=}O + 2Na \xrightarrow[25°/3d]{THF} [O{-}C(CF_3)_2C(CF_3)_2{-}O]^{2-} + 2Na^+ \qquad (65)$$

This reactive, easily prepared reagent is convenient for the preparation of a variety of covalent main-group derivatives of PFP^{2-} by reaction with dichlorides, and in this way the alkoxides $Me_2M(PFP)$ ($M = Si, Ge, Sn$) were synthesized, together with the cyclic borate PhB(PFP), the sulphite (PFP)S=O and the sulphate $(PFP)SO_2$ [27]. The complex borate anion $[B(PFP)_2]^-$ is readily formed in aqueous solution. Reaction of H_2PFP with $Si(OMe)_4$ in the presence of ethanolamine gives the five-coordinate silicon complex **22** [196]:



22

When PFP^{2-} reacts with SCl_2, the sulphur disproportionates to give the sulphur(IV) *spiro* complex **23** [27]:



23

(66)

The same product may be made by the reaction of H_2PFP with SCl_2 in ether in the presence of pyridine [197]. The tellurium analogue $Te(PFP)_2$ is made directly from $TeCl_4$ and $[PFP]^{2-} \cdot 2\,Na^+$ [27]. The ^{19}F NMR spectrum of **23** has been examined in detail by Astrologes and Martin [197], who find that the two inequivalent CF_3 resonances observed at 25 °C show further splittings down to −150 °C, consistent with a TBP geometry at sulphur with the non-bonding pair equatorial; this has been confirmed by a solid state crystal structure determination [198]. Curiously, $Te(PFP)_2$ shows only a single ^{19}F resonance at 25 °C, suggesting rapid inversion of the two rings [27]; the same effect has been noticed with $Te(OCH_2CF_3)_4$ [134].

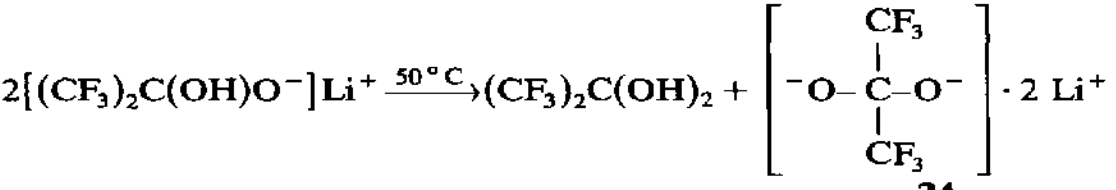
A great deal of work has been carried out on phosphoranes in which the five-membered ring $\overline{P{-}O{-}C(CF_3)_2{-}C(CF_3)_2{-}O}$ is present; it has been extensively reviewed recently [9] and only a brief outline will be given here. The formation of this system by the reaction of HFA with $(EtO)_3P$ has been mentioned (eqn. (9)); the mechanism has been studied by Ramirez and coworkers [199]. Bone and coworkers have synthesized a number of *spiro* phosphoranes such as $\overline{O{-}N(Me){-}P}(PFP){-}OPh$ and studied their pseudo-rotation by NMR [200].

Roeschenthaler, Schmutzler and coworkers have published a number of synthetic, structural and NMR studies on various phosphoranes including

$(PFP)PF_2-N(SiMe_3)_2$ [201], $(PFP)PH$ [202], $(PFP)PX$ [202,203], $(PFP)PX_3$ (X = halogen) and $[(PFP)P(O)]_2O$ [203], $(PFP)P-NR_2$ [204], $(PFP)PCl(\mu\text{-}NMe)_2PCl(PFP)$ [205], $(PFP)PHPh_2$ [206], and the mixed fluoro-alkoxy complexes $(PFP)PEt_2-OCH(CF_3)_2$ [207] and $(PFP)P(NR_2)[OCH(CF_3)_2]_2$ [208]. The hydride $(PFP)_2PH$ may be deprotonated with Et_3N to give $Et_3NH^+[(PFP)_2P^-]$ [209]. The complex $Me_3P \rightarrow PF_3(PFP)$ contains a coordinate bond from phosphorus(III) to phosphorus(V) [210].

(b) Other fluorinated diols

The simplest fluorinated diol, hexafluoro-2,2-propanediol, ("hexafluoroacetone hydrate" $(CF_3)_2C(OH)_2$) forms an interesting study. With a first pK_a value of 6.58, it may easily be titrated in aqueous solution [10]. Monosalts of the group I metals, $M^+[^-OC(CF_3)_2OH]$, may be isolated, but the addition of further base causes decomposition to CF_3COO^- and CF_3H [211]. However, controlled pyrolysis of the solid monolithium salt in vacuo leads to evolution of the diol and formation of the dilithium salt **24**, stable to 150 °C:



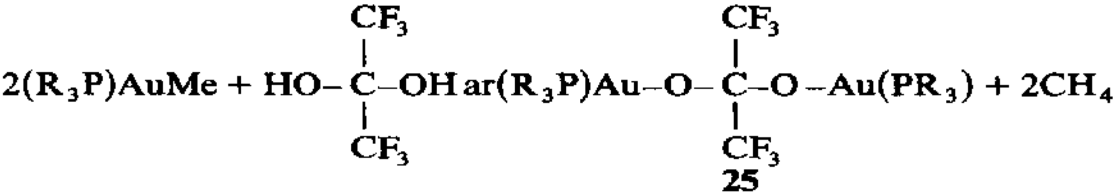
$$2[(CF_3)_2C(OH)O^-]Li^+ \xrightarrow{50^{\circ}C} (CF_3)_2C(OH)_2 + \left[{}^-O-\overset{CF_3}{\underset{CF_3}{C}}-O^-\right]\cdot 2\,Li^+ \qquad (67)$$

24

With the large tetraphenylphosphonium cation, a salt of the diol has been isolated and structurally characterized. It has the composition $[Ph_4P^+]_2[\{(CF_3)_2C(OH)O\}_2\{(CF_3)_2C(OH)_2\}_2]^{2-}$, the unionized and monoionized diol molecules being held together by hydrogen bonding in the tetrameric dianion [212].

Compound **24** reacts with Me_3SiCl to give $(CF_3)_2C(OSiMe_3)_2$ [211]. The hemi-substituted product, $Me_3SiOC(CF_3)_2OH$, has been made by the direct reaction of HFA with trimethylsilanol [213].

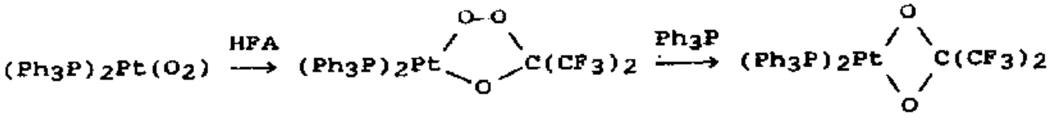
When a gold(I) alkyl reacts with the diol, the product is the alkoxide **25** in which the fluorinated group bridges two metal atoms [214]:



$$2(R_3P)AuMe + HO-\overset{CF_3}{\underset{CF_3}{C}}-OH\ \mathrm{ar}(R_3P)Au-O-\overset{CF_3}{\underset{CF_3}{C}}-O-Au(PR_3) + 2CH_4 \qquad (68)$$

25

Acting as a chelating ligand, $(CF_3)_2C(OH)_2$ would form a four-membered ring. The first complex of this type, **27**, was prepared indirectly by Hayward and Nyman via the reduction of a peroxy complex of platinum, **26** [215]:



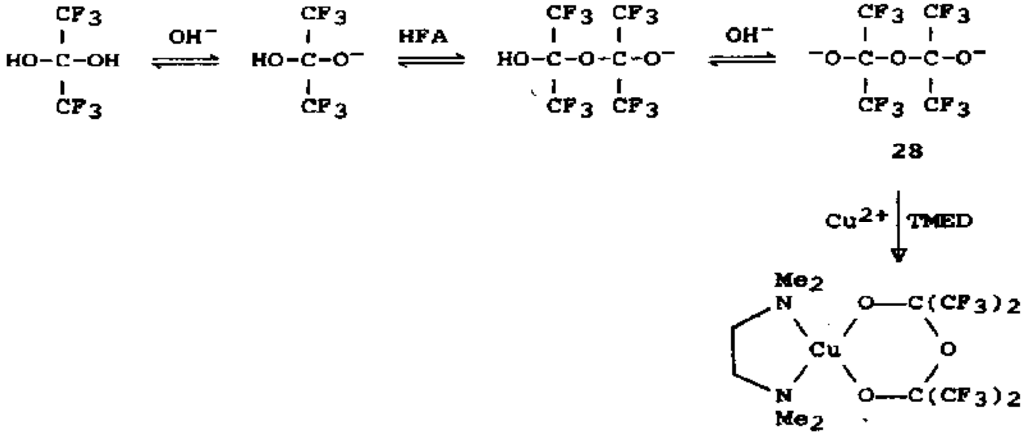
(69)

26 27

A similar sequence has been suggested in the reaction of the nickel peroxide complex $(Bu^tNC)_2Ni(O_2)$ with HFA [216].

Recent work on the solution chemistry of $(CF_3)_2C(OH)_2$ has shown that complexes containing four-membered chelate rings may be prepared by the reaction of the diol with metals such as Ni^{2+} or Cu^{2+} in the presence of a sterically demanding co-ligand [217]. However, an alternate mode of coordination is also found.

As mentioned previously (eqn. (6)), nucleophilic attack on HFA leads to "head-to-tail" dimerization and the formation of C–O–C linkages. It is now clear that a similar equilibrium is set up in aqueous/ethanolic solution when base is added:



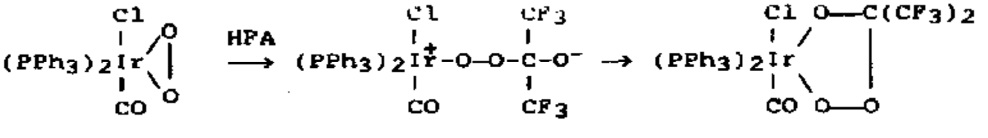
(70)

28

29

The parent alcohol of the dianion **28**, $HOC(CF_3)_2OC(CF_3)_2OH$, is not stable with respect to $(CF_3)_2C(OH)_2$ and HFA, but the six-membered chelate ring is stabilized by coordination to copper(II) or other metals [217]. The same ring is present in the complex $(PR_3)_2\overline{\text{Pt–O–C(CF}_3)_2\text{–O–C(CF}_3)_2\text{–O}}$, prepared and structurally characterized by Modinos and Woodward [218]. However, this was made by the reaction of a platinum azadiene complex with HFA containing small amounts of the hydrate, and it was not clear whether or not it was the thermodynamically favoured product. Current results suggest that this six-membered ring is stable in a variety of environments.

The usual ability of the perfluoroalkyl groups to stabilize peroxy linkages is demonstrated by the ready formation of stable complexes such as **26** above. Reaction of **26** with additional HFA results in expansion of the ring from five to seven members in the complex $(PR_3)_2Pt–O–C(CF_3)_2–O–C(CF_3)_2–O–O$ [215]. The reaction of HFA with iridium(III) peroxy complexes such as $(PPh_3)_2IrCl(CO)(O_2)$ has been studied in detail, and the results were interpreted in terms of electrophilic attack by HFA on coordinated O_2 to give an ionic transition state, **30**, followed by ring closure to give the product **31** [219]:



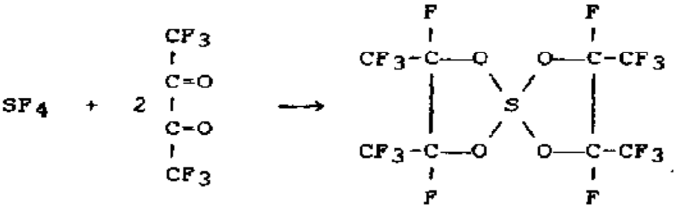
(71)

30 **31**

The peroxydiol $HO–C(CF_3)_2–O–OH$ (made by the reaction of HFA with H_2O_2) and its monolithium and monosodium salts are known [220], and the disodium salt $2Na^+[^-OC(CF_3)_2–O–O–C(CF_3)_2O^-]$ may be prepared by the reaction of HFA with Na_2O_2 in CH_3CN [221]; the position of the peroxy link was not definitely established. However, these compounds do not appear to have been used as intermediates in the preparation of alkoxide complexes of other metals.

The range of diols which might be prepared by the reductive dimerization of fluorinated ketones is limited by the difficulty of preparing this class of compound. Octafluoroacetophenone $C_6F_5C(O)CF_3$ is readily available; it undergoes reductive coupling much less easily than HFA, probably because of steric hindrance [17]. The product $[C_6F_5(CF_3)C(OH)–]_2$, **32**, contains two chiral centres; both *meso* and *dl* forms are produced in the coupling, and they have been separated. The optical isomers of **32** have been resolved by formation of a salt with the chiral base cinchonidine. This diol has pK_a of 8.85 and is a weaker ligand than H_2PFP, but metal complexes were isolated using Ni^{2+} and Cu^{2+} with neutral co-ligands; based on their circular dichroism (CD) spectra, absolute configurations of the enantiomers were assigned [222]. Coupling of $C_6H_5C(O)CF_3$ gives the partially fluorinated diol *meso*-$[C_6H_5(CF_3)C(OH)–]_2$; with a pK_a of 11.4, it is even less acidic than **32**, but some complexing ability towards Ni^{2+} is shown [222]. The semi-fluorinated aromatic diol $[C_6H_5(C_6F_5)C(OH)–]_2$ has been prepared by Filler and Kang [35] by reductive coupling in 2-propanol. They were unable to make $[(C_6F_5)_2C(OH)–]_2$ from $(C_6F_5)_2C{=}O$ by this route, but Dedinas showed that the fully fluorinated benzopinacol could be made by the irradiation of the ketone in perfluoro(methylcyclohexane) solution containing small amounts of 2-propanol [223]. Although stable up to its melting point of 140 °C, this diol rapidly decomposes to $(C_6F_5)_2CHOH$ and $(C_6F_5)_2C{=}O$ in solution in alcohols, apparently through radical disproportionation. Clearly, these aromatic diols are too sterically demanding to be effective ligands.

The fully fluorinated 2,3-butanediol $CF_3CF(OH)CF(OH)$-CF_3 is not known and would not be expected to be stable, but the sulphur(IV) derivative **33** has been made by Hodges et al. in an interesting reaction in which fluoride adds to the carbonyl groups in perfluorobiacetyl [224]:



33

(72)

The *spiro*sulphurane **33** has the expected TBP geometry at sulphur.

The similar partially fluorinated stable butanediol $CF_3CH(OH)CH(OH)$-CF_3 is known (made in poor yield by the reaction of SF_4 with tartaric acid [225]), but its potential use as a chelating ligand has not been studied.

(vii) Fluorinated phenols

As mentioned in Section B(iv), the effect of complete fluorination is much less in aromatic systems than it is for the aliphatic alcohols. Pentafluorophenol has a pK_a of 5.52 [36], only 4.4 units less than that of phenol. As a result, its acidity falls into the same range as that of the fluorinated alcohols, its derivatives have properties comparable with those of the fluorinated alkoxides, and they are considered in this section. The only significant compounds of this type to have been studied are pentafluorophenol and tetrafluorocatechol. Because of the availability of a variety of substituted phenols and the readiness with which they yield metallic complexes, many studies on C_6F_5OH derivatives place them among a number of related aryloxides, often including the thio analogue C_6F_5SH.

Pentafluorophenoxides are easily prepared, either from the phenol itself or from group I derivatives C_6F_5OLi or C_6F_5ONa.

Early work on complexes of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} by Nyholm and Hollebone characterized $C_6F_5O^-$ as a pseudo-halide ion similar to $C_6Cl_5O^-$ [226]. With large cations, tetrahedral complexes $[M(OC_6F_5)_4]^{2-}$ may be isolated, where M = Co, Cu or Zn, while nickel gives only $Ni(OC_6F_5)_2$. The blue Co^{2+} complexes give crystal-field splittings of 3920 cm and 3850 cm^{-1} for $C_6F_5O^-$ and $C_6Cl_5O^-$ respectively, comparable to that found in $[CoCl_4]^{2-}$ (3100 cm^{-1}), and the phenoxides have the normal properties of oxygen-donor ligands. The nickel derivative, a brown apparently polymeric solid, has also been made by the reaction of bis(2-methylallyl)nickel with C_6F_5OH [227].

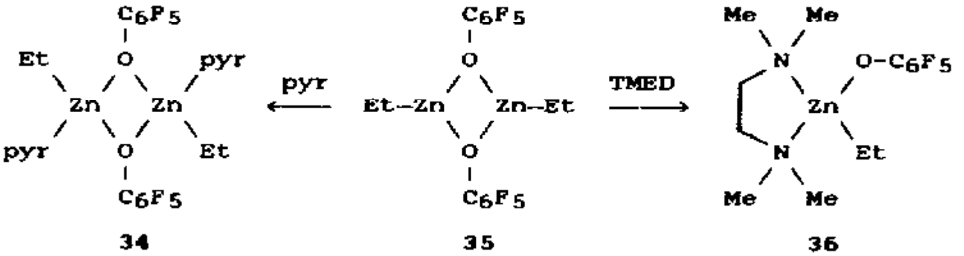
The six-coordinate titanium(IV) complex $(acac)_2Ti(OiPr)_2$ undergoes exchange with C_6F_5OH to yield *cis*-$(acac)_2Ti(OC_6F_5)_2$ [228]. In contrast, $(cp)_2TiCl_2$ reacts with $NaOC_6F_5$ more slowly than with $NaOCH(CF_3)_2$ and only one halide is replaced, giving $(cp)_2TiCl(OC_6F_5)$ [148].

Studies on molybdenum and tungsten complexes are consistent with the pseudo-halide character of the ligand. Complete exchange occurs between WCl_6 and C_6F_5OH, leading to $W(OC_6F_5)_6$ [229], while compounds $WF_n(OC_6F_5)_{6-n}$ may be prepared by the reaction of WF_6 with silicon pentafluorophenoxides [230,231]. The reaction of Mo_6Cl_{12} with aqueous $NaOC_6F_5$ in the presence of hexamethylphosphoramide (HMPA) gives the cluster compound $Mo_6Cl_8(OC_6F_5)_4(HMPA)_2$, volatile at 300 °C [232].

Several derivatives of platinum are known. The reaction of bis(tricyclohexylphosphine)platinum(0) with C_6F_5OH gives the hydride, *trans*-$(Cy_3P)_2PtH(OC_6F_5)$, in which ^1J(Pt, H) is 14.0 Hz, marginally less than the value of 14.6 Hz found in the analogous unfluorinated phenoxide [233]. NMR studies have also been carried out on the complexes (*o*-$Me_2N{-}C_6H_4{-}C(CH_3){=}CH_2)PtCl(OR)$, where $R = C_6F_5$ etc., and values of J(Pt, H) have been shown to increase as the acidity of ROH increases [234]. A structural study has been made of the similar complex (*o*-$Me_2N{-}C_6H_4{-}CH{=}CH_2)PtCl(OC_6F_5)$ and its $C_6F_5S^-$ analogue [235].

The reaction of *trans*-$(PPh_3)_2IrCl(CO)$ with $NaOC_6F_5$ gives *trans*-$(PPh_3)_2Ir(OC_6F_5)(CO)$, whose structure has been determined [236]. Bond lengths of the $C_6F_5O{-}$ ligand are the following: $r(C{-}O) = 1.302(6)$ Å; $r(Ir{-}O) = 2.058(3)$ Å. The angle at oxygen is 135.4(3)°. The authors compare these dimensions with the corresponding values for the analogous unfluorinated phenoxide, which are 1.324(6) Å and 2.049(4) Å and 126.5(3)° respectively. The greater bond angle at oxygen in the fluorinated derivative indicates some π bonding; the absence of available vacant orbitals on the d^8 iridium(I) atom makes π bonding to the metal unlikely, so they conclude that there is probably increased π donation from oxygen to the fluorinated aromatic ring, consistent with the shorter C–O bond length.

The zinc complex $EtZnOC_6F_5$ is dimeric in solution, and a structure with phenoxide bridging three-coordinate zinc, **35**, is suggested. Pyridine gives a 1 : 1 dinuclear complex **34**, whereas TMED gives a mononuclear complex **36** [237]:



34 **35** **36**

(73)

NMR studies have been made on a series of mercury complexes CH_3HgOR, including $CH_3HgOC_6F_5$; again, it has been found that ^2J(H, Hg) increases as the acidity of ROH increases [238].

In main-group compounds, Graham and coworkers prepared the derivatives $Me_3M(OC_6F_5)$ and $Ph_3M(OC_6F_5)$, where M = Si, Ge, Sn or Pb, and carried out NMR studies [239]. Ramirez and Maracek prepared $Mg(OC_6F_5)_2$ in aqueous solution and characterized its adducts with nitrogen bases [240]. The germanium(II) derivative $Ge(OC_6F_5)_2$, made by the reaction of $GeCl_2$ with $LiOC_6F_5$ in dioxane, appears to be polymeric [241]. Sharp and coworkers have made a number of sulphur derivatives, including $(C_6F_5O)_3S(O)F$ [242], $(C_6F_5O)_3SF$ and $(C_6F_5O)SF_2CF_3$ [243]; the last compound has the expected TBP geometry with apical fluorine atoms. Pentafluorophenol reacts with $POCl_3$ to give $(C_6F_5O)_nP(O)Cl_{3-n}$, where $n = 1$–3 [244].

In summary, it is clear that any number of derivatives of pentafluorophenol may be prepared. The acidity of the phenol is comparable to that of the most acidic fluorinated aliphatic alcohol, $(CF_3)_3COH$, but its much smaller steric bulk facilitates the preparation of many more derivatives, including the unusual anionic complexes $[M(OC_6F_5)_4]^{2-}$. Comparison with a halide ion is probably more appropriate for $C_6F_5O^-$ than for other fluorinated alkoxide ions.

The dihydric phenol, tetrafluorocatehcol, $o\text{-}C_6F_4(OH)_2$ (H_2TFC), is obviously a potential chelating ligand because of the suitable distribution of the –OH groups and two studies have been reported [245,246]. Despite the favourable geometry and the possibility of additional stabilization through conjugation of metal–ligand π bonding with the aromatic ring, TFC^{2-} shows only limited applicability. It interacts with a variety of metal ions in solution, but complexes are less stable than those of perfluoropinacol or of pentafluorophenol. Decomposition can occur easily through oxidation of the ligand, very often accompanied by fluoride elimination.

Only Cu^{2+} forms an anionic complex $[Cu(TFC)_2]^{2-}$, analogous to $[Cu(PFP)_2]^{2-}$ [245]. Nickel forms neutral complexes $L_2Ni(TFC)$ with amine or phosphine co-ligands, while Fe^{3+} gives an apparently six-coordinate neutral complex (TMED)Fe(TFC)(HTFC) in which the phenol is incompletely ionized. Germanium gives a reasonably stable complex with dimethylformamide (DMF) as co-ligand, $Ge(TFC)_2(DMF)_2$, but analogous derivatives of other group IV elements could not be characterized [245]. In a later study on manganese complexes, it was found that TFC^{2-}, out of a group of similar ligands studied, was the least suitable for stabilization of Mn^{3+}, because of its relative ease of oxidation [246].

Tetrafluorocatechol is unusual in that its ligand properties are markedly inferior to those of its chlorinated or brominated analogues. The evidence suggests that this is due to the ready transmittance of electron density through the π system to the fluorine substituents on the aromatic ring, leading to fluoride elimination and general decomposition of the system. With chlorine or bromine, the carbon–halogen bond is less polar and this does not occur so easily [245].

D. HYBRID LIGANDS: COMPLEXES OF MULTIFUNCTIONAL FLUORINATED ALCOHOLS

(i) Stability and preparation of ligands

In previous sections of this review, the ligands considered have been alcohols or diols in which the only potential donor sites present have been alkoxide groups. However, in the majority of stable complexes of metal ions, co-ligands of different character (either anionic or neutral) are also present. It is clearly of interest to combine the two potential donors in the same molecule, producing a difunctional or multifunctional ligand; since the donor sites are chemically different, the term "hybrid ligand" is often applied in such cases. By suitable choice of molecular geometry, complexes of these ligands can be stabilized by the chelate effect. It is also possible to combine the hard alkoxide donor with a soft donor, such as phosphine or thioether, thus stabilizing complexes of the softer heavy transition elements.

Ligands of this type are derived from tertiary fluorinated alcohols, and the great majority have compositions based on the units $X–CH_2–C(CF_3)_2–OH$ or o-$X–C_6H_4–C(CF_3)_2–OH$, where the group X contains a second donor site. The fluorinated alcohol function is therefore stable to fluoride elimination and a pK_a in the region 9–10 would be expected. Synthetic routes to a variety of stable ligands have been developed, almost invariably based upon hexafluoroacetone, and are described for individual ligands in the following sections. However, there are two important classes of complex where the parent ligand is unstable and the complex has to be made directly by template synthesis methods. The first of these occurs where the second donor site is carbon, i.e. the complex is organometallic (Section D(ii)). These are generally made by reaction of HFA with a low valency metal complex, and the ligand has no independent existence. The other class of "unstable" ligand is found where the second donor site is an imino group (Section D(iii)); these are made by amine condensations familiar in the chemistry of Schiff bases. The ligand cannot be removed from the metal with the imino group intact, but hydrogenation of the C–N bond in situ generally gives a stable difunctional amino alcohol.

(ii) Alkoxide and carbon donor

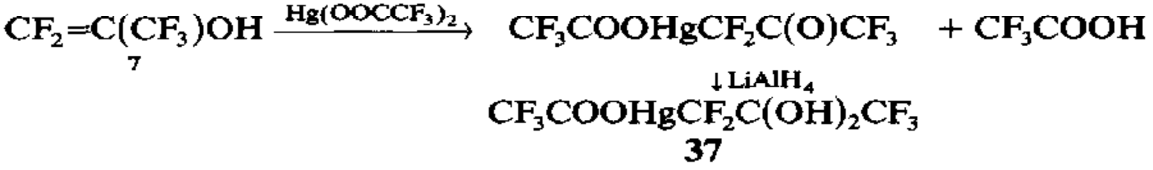
Complexes in which coordination to the metal occurs from carbon in conjunction with a fluorinated alkoxide are generally prepared by the direct reaction of low valency metal complexes with HFA. (In many cases, the analogous reaction may be carried out with hexafluoroisopropylimine, $(CF_3)_2C{=}NH$.) It is therefore the exception for the parent alcohol to be isolated, but some examples are known. A fluorinated alcohol containing an organo-iron substituent is made by the sequence [148]

$$Na^+[cpFe(CO)_2]^- \xrightarrow[Et_2O]{(1)\ HFA\ (2)\ HCl} cpFe(CO)_2C(CF_3)_2OH \tag{74}$$

In a reaction utilizing the activity of an alkynyl proton toward HFA, a platinum-substituted alcohol has been prepared [247]:

$$(PPhMe_2)_2Pt(C{\equiv}CH)_2 \xrightarrow{HFA} (PPhMe_2)_2Pt\{C{\equiv}CC(CF_3)_2OH\}_2 \tag{75}$$

When the vinylic alcohol $CF_2{=}C(CF_3)OH$, **7**, reacts with $Hg(OOCCF_3)_2$, the mercury becomes attached to carbon rather than oxygen, and the resulting ketone can be hydrogenated to a mercuriated *gem* diol, **37** [183]:



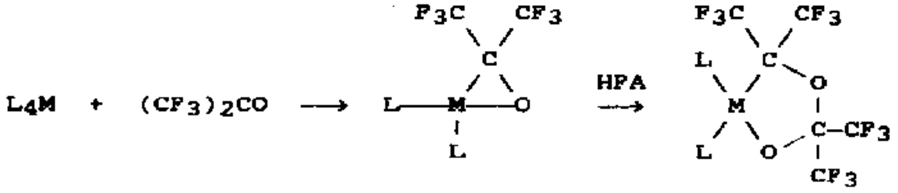
$$\begin{array}{ccl} \underset{\mathbf{7}}{CF_2{=}C(CF_3)OH} & \xrightarrow{Hg(OOCCF_3)_2} & CF_3COOHgCF_2C(O)CF_3 \quad + CF_3COOH \\ & & \qquad\qquad \downarrow LiAlH_4 \\ & & \underset{\mathbf{37}}{CF_3COOHgCF_2C(OH)_2CF_3} \end{array} \tag{76}$$

In general, however, ligands in which carbon and fluorinated alkoxide coordinate to a metal may be formed in one of two ways. Often, the metal–oxygen and metal–carbon bonds are formed simultaneously in reaction with HFA. Alternatively, an organometallic compound may undergo reaction of the organic ligand with HFA, the latter being converted to an alkoxide bonded to the metal. In either case, these may be classified as template synthesis reactions, i.e. the ligand is formed by reactions occurring on the metal which is to be complexed.

The metals of the nickel triad are particularly suited to oxidative addition reactions, and many derivatives have been reported, mainly by Stone, Green and coworkers. Other metals used have included iron, molybdenum, rhodium, iridium and gold. The topic has recently been reviewed by Witt et al. [9].

An interesting example of the reaction of HFA with a metal in a low oxidation state is found in studies by Walczak et al. on the chemisorption of the ketone on a ruthenium surface [248]. They find bonding interactions of the order of 66–87 kJ mol^{-1} which they attribute to donation of electron density from the metal into C=O π^* orbitals.

Two types of product are seen when a low valency metal complex reacts with HFA; an initial adduct with a three-membered ring **8**, and a complex of the type **9**, formed by the addition of a second HFA molecule to give a five-membered ring:


(77)

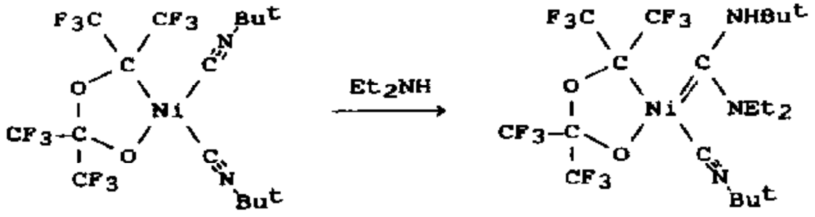
8 **9**

With nickel, the co-ligands L may be cyclooctadiene [249], triphenylphosphine [250], or *t*-butyl isocyanide [216,251]. There was initial debate as to whether the complexes of type **8** should be regarded as cyclic derivatives of a divalent metal, or as π complexes of the ketone with a zerovalent metal. In a structural report on $(Ph_3P)_2Ni(HFA)$ [252], Countryman and Penfold, by comparison of bond lengths with those of nickel–alkene complexes, suggested that the latter view is more appropriate. Stone and coworkers prefer to regard the reaction of HFA with low valent metal complexes as a two-electron oxidation reaction. They note that the type **8** complexes do not show a C=O IR absorption about 180 cm^{-1} lower than that of free HFA, typical of a coordination shift for π-bonded ketones. Furthermore, in the iridium complex $(PR_3)_2IrCl(CO)(HFA)$, the absorption frequency of coordinated CO is typical of that found in Ir^{3+} rather than Ir^{+} complexes [253].

More recent work has established the stability of fluorinated alkoxides of the nickel triad in complexes where soft co-ligands are present, and there seems no reason to doubt that the complexes with three-membered rings are correctly included as such, and that these reactions of HFA should be thought of as oxidative additions to the metal.

To some extent, the description of the mode of coordination of HFA to the metal is arbitrary, and Chisholm and Rankel describe the metal atom in the complex $(MeC{\equiv}C)_2(AsMe_3)_2Pt(HFA)$ as "either five- or six-coordinate", depending on which view is taken [247].

The coordinated alkoxide ring systems in the nickel complexes are often stable to reactions of the co-ligands. The type **8** complex (COD)Ni(HFA) reacts with diars to give (diars)Ni(HFA), which then adds further HFA to give a type **9** complex [254]. When the type **9** complex $({}^tBuNC)_2Ni(HFA)_2$ is treated with secondary amine, a nickel carbene complex, **38**, is produced [255].


(78)

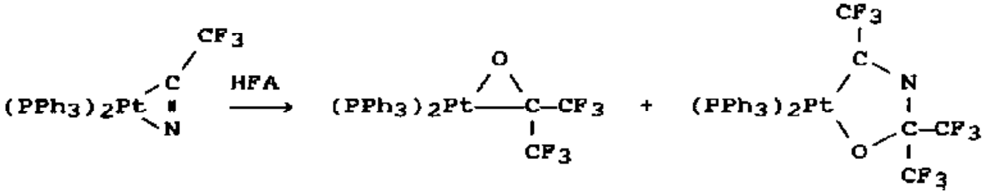
38

In reactions of this type, the five-membered alkoxy heterocycle is behaving in the same way as the fluorinated organometallic ring $(CF_2)_4Ni$ [255].

With palladium or platinum, phosphines are the most generally useful co-ligands, and reaction of $(Ph_3P)_4M$ with HFA gives type **8** complexes [253]. Both types **8** and **9** complex are produced if the co-ligands are $PMePh_2$ or diphos [190,256] or PEt_3 [257], or if the ring contains one HFA and one $(CF_3)_2C{=}NH$ unit [258]. In the reactions of these and the analogous NiL_4 and $L_2Ni(HFA)$ complexes, the activity of phosphine complexes towards both HFA and $(CF_3)_2C{=}NH$ increases in the general order: $P(OPh_3) \approx PPh_3 \ll PMePh_2 \approx (Ph_2PCH_2)_2 < P(OMe)_3$.

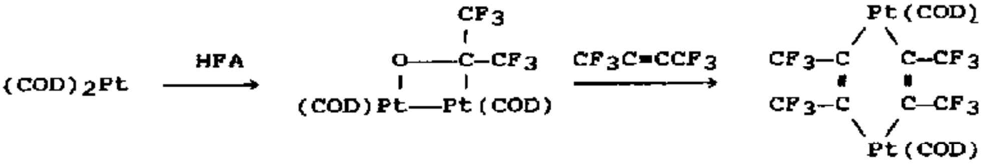
Expansion from a three- to a five-membered ring presumably involves the intermediate coordination of a second ketone molecule, followed by rearrangement of the coordinated ligands and "head-to-tail" dimerization. On the assumption that HFA is a strong π acceptor, this will be favoured by increased nucleophilicity on the metal. This is consistent with the observation that the more strongly σ-donating phosphines give greater reactivity [190,216,251,256]. However, steric hindrance from the bulkier phosphine ligands may also be a factor in determining what product is formed.

With the complex $(PPh_3)_2Pt(\pi\text{-}N{\equiv}CCF_3)$, reaction with HFA gives both displacement and ring expansion [259]:



(79)

Interesting studies have been reported on fluorinated alkoxides containing Pt–Pt bonds. Reaction of the triangulo cluster compound $Pt_3(Bu^tNC)_6$ with HFA leads to complete breakdown of metal–metal bonds and formation of the type **8** complex $(Bu^tNC)_2Pt(HFA)$ [260], but a dinuclear complex **39** may be prepared by the reaction of $Pt(COD)_2$ with HFA [261,262]. When this complex reacts with hexafluoro-2-butyne, the HFA is displaced and a platinum-containing heterocycle (**40**) is formed [263]:



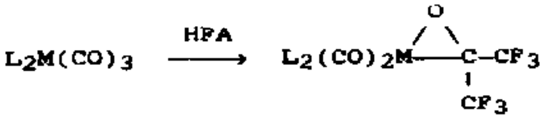
(80)

39 **40**

HFA adducts of Ir, Rh and Os have been prepared by reactions of low valency metal carbonyls. When $L_2IrCl(CO)$ reacts with HFA, the product is

$L_2IrCl(CO)(HFA)$ ($L = PPh_3$ or PPh_2Me); the phosphines are *trans* [253]. Reaction of the iridium complex $(PPh_3)_3Ir(NO)$ with HFA gives the type **8** complex $(PPh_3)Ir(NO)(HFA)$; the geometry cannot be deduced from the NMR data [264].

Zerovalent metal carbonyls may lose CO on reaction with HFA:



(81)

where $M = Ru$, $L = P(OR)_3$ [265] or PR_3 [266]; the ligands L in the product are *cis* in the former and *trans* in the latter. With $M = Os$, $L = PPhMe_2$, the phosphines in the product are *cis* [267].

Some interesting oxidative addition reactions occur when iron complexes containing π-bonded dienes react with HFA. An intermediate adduct **41** is formed in some cases, but in the final product **42** one double bond attacks the ketone, the resulting alcohol being coordinated to the metal. The second double bond remains bonded to the metal as a π-allyl function:

$$(\pi\text{-}CH_2{=}CHR{-}CHR{=}CH_2)FeL_n$$

$$\xrightarrow{HFA} (\pi\text{-}CH_2{=}CHR{-}CHR{=}CH_2)FeL_{(n-1)}(HFA) \qquad (82)$$

41 ↓

$$\overline{CH_2{-}CHR{=}CHR{-}CH_2{-}C(CF_3)_2{-}O{-}Fe}L_{(n-1)}$$

42

When the diene is tetramethylcyclobutadiene ($L = CO$), rearrangement of **41** to **42** is initiated by reaction with $P(OMe)_3$ [268]. With 2-methylbutadiene or 2,3-dimethylbutadiene ($L = CO$) insertion occurs on irradiation [269]. A rhodium complex with the first diene and η^5-cp as co-ligand reacts similarly, but when the diene is $CH_2{=}CHMe{-}CHMe{=}CH_2$, one HFA unit inserts between diene and metal and a second adds to a C–H bond in the cp ligand to give a free $-C(CF_3)_2OH$ group. With the complex (HMDB)Rh(cp) (HMDB = hexamethyldewarbenzene), the diene is unaffected and two HFA units add into C–H bonds in the cp ring [269].

The molybdenum(I) hydride $(cp)MoH(CO)_2(PPh_3)$ adds one molecule of HFA, but the structure of the apparent dinuclear product is unclear [270].

An interesting difference in behaviour is found with gold, clearly associated with the preference of that element for linear coordination in the +1 oxidation state. Reaction of $(PR_3)AuMe$ with HFA gives addition across the C=O bond, but the product is the dinuclear complex $(PR_3)Au{-}O{-}C(CF_3)_2{-}Au(PR_3)$ rather than a cyclic type **8** complex [214]. The related reaction in the presence of water was noted in Section C(vi)(b) above.

(iii) Alkoxide and nitrogen donor

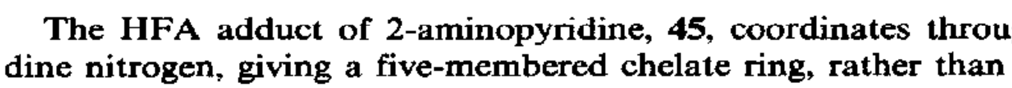
A molecule containing a fluorinated alcohol and an amino function is very suitable for coordination to harder transition metal ions. When these complexes are stabilized by chelation, complexes of such ions as Cu^{2+}, Ni^{2+}, Co^{2+}, Co^{3+}, Fe^{3+} and Ce^{4+} may be prepared by straightforward reaction in solution. Early work on ligands of this type was directed to the synthesis of the parent molecules, but the range of available complexes was very much extended by the discovery that template condensation reactions could be used. Since reactions of this type start with any primary amine, a great variety of ligands, many of them containing additional functional groups, may be prepared.

Direct addition of HFA to $R_2N{-}H$, leading to $R_2N{-}C(CF_3)_2{-}OH$ ($R = H$, alkyl etc.) is easy [8,9] but such molecules are unsuitable as chelating ligands because of the small ring which would result and because of the ease with which HFA is lost.

Three routes have been used to synthesize fluorinated alcohols containing primary or secondary amino or pyridino substituents at a suitable separation from the alcohol function for chelation to occur [50]:

$$CH_2(CN)COOH \xrightarrow{HFA} (CF_3)_2C(OH)CH_2CN \xrightarrow{H_2/Ni} (CF_3)_2C(OH)CH_2CH_2NH_2 \qquad (83)$$

43



$$CH_2N_2 \xrightarrow{HFA} (CF_3)_2\overset{O}{C{-}CH_2} \xrightarrow{RNH_2} (CF_3)_2C(OH)CH_2NHR\ (R = H \text{ or } CH_3) \qquad (84)$$

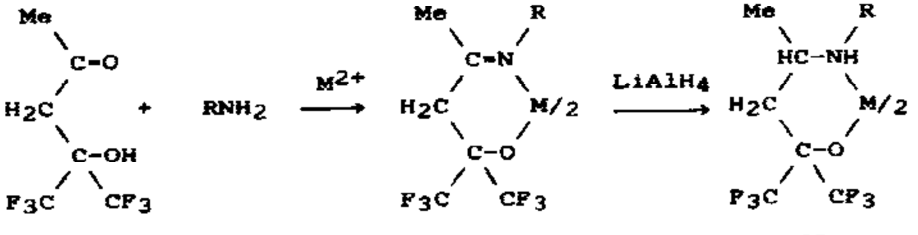
44

$$2\text{-}(C_5H_4N){-}NH_2 \xrightarrow{HFA} 2\text{-}(C_5H_4N){-}NH{-}C(CF_3)_2{-}OH \qquad (85)$$

45

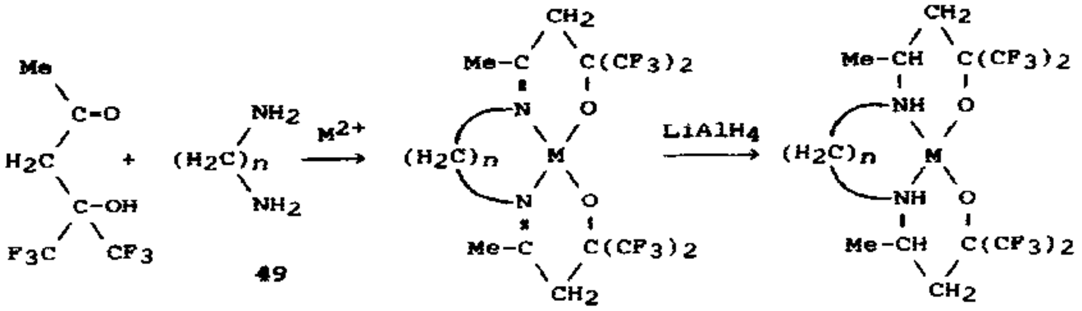
The HFA adduct of 2-aminopyridine, **45**, coordinates through the pyridine nitrogen, giving a five-membered chelate ring, rather than through the secondary amine. The amino alcohol **44** also gives a five-membered ring, while **43** gives a six-membered chelate. Neutral 2:1 complexes of Co^{2+}, Ni^{2+} and Cu^{2+} were obtained with all three ligands. Formation constants showed the usual stability trend among these elements: $Cu^{2+} > Ni^{2+} > Co^{2+}$, and in each case the complexes were less stable than those of analogous amino acids. The structures appeared to be square planar with Ni^{2+} and Cu^{2+}, whereas Co^{2+} complexes were less stable and tended to crystallize as octahedral dihydrates. Solvation to give five-coordinate species was observed when the nickel or copper complexes reacted with pyridine.

In later work, the range of available ligands of this type has been considerably extended through the use of template condensation reactions between primary amines and the fluorinated keto alcohol $CH_3C(O)CH_2C(CF_3)_2OH$ (**46**); the latter is readily made by the reaction of acetone with HFA. Two types of complex have been prepared, using either monofunctional or difunctional amines. In each case, the C=N bond may be hydrogenated and the resulting stable amino-alcohol ligand then transferred to another metal:



46 **47** **48**

(86)



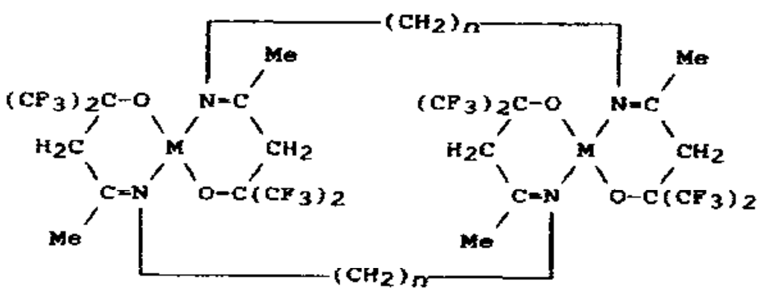
49 **50** **51**

(87)

Neither of the Schiff-base-type condensations in eqns. (86) and (87) occurs in the absence of a metal ion, and coordination of the reactants to the metal ion is clearly necessary to bring about reaction.

The reactions of difunctional amines, **49**, with $n = 2$ or 3 and M = Cu or Ni, were investigated first [271,272]. The four-coordinate square-planar complexes, **50**, could in many cases be solvated to five- but not six-coordinate adducts with pyridine.

The use of long-chain diamines with $n = 5$–12 gave a different type of product, **52**, with the diamine residue bridging instead of chelating:



52

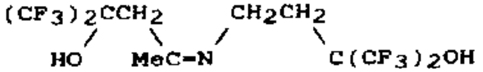
Structures of type **52** complexes have been determined with $n = 6$ and M = Ni [273], and with $n = 5$ and M = Cu [274]; there is no metal–metal interaction in either case. In **50** and **51** with $n = 2$ or 3, the bulky fluorinated alkoxide groups are required to be *cis*, whereas in **52** the constraint of the chelate ring is removed and they are *trans* disposed.

An interesting variation on reaction (87) was found where **49** is ethylenediamine and the metal is Ce^{3+}. Air oxidation occurs readily and a neutral eight-coordinate Ce^{4+} complex containing two quadridentate ligands is formed; the geometry at the metal is roughly a square antiprism [275].

Since the ready condensation of long-chain diamines to give type **52** complexes did not depend on chelation by the reactant diamine, it was to be expected that monofunctional amines would also condense with **46** (eqn. (86)) [276]. Hydrogenation of the C=N bond in **47** introduces a chiral centre at carbon; through the use of a chiral R group, it was shown that the reaction is stereospecific and an absolute configuration was assigned [276].

A variety of multidentate ligands and their complexes have been made through condensation of **46** with long-chain diamines containing other amine or ether functions. Complexes of the following imino diols have been prepared; in most cases they have been reduced to the corresponding amino diols:

53



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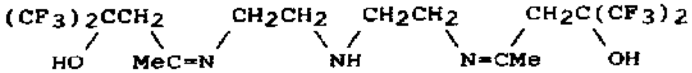

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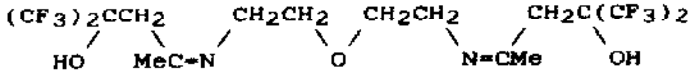
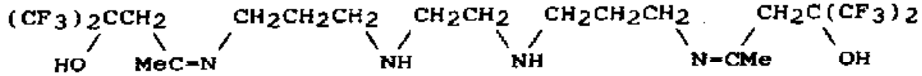
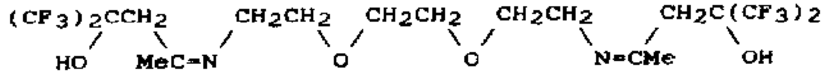


56



57



Ligand **53** is tridentate, and four- and five-coordinate complexes of Ni^{2+} are formed with pyridine or TMED as co-ligands [277].

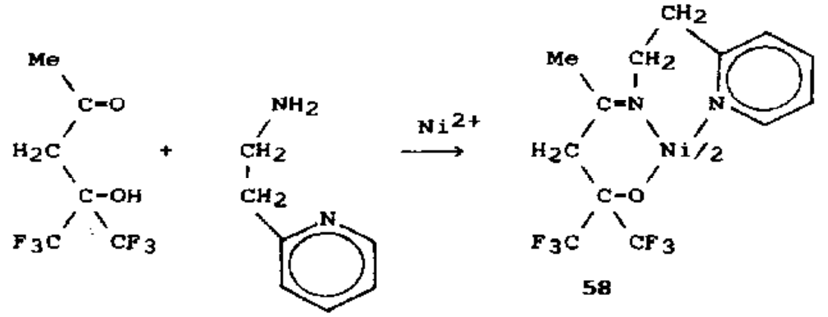
Ligand **54** gives five-coordinate complexes with Cu^{2+} or Ni^{2+} [271]. With **55**, the extra donor is ether rather than amine, and it remains uncoordinated in Cu^{2+} and Ni^{2+} complexes, which are of the dinuclear **52** type, although the Co^{2+} analogue appears to be five-coordinate and mononuclear [276].

When C=N bonds in **55** are hydrogenated, the greater flexibility of the ligand enables the Ni^{2+} complex to be five-coordinate and mononuclear.

The potentially hexadentate ligands **56** and **57** are able to fill all coordination sites at an octahedral centre. The stronger donor **56** gives six-coordinate complexes with Ni^{2+} and Co^{3+}. With **57**, both ethereal oxygen atoms are coordinated in a six-coordinate Co^{2+} complex which has been structurally characterized [278], but with Ni^{2+} the ligand fills only four sites in *trans* square-planar coordination, with the eight-membered di-ether chain apparently bridging across the metal ion without coordinating [278].

A hexadentate ligand is also produced by template condensation of **46** with tris(aminomethyl)ethane, $CH_3C(CH_2NH_2)_3$, and reaction in the presence of Fe^{3+} has been found to produce complexes of both the fully condensed ligand $CH_3C\{CH_2N{=}C(CH_3)CH_2C(CF_3)_2OH\}_3$ and a partially condensed ligand with one unreacted amino group. The latter, which has been structurally characterized, contains an Fe–O–Fe bridge [279].

Potentially tridentate Schiff-base-type ligands may be obtained by condensation of **46** with primary amines containing an additional donor site. Because of the presence of the bulky fluorinated alkoxide, these additional donor sites do not coordinate in all cases, but a six-coordinate Ni^{2+} complex, **58**, can be formed from 2-(2-aminoethyl)pyridine [280]:

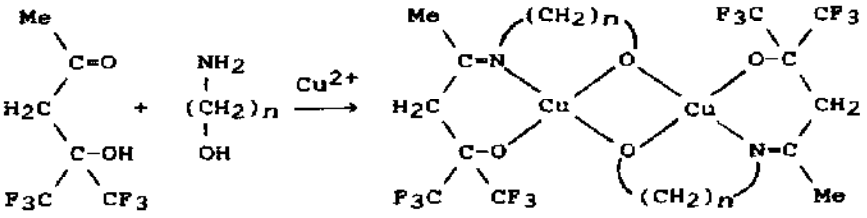


58

(88)

All similar donors are *trans* in **58** which is crystallographically centrosymmetric.

Template condensation of **46** with amino alcohols on Cu^{2+} gives a range of dinuclear complexes, **59**, in which the unfluorinated alkoxide bridges two metal ions [281]:



59

(89)

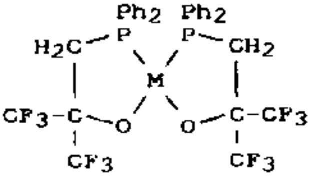
Strong antiferromagnetic interactions between copper atoms are found in type **59** imino-alkoxide complexes when $n = 3$ or 4, and a structural study shows this to correlate with the degree of coplanarity of the two coordination planes and the bridging alkoxides [282]. The degree of antiferromagnetic interaction is less in the Cu^{2+} complexes of the corresponding amino-alkoxide ligands [281] or when substituents are present in the original amino alcohol $H_2NCH(R)CH_2OH$ [283].

(iv) Alkoxide and phosphorus donor

As mentioned in Section C(vi)(a), work on perfluoropinacol derivatives has shown that their complexes with the heavier transition metals are stabilized when the hard alkoxide donor is combined with a soft co-ligand, of which tertiary phosphine is the most suitable [30,190,191]. Rather than use separate ligands, it is clearly easier to combine the two functions in one molecule, and this was accomplished by the reaction of HFA with lithiated methyldiphenylphosphine [284]:

$$Ph_2PCH_3 \xrightarrow{BuLi} Ph_2PCH_2Li \xrightarrow{(1)\ HFA\ (2)\ H_3O^+} \underset{\mathbf{60}}{Ph_2PCH_2C(CF_3)_2OH} \qquad (90)$$

Complexes of the phosphino alcohol **60** are readily formed with a variety of transition metals; either neutral bis-chelate complexes **61** with Ni^{2+}, Pd^{2+} or Pt^{2+}, or the complex **62** with phosphine co-ligands and Cu^+ or the anionic $[(\overline{OC(CF_3)_2CH_2PPh_2)_2Rh}Cl_2]^-$ with Rh^{3+} [284]:



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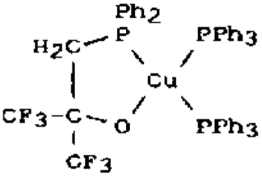
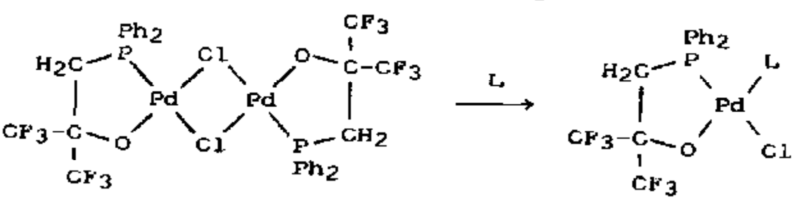


62

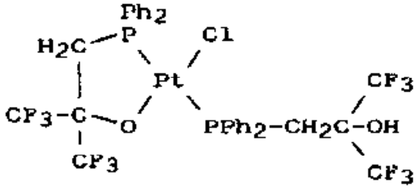
The Pd^{2+} and Pt^{2+} complexes have the *cis* geometry shown, whereas the Ni^{2+} complex shows a solvent-dependent *cis–trans* equilibrium in solution, with a *trans* structure in the solid state; the latter, although square planar and diamagnetic, has a significant axial interaction of the nickel atom with two CF_3 groups [283]. The Pd^{2+} complex reacts with $PdCl_4^{2-}$ to give the chloro-bridged dinuclear complex **63**, which in turn may be cleaved with phosphines or other ligands to give mixed-ligand complexes **64**; a structure has been determined for $L = PPh_2Me$ [285]:

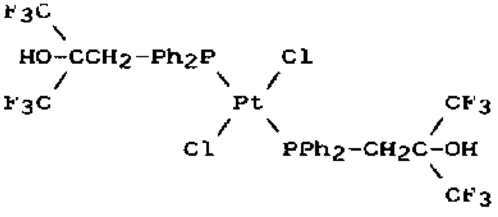


(91)

63 64

There is an extensive chemistry for the platinum complexes of this ligand, which can be either bidentate (anionic) or unidentate (neutral, unionized), coordinating through the phosphine only. Both *cis* and *trans* isomers of **65** and **66** have been prepared, and various interconversions between them and the type **61** complex may be carried out [44]:


65


66

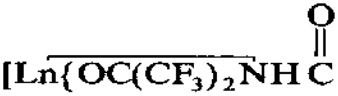
The bis-chelate Pt^{2+} complex **61** reacts with chlorine to give the platinum(IV) complex $\{\overline{OC(CF_3)_2CH_2PPh_2\}_2P}tCl_2$ which contains *trans* phosphines and *trans* chlorides [44].

(v) Alkoxide and oxygen donor

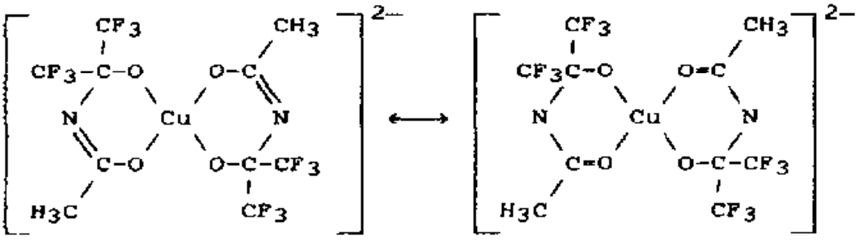
The use of the keto alcohol $CH_3C(O)CH_2C(CF_3)_2OH$, **46**, in template synthesis, referred to in Section D(iv), requires that it coordinates to the metal ion during the reaction, presumably chelating through the alkoxide and carbonyl functions. The latter is generally a weak donor, and it was only possible to isolate stable complexes of **46** as a bidentate uninegative ligand with Cu^{2+} and Ni^{2+} through the use of a bulky tridentate macrocyle as co-ligand [271].

With the keto diol $HOC(CF_3)_2CH_2C(O)CH_2C(CF_3)_2OH$, the mode of coordination to Ni^{2+} and Cu^{2+} appears to be bidentate through alkoxide and carbonyl, presumably because the geometry of the ligand disfavours a tridentate mode of coordination [277].

Another ligand chelating through alkoxide and carbonyl is the adduct of HFA with acetamide, $CH_3C(O)NHC(CF_3)_2OH$. Neutral complexes were prepared with a variety of metals including Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+} and Ce^{4+}, whereas lanthanide(III) ions gave anionic complexes $[Ln\{\overline{OC(CF_3)_2N}H\overset{\overset{\displaystyle O}{\|}}{C}CH_3\}_4]^-$ [286]. In the absence of structural data, it is difficult to establish the exact mode of coordination of this ligand, but IR data suggest that it is bonded through alkoxide and carbonyl oxygen in all cases except for copper, where coordination may be through amido nitrogen.



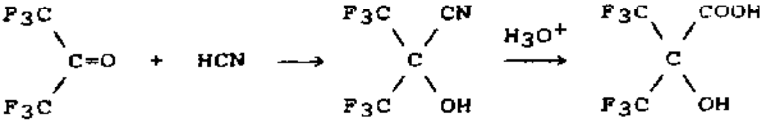
The Cu^{2+} complexes may be deprotonated to the anionic complex **67** which is stabilized by delocalization:



(92)

67 **68**

Since carboxylate is a stronger donor than carbonyl, it would be expected that a donor combining –COOH with a fluorinated alcohol would give more stable complexes than the above keto alcohols. A synthetic route to hydroxyhexafluoroisobutyric acid, **69**, is available via the cyanohydrin of HFA:



(93)

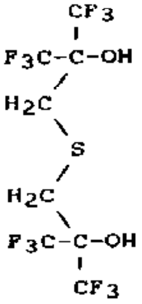
69

This ligand, which is similar to oxalic acid, has the potential to form a five-membered chelate ring, and complexes have been prepared with Al^{3+} and a variety of first-row transition metal ions including VO^{2+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} [287]. From the visible spectrum of the Cr^{3+} complex $[Cr\{OC(CF_3)_2COO\}_3]^{3-}$, the ligand-field splitting, $10Dq$, was calculated to be 17 000 cm^{-1}, which is greater than that for Cl^- (13 800 cm^{-1}), essentially the same as that for water and very similar to that for oxalate ion (17 400 cm^{-1}). The Ni^{2+} complex $[Ni\{OC(CF_3)_2COO\}_2]^{2-}$ differs from the PFP^{2-} analogue in being paramagnetic, with a visible spectrum typical of octahedral Ni^{2+}; this is ascribed to a tridentate mode of coordination, probably involving bridging carboxylate groups.

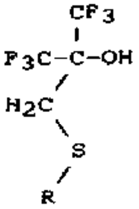
Examples of coordination from ethereal oxygen were mentioned in Section D(iii) for multidentate ligands where other stronger donors were also present in the molecule, but oxygen in this environment appears to be too weak a donor to coordinate in a ligand containing fluorinated alkoxide and ether only.

(vi) Alkoxide and sulphur donor

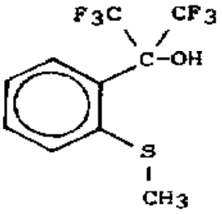
Studies on PFP^{2-} complexes of soft transition metals showed that the metal–oxygen bond could be stabilized by the presence of the soft thioether as co-ligand, e.g. in $(Me_2S)_2Pt(PFP)$ [191]. As with the analogous phosphine complexes, this has been extended to the study of hybrid ligands with both functional groups in the same molecule. Three types of compound, giving five- or six-membered chelate rings, have been successfully applied as ligands:



70



71



72

The potentially trifunctional ligand **70** is made by the irradiation of HFA with $(CH_3)_2S$ [288]. Stable complexes may be made with the first-row transition metals Co^{2+}, Ni^{2+} and Cu^{2+}; no success was achieved with heavier transition metals [289]. It appears that the presence of only one soft ligand is insufficient to stabilize complexes with two hard alkoxides coordinated to a soft transition metal ion; moreover, the geometry of the ligand is unsuitable for coordination at a square-planar centre. The ligand is dinegative and tridentate in complexes, and a structural determination on the five-coordinate Co^{2+} complex $(pyr)_2\overline{CoS\{CH_2C(CF_3)_2O}\}_2$ shows TBP geometry with the sulphur atom apical and the two alkoxides equatorial; the $CH_2{-}S{-}CH_2$ angle is 100.4(3)°.

With type **71** ligands (R = Me or Ph), where a ratio of one fluorinated alkoxide to one thioether function is present, the situation is reversed, and only complexes of softer transition metal ions (Pd^{2+} or Pt^{2+}) could be isolated [290]. The neutral bis complexes $\overline{M\{RSCH_2(CF_3)_2O}\}_2$ have *cis* alkoxide groups for M = Pt, whereas both *cis* and *trans* isomers are observed for M = Pd. From dynamic NMR measurements, the barrier to inversion of the coordinated thioether may be found [290].

By the use of other co-ligands, neutral mixed-ligand complexes $Ph_3P\overline{MCl\{RSCH_2C(CF_3)_2O}\}$ and cationic $[(R'_3P)_2\overline{M\{RSCH_2C(CF_3)_2O}\}]^+$ may be isolated [291]. Again, dynamic NMR measurements enable the thioether inversion barrier to be measured. For the cationic species (as the BF_4^- salts) complete structural determinations have been made for $R'_3P = Ph_3P$ and Ph_2PMe and a consideration of structural data in conjunction with NMR results suggests that a preferred ring conformation persists in solution [292].

The substituted thioanisole ligand **72** reacts similarly with Pd^{2+} and Pt^{2+}, giving neutral bis complexes in a *cis–trans* mixture [293]. The Pd^{2+} complex reacts with $PdCl_4^{2-}$ to give a Cl-bridged dinuclear complex similar to that found for the phosphino-alkoxide complex (eqn. (91)). Reaction of the latter with other ligands leads to cleavage of the chloride bridge, and a structural determination on the complex $(PPh_2Me)\overline{PdCl\{S(Me)-C_6H_4-C(CF_3)_2O}$ shows phosphine *trans* to alkoxide and thioether *trans* to chloride [293].

E. PROPERTIES OF FLUORINATED ALKOXIDE LIGANDS

(i) General properties

The preceding sections have outlined the general properties of the fluorinated alkoxide as a ligand. Its outstanding chemical characteristic is its low basicity. As a result, the ligands show much less of a tendency to bridge between metal ions than do their unfluorinated analogues, and complexes tend to have relatively simple structures rather than the bridged aggregates common among other alkoxides. The bond from metal to oxygen has considerable ionic character, and the metal atom is correspondingly electrophilic. The "hard" nature of the ligand coordinating through oxygen means that the most stable complexes are formed with the first-row transition elements, with stabilities following the usual Irving–Williams series. Complexes of softer acceptor ions derived from heavier elements may be stabilized by the presence of soft co-ligands.

The low basicity of the oxygen means that complexes are generally stable to attack by water or other protonic solvents, which therefore serve as convenient synthetic media. Provided that the problem of fluoride elimination is not present, the fluorinated alkoxides show considerable chemical stability. In particular, they are very resistant to oxidation and are therefore suitable for stabilizing metals in high oxidation states. Perfluoro-*t*-butanol and perfluoropinacol are each virtually impossible to oxidize and are especially valuable in this respect.

In the final sections of this review, some additional specific properties of the fluorinated alkoxide ligand are considered under two general headings: those deduced from spectroscopic measurements, and those relating to structural data. Applications of these ligands are then briefly considered.

(ii) Spectroscopic properties

The synthesis of many coloured complexes of fluorinated alkoxides has made it easy to place the ligands in the spectrochemical series. As mentioned in Section C(vii), early spectroscopic studies on pentafluorophenoxide complexes gave the $C_6F_5O^-$ ligand a crystal-field strength comparable to that of Cl^- and other oxygen-donor ligands [226]. Similar results were found in a study of square-planar Ni^{2+} complexes $(Et_3P)_2NiX_2$ [30], for which the first transition in the visible region is found at 610 nm, 542 nm, 490 nm and 460 nm for $X^- = I^-$, $X^- = Br^-$, $X^- = Cl^-$ and $X^- = (PFP^{2-})/2$ respectively. The substitution of carboxylate for one fluorinated alkoxide in the last complex, giving $(Et_3P)_2\overline{Ni\{OOCC(CF_3)_2O}\}$, gives no detectable change in the position of this absorption [287]. The similarity between the spectra of Cr^{3+} complexes of the same ligand and its aquo and oxalato analogues was mentioned in Section D(v).

All of these results lead to the placement of the fluorinated alkoxide slightly to the high energy side of the halides in the spectrochemical series, comparable to other ligands coordinating through oxygen with a bond of considerable ionic character.

Through a detailed study of some PFP^{2-} complexes of Pt^{2+}, information has been obtained on the *trans* influence and the *trans* effect of this ligand [191]. Phosphorus–platinum coupling constants are generally accepted as a reliable indicator of the *trans* influence of ligands, and a comparison of the ^1J(Pt, P) values for $(R_3P)_3Pt(PFP)$ with those for a series of complexes $(R_3P)_2PtX_2$ ($X^- = Cl^-$, Br^- or I^-) gives the order $Cl^- < Br^- \approx -C(CF_3)_2O^- < I^-$.

Again, PFP^{2-} is in the pseudo-halide class, although its ordering against the halogens is slightly different from that demonstrated by the spectrochemical series. By comparison with other ligands coordinating to platinum through oxygen, the static *trans* influence of the fluorinated alkoxy group may be placed in an order which corresponds to their increasing basicity: $ONO_2^- < CH_3COO^- \approx -C(CF_3)_2O^- < p\text{-}CH_3OC_6H_4O^- < OH^-$.

A direct comparison of the *trans* influence of fluorinated and unfluorinated alkoxides in complexes of the same geometry is available following the preparation of *cis*-$\overline{Pt\{PPh_2CH_2C(CH_3)_2O}\}_2$ by Alcock et al. [294]. This complex has ^1J(Pt, P) = 3303 Hz, considerably less than the value of 3517 Hz found in *cis*-$\overline{Pt\{PPh_2CH_2C(CF_3)_2O}\}_2$ (**61**) and showing a greater *trans* influence for the more basic unfluorinated alkoxide. When the ligand contains neutral methoxy instead of anionic alkoxide, as in the cationic complex *cis*-$[\overline{Pt\{PPh_2CH_2C(CH_3)_2O}CH_3\}_2]^{2+}$, the *trans* influence is much weaker and ^1J(Pt, P) is 4220 Hz [295].

Slightly contrasting results are found when the dynamic *trans* effect of the PFP^{2-} ligand is estimated from its ability to lower the activation energy barrier to inversion at sulphur in thioether complexes [191]. The value of ΔG^* is 75.5 kJ mol^{-1} in $(SEt_2)_2Pt(PFP)$, slightly greater than the value of 70.3 kJ mol^{-1} in *cis*-$(SEt_2)_2PtCl_2$. Using 2,5-dithiahexane, $CH_3S(CH_2)_2$-SCH_3, (DTH) as a co-ligand, the barrier to inversion at sulphur was found to be 86 kJ mol^{-1} for (DTH)Pt(PFP), again greater than the values of 81.4 kJ mol^{-1} and 75.3 kJ mol^{-1} found for (DTH)$PtCl_2$ and (DTH)PtI_2 respectively. Because of its weaker *trans* effect, it is suggested that fluorinated alkoxide *trans* to thioether is more strongly electron withdrawing than is chloride.

There is therefore a difference in the ordering of fluorinated alkoxide and chloride; the former has the greater static *trans* influence, but the latter the greater dynamic *trans* effect. This has been rationalized in terms of the relative importance of ionic and covalent contributions to the metal–ligand bonding in each case [191].

(iii) Structural properties

The structural effects of the fluorinated alkoxides may be considered under two headings: the steric bulk of the fluorinated ligands, and the effect of a high degree of fluorination on bond lengths within complexes.

The trifluoromethyl group is significantly larger than the methyl group. An empirical estimate of their relative size may be obtained from the molar volumes of liquid alkanes and their fluorinated analogues, where only van der Waals interactions are present. For C_2–C_6 alkanes, the molar volume of the fully fluorinated version is 45%–55% greater, corresponding to an increase of 14%–16% in the linear dimensions of the molecule. An estimate using the usual values of the C–H and C–F bond lengths and van der Waals radii of the atoms gives a similar result.

Although this difference is significant, its effect on the stability and geometry of complexes is somewhat reduced by the three-bond separation of the CF_3 group from the metal atom. This contrasts with such sterically hindered ligands as phosphines R_3P where the bulk of R groups, only two bonds removed from the metal, has profound effects on complexes. Thus there are stable complexes known such as $\{(CF_3)_3CO\}_4Ti$, $[(PFP)_3Al]^{3-}$ and $[(PFP)_3Fe]^{3-}$, in each of which no less than 12 CF_3 groups are three bonds removed from the small central metal atom. The bulk of the fluorinated ligand will be primarily determined by the geometry of the carbon framework, as in the case of the unfluorinated analogues, but there may be other factors present which compensate for the slight destabilization of complexes associated with the greater bulk of the fluorinated groups.

The phosphino alcohol $Ph_2PCH_2C(CF_3)_2OH$, **60**, forms the stable complex *trans*-$PtCl_2\{Ph_2PCH_2C(CF_3)_2OH\}_2$, **66**, in which only phosphine is coordinated [44]. This has been structurally characterized, and profile calculations give an average cone angle for the phosphine of 159°, greater than that of Ph_3P (145°) and comparable to those of Ph_2P–^tBu (157°) and Ph_2P–C_6F_5 (158°). It is the steric influence of these ligands that makes the *trans* isomer the preferred form of their $PtCl_2$ complexes. When the phosphino alcohol is ionized and chelating, its effective bulk is reduced, the antisymbiotic effect of the soft phosphine ligand predominates, and only *cis*-$\overline{\mathrm{Pt}\{\mathrm{PPh_2CH_2C(CF_3)_2O}}\}_2$ **61** can be isolated [44].

Some crystallographically determined structural data for fluorinated alkoxy derivatives of various metallic and non-metallic elements M are summarized in Table 10.

The first part of the table refers to terminal alkoxides, mainly hexafluoroisopropoxides. While there are insufficient data to draw any definite conclusions, the tendency is for the C–O bond to be longer in derivatives of phosphorus than in those of the metals. This is to be expected, following the discussion of derivatives of trifluoromethanol (Section C(iii)(a)). The more electropositive the atom attached to oxygen, the greater the partial negative charge it acquires; this electron density is then removed into orbitals of π character, effectively shortening the C–O bond.

The noticeable shortening of the C–O bond in the iridium complex of pentafluorophenol has been discussed earlier (Section C(vii)).

For the PFP^{2-} derivatives listed in Section (b) of Table 10, this effect is less pronounced. In derivatives of phosphorus and sulphur, the longer axial M–O bonds correspond in each case to a shorter C–O bond. Bonds from carbon to axial oxygen average 1.376 ± 0.012 Å, while bonds to equatorial oxygen average 1.400 ± 0.012 Å. Again, this is to be expected, since the shorter bond from oxygen to the electronegative non-metal would remove more electron density from the C–O bond, weakening and lengthening it. In the three metal complexes of PFP^{2-} for which data are available, the C–O bond lengths fall in the same range as for the non-metals.

A point of some interest in complexes of PFP^{2-} is the length of the central C–C bond in the ligand. For the ten listed derivatives, this averages 1.606 ± 0.025 Å, significantly greater than a normal C–C bond length of 1.54 Å. There is little doubt that this lengthening is the result of steric repulsion between vicinal CF_3 groups, as suggested by Sheldrick et al. [210]. Brown et al. have carried out molecular mechanics calculations on PFP^{2-} *spiro* complexes of phosphorus, which lead them to conclude that vicinal CF_3 interactions are minimized by the conformation adopted by the five-membered ring [299].

Independent support for this idea is provided by structural data on the fluorocarbon p-$F{-}C_6H_4{-}C(CF_3)_2{-}C(CF_3)_2{-}C_6H_4{-}F$ where the length of the central C–C bond is no less than 1.671(4) Å, an effect attributed to steric repulsion between the vicinal substituent groups [300]. It is also interesting to note that in acetonitrile solution the PFP^{2-} dianion dissociates into HFA ketyl radicals, $[(CF_3)_2CO]^-$ [301]. While this is partly due to stabilization of the radical by the presence of electronegative substituents, a long weak C–C bond in PFP^{2-} is probably a contributing factor.

TABLE 10

Bond lengths and angles in fluorinated alkoxides

(a) Complexes of unidentate alkoxides

M	Ligand	M–O (Å) [a]	C–O (Å) [b]	∠ M–O–C (°)	Ref.
P(V)	$OCH(CF_3)_2$	1.652 (3)	1.401 (5)	130 [b]	164
		1.586 (4) [b]	1.428 (7) [b]		
P(V)	$OCH(CF_3)_2$	1.667 (2)	1.396 (6)	132 [b]	296
		1.610 (2)	1.419 (5)		
W(VI)	$OCH(CF_3)_2$	1.958 (12) [b]	1.404 (22) [b]	133 [b]	153
W(VI)	$OCH(CF_3)_2$	1.957 (9) [b]	1.345 (18) [b]	137	154
Mo(VI)	$OCH(CF_3)_2$	1.970 (3) [b]	1.375 (6) [b]	135 [b]	156
Mo(VI)	$OCH(CF_3)_2$	2.021 (2)	1.368 (4)	130.5 (2)	155
Mo(VI)	$OC(CF_3)_3$	1.87 (6) [b]	1.34 (13) [b]	151 [b]	173
Pt(II)	OC_6F_5	2.017 (5)	1.341 (9)	123.0 (4)	235
Ir(I)	OC_6F_5	2.058 (3)	1.302 (6)	135.4 (3)	236

(b) Complexes of chelating PFP^{2-} ligands

M	Ligand	M–O (Å)	C–O (Å)	C–C (Å)	Ref.
P(V)	$^-$O–C–C–O$^-$	1.773 (2)	1.375 (4)	1.579 (5)	206
		1.681 (2)	1.396 (4)		
P(V)	$^-$O–C–C–O$^-$	1.682 (4)	1.377 (6)	1.589 (6)	204
		1.624 (3)	1.415 (6)		
P(V)	$^-$O–C–C–O$^-$	1.697 (7)	1.370 (12)	1.588 (13)	210
		1.673 (8)	1.384 (13)		
P(V)	$^-$O–C–C–O$^-$	1.715 (2)	1.379 (3)	1.595 (4)	295
		1.646 (2)	1.413 (4)		
P(V)	$^-$O–C–C–O$^-$	1.709 (4)	1.387 (7)	1.575 (8)	299
		1.648 (4)	1.405 (7)		
P(V)	$^-$O–C–C–O$^-$	1.685 (3)	1.354 (6)	1.637 (7)	299
		1.668 (3)	1.387 (6)		
S(IV)	$^-$O–C–C–O$^-$	1.741 (6) [b]	1.391 (10) [b]	1.615 (11) [b]	198
		1.638 (6) [b]	1.403 (10) [b]		
Ni(II)	$^-$O–C–C–O$^-$	1.852 (3)	1.380 (5)	1.601 (6)	188
Pd(II)	$^-$O–C–C–O$^-$	1.043	1.341	1.643	190, 297 [c]
		2.016	1.388		
W(VI)	$^-$O–C–C–O$^-$	2.053 (3)	1.369 (4)	1.633 (5)	195, 298 [d]
		2.019 (2)	1.369 (4)		

(c) Complexes of chelating hybrid ligands

M	Ligand	M–O (Å)	C–O (Å)	Ref.
Ni(II)	$^-$C–O$^-$	1.87 (1)	1.32 (2)	252
Pt–Pt [c]	$^-$C–O$^-$	1.954(11)	1.406(18)	261
Pt(II)	$^-$C–O–C–O$^-$	1.992 (5)	1.347 (12)	261
Co(II)	RS–C–C–O$^-$	1.911(6) [b]	1.352 (10) [b]	289
Pt(II)	RS–C–C–O$^-$	2.058 (6)	1.377 (17)	292
Pt(II)	RS–C–C–O$^-$	2.041 (5)	1.366 (8)	292
Pt(II)	$^-$O–C–O–C–O$^-$	2.03 (3) [b]	1.30 (5) [b]	218
Pt(II)	$^-$O–C–O–C–O$^-$	2.04 (1) [b]	1.32 (1) [b]	218
Ni(II)	Ph_2P–C–C–O$^-$	1.840 (8) [b]	1.38 (1) [b]	284
Pd(II)	Ph_2P–C–C–O$^-$	2.046 (2)	1.365 (3)	285
Pt(II)	Ph_2P–C–C–O$^-$	2.032 (8) [b]	1.37 (1) [b]	44
Fe(III)	RN=C–C–C–O$^-$	1.972 (3) [b]	1.355 (6) [b]	279
Co(II)	RN=C–C–C–O$^-$	1.943 (6) [b]	1.348 (9) [b]	278

TABLE 10 (continued)
(c) Complexes of chelating hybrid ligands

M	Ligand	M–O (Å)	C–O (Å)	Ref.
Ni(II)	RN=C–C–C–O$^-$	1.842 (3) [b]	1.358 (6) [b]	273
Ni(II)	RN=C–C–C–O$^-$	2.033 (3)	1.346 (6)	280
Cu(II)	RN=C–C–C–O$^-$	1.864 (9) [b]	1.36 (1) [b]	274
Cu(II)	RN=C–C–C–O$^-$	1.895 (3) [b]	1.38 (4) [b]	282
Cu(II)	RN=C–C–C–O$^-$	1.920 (11) [b]	1.34 (2) [b]	276
Ce(IV)	RN=C–C–C–O$^-$	2.211 (4) [b]	1.365 (8) [b]	275
Pd(II)	MeS–C_6H_4–C–O$^-$	2.053 (3)	1.359 (7)	293

[a] Where two bond lengths are given for the same compound, one refers to the axial and the other to the equatorial ligand.

[b] Denotes an average value for chemically equivalent groups. Error estimates on averages are calculated by taking the square root of the mean of the squares of uncertainties on each bond length. Error estimates on average bond angles are not given when there is considerable variation between chemically equivalent groups in the solid state structure.

[c] Additional data kindly supplied by Dr. D.W.T. Chan.

[d] Additional data kindly supplied by Professor B.R. Penfold.

[e] HFA is coordinated to a dinuclear Pt(I)–Pt(I) unit, forming a four-membered ring.

In the first complex listed in part (c) of Table 10, the unusually short C–O bond length of 1.32(2) Å is associated with a high degree of π character in the three-membered ring, as discussed by Countryman and Penfold [252]. In contrast, the second complex listed in the group, (COD)$\overline{\mathrm{Pt{-}Pt(COD)C(CF_3)_2{-}O}}$, has the long C–O bond length of 1.406(18) Å, possibly because the HFA molecule is bridging across two platinum(I) atoms at a separation of 2.585 Å.

The remaining 18 complexes in Table 10(c) containing five- and six-membered chelate rings show no significant differences in their C–O bond lengths which average 1.355 ± 0.020 Å. As would be expected, the C–O bond length of the unionized free alcohol groups in *trans*-$PtCl_2\{Ph_2PCH_2\text{-}C(CF_3)_2OH\}_2$ is significantly longer at 1.388(7) Å [44].

The effect of fluorination on the C–O bond length in alkoxides is clearly seen if the data discussed above are compared with those for unfluorinated derivatives, for which some typical values are shown in Table 11.

The average of the C–O bond lengths in the first eight compounds listed in Table 11 is 1.43 ± 0.02 Å, significantly greater than the range of values in Table 10 and showing a correspondingly lower C–O bond order. The metal–oxygen bond would be expected to show the reverse effect, being longer through reduced π bonding in the fluorinated alkoxides. However, the effect would be masked by other variables (particularly the nature of other ligands on the metal) and no systematic trend is discernible from the limited data available.

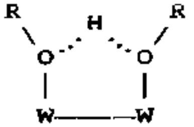
TABLE 11

Bond lengths in complexes of unidentate unfluorinated ligands

M	Ligand	M–O (Å)	C–O (Å)	∠ M–O–C (°)	Ref.
Nb(V)	$O{-}C_2H_5$	1.87 (4)	1.41 (6)	149	302
Nb(V)	$O{-}CH_3$	1.898 (7) [a]	1.42 (1) [a]	149 [a]	303
Nb(V)	$O{-}CH(CH_3)_2$	1.806 (7) [a]	1.47 (3) [a]	159 [a]	304
Mo(VI)	$O{-}CH(CH_3)_2$	1.814 (3) [a]	1.443 (6) [a]	145 [a]	305
W(VI)	$O{-}C_2H_5$	1.824 (4) [a]	1.416 (9) [a]	144.6 (6) [a]	306
W(VI)	$O{-}CH(CH_3)_2$	1.883 (6) [a]	1.417 (15) [a]		307
Co(III)	$O{-}C(C_6H_{13})_3$	1.798 (4)	1.427 (8)	145.2 (4)	308
		1.763 (5)	1.447 (8)	158.1 (5)	
Co(III)	$O{-}C(C_6H_5)_3$	1.813 (4) [a]	1.418 (9) [a]	133.0 [a]	308
W(VI)	$O{-}CH_3$	1.950 (5) [a]	1.47 (2) [a]	131.1 (5) [a]	309
W(VI)	$O{-}C_2H_5$	1.991 (6) [a]	1.47 (2) [a]	130.3 (6) [a]	309

[a] Indicates an average of bond lengths in chemically similar groups.

In the last two compounds in Table 11, the ligand is intermediate between an alkoxide and an alcohol, i.e. two RO^- groups are coordinated, with a proton hydrogen bonded between the two oxygen atoms. The compounds have the overall composition $W_2Cl_4(OR)_4(ROH)_4$, and the relevant portion of the structure is shown as **73** [308]:



73, R = CH_3 or C_2H_5

This has the effect of reducing π bonding and lengthening both the metal–oxygen and metal–carbon bonds. A similar increase in bond lengths is found when alkoxy groups bridge two metal atoms [303,305–308].

Additional information on π bonding comes from the bond angles at oxygen in monodentate alkoxide ligands. (In bidentate ligands, this is largely determined by ring geometry.) A comparison of data in Table 10(a) and Table 11 shows that bond angles in the fluorinated alkoxides are significantly less than in the unfluorinated analogues, indicating a decrease in π bonding. (A greater angle at oxygen in the perfluoro-*t*-butoxide may be attributed to the steric bulk of this group.) Again, the last two entries in Table 11 are anomalous, because of hydrogen bonding in **73**, whose M–O–C bond angles are little more than the value of 129.4(4)° found in a complex where neutral methanol is coordinated to six-coordinate Mo(V) [310].

It appears that the effect on the bond angle at oxygen of fluorination of the R group is similar to that of the "semi-protonation" shown as **73**, i.e. electron density is removed from oxygen by the inductive effect of the R_f

groups and $p_\pi \rightarrow d_\pi$ bonding from oxygen to element M (metal or phosphorus) is reduced. Interaction between metal and oxygen is more important in determining the bond angle at oxygen than interaction with carbon because of the availability of *d* orbitals on the metal. Fluorination of the ligand therefore causes both the C–O bond length and the M–O–C bond angle to decrease, whereas protonation causes the C–O bond length to increase while the angle at oxygen decreases.

(iv) Applications of fluorinated alkoxides

Complexes of metal ions with fluorinated alkoxides are generally chemically unreactive, with the exception of those discussed in Section D(ii) where very small strained chelate rings are present. Rather than acting as a reactive centre, the ligand serves as an electron-withdrawing group comparable to halide ion, but more resistant to oxidation and possessing a greater overall bulk. Because the steric effects of the ligand $RC(CF_3)_2O^-$ can easily be varied by changing the nature of the group, it can be used in the design of catalytic species, the reactivity usually being associated with some other functional group in the molecule. This has been demonstrated in several complexes discussed in this review, including the olefin and acetylene metathesis reactions studied by Schrock and coworkers, where $HC(CF_3)_2O^-$ and similar ligands are used in catalysts incorporating tungsten or molybdenum [152–156], and in the work on ruthenium-based hydrogenation catalysts by Hayashi et al. [16].

The increased acidity of fluorinated alkoxides leads to their increased activity as polymerization catalysts [111,127]. A perfluoropinacol complex of tungsten has been suggested as a model for active sites in homogeneous propylene ammoxidation [195], while the possible use of fluorinated complexes as models for biological systems has been demonstrated by the observation that the Co^{2+} complex $[Co(PFP)_2]^{2-}$ reversibly adds molecular oxygen [311].

As the discussion in Section D demonstrates, the versatility of fluorinated alkoxides has been considerably extended in recent years by their incorporation into hybrid ligands. Synthetic routes to compounds $RC(CF_3)_2OH$ containing a variety of functional groups are now well established, as are the conditions under which they will complex to metal ions of various characters. The fluorinated alkoxide ligand is more than a bulky pseudo-halide ion; it is a valuable means of connecting an organic group to virtually any metal ion. There is little doubt that the application of this class of compound will lead to many developments in coordination chemistry in the future.

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REFERENCES

1 (a) D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Metal Alkoxides, Academic Press, London, 1978.
(b) R.C. Mehrotra, Adv. Inorg. Radiochem., 26 (1983) 269.
2 (a) S.K. De and S.R. Palit, Adv. Fluorine Chem., 6 (1970) 69.
(b) R.E. Banks, Fluorocarbons and their Derivatives, Elsevier, New York, 1970, p. 165.
(c) R.D. Chambers, Fluorine in Organic Chemistry, Wiley, New York, 1973, p. 225.
3 J.A. Young, J. Chem. Educ., 47 (1970) 733.
4 L. Batt and R. Walsh, Int. J. Chem. Kinet., 14 (1982) 933; 15 (1983) 605.
5 G. Klöter and K. Seppelt, J. Am. Chem. Soc., 101 (1979) 347.
6 S. Andreades and D.C. England, J. Am. Chem. Soc., 83 (1961) 4670.
7 R.A. Bekker, G.G. Melikyan, E.P. Lur'e, B.L. Dyatkin and I.L. Knunyants, Dokl. Akad. Nauk SSSR, 217 (1974) 1320.
8 C.G. Krespan and W.J. Middleton, Fluorine Chem. Rev., 1 (1967) 145.
9 M. Witt, K.S. Dhathathreyan and H.W. Roesky, Adv. Inorg. Radiochem., 30 (1986) 223.
10 W.J. Middleton and R.V. Lindsey, J. Am. Chem. Soc., 86 (1964) 4948.
11 H.E. Simmons and D.W. Wiley, J. Am. Chem. Soc., 82 (1960) 2288.
12 I.L. Knunyants, T.-Y. Chen and N.B. Gambaryan, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1960) 686.
13 A.F. Janzen and C.J. Willis, Can. J. Chem., 43 (1965) 3063.
14 A.F. Janzen and C.J. Willis, Inorg. Chem., 6 (1967) 1900.
15 W.R. Cullen and G.E. Styan, Inorg. Chem., 4 (1965) 1437.
16 Y. Hayashi, S. Komiya, T. Yamamoto and A. Yamamoto, Chem. Lett., (1984) 1363.
17 I.S. Chang, J.T. Price, A.J. Tomlinson and C.J. Willis, Can. J. Chem., 50 (1972) 512.
18 (a) P. Tarrant, P. Johncock and J. Savory, J. Org. Chem., 28 (1963) 839.
(b) F.G. Drakesmith, D.R. Richardson, O.J. Stewart and P. Tarrant, J. Org. Chem., 33 (1968) 286.
(c) P. Tarrant, R.H. Somerville and R.W. Whitfield, J. Org. Chem., 35 (1970) 2742.
19 C. Tamborski, W.H. Burton and L.W. Breed, J. Org. Chem., 31 (1966) 4229.
20 (a) W.T. Miller, J.H. Fried and H. Goldwhite, J. Am. Chem. Soc., 82 (1960) 3091.
(b) W.T. Miller, W. Frass and P.R. Resnick, J. Am. Chem. Soc., 83 (1961) 1767.
21 D.P. Graham and V. Weinmayr, J. Org. Chem., 31 (1966) 957.
22 (a) R.D. Chambers and R.H. Mobbs, Adv. Fluorine Chem., 4 (1965) 50.
(b) R.E. Banks and J.C. Tatlow, in R.E. Banks, D.W.A. Sharp and J.C. Tatlow (Eds.), Fluorine, The First Hundred Years, Elsevier, New York, 1986, p. 227.
23 (a)I.L. Knunyants and B.L. Dyatkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 923.
(b) B.L. Dyatkin, E.P. Mochalina and I.L. Knunyants, Tetrahedron, 21 (1965) 2991.
24 R. Filler and R.M. Schure, J. Org. Chem., 32 (1967) 1217.
25 (a) F.J. Pavlik and P.E. Toren, J. Org. Chem., 35 (1970) 2055.
(b) R.E.A. Dear, Int. J. Methods Syn. Org. Chem., 7 (1970) 361.
26 V. Weinmayr, U.S. Patent 3 317 616, 1967.
27 M. Allan, A.F. Janzen and C.J. Willis, Can. J. Chem., 46 (1968) 3671.

28 C.L. Frye, R.M. Salinger and T.J. Patin, J. Am. Chem. Soc., 88 (1966) 1026.
29 N.P. Gambaryan, Yu.A. Cheburkov and I.L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 1526.
30 W.S. Cripps and C.J. Willis, Can. J. Chem., 53 (1975) 809.
31 I.L. Knunyants, N.P. Gambaryan, C.-Y. Ch'en and E.M. Rokhlin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1962) 684.
32 A.R. Lepley, W.A. Khan, A.B. Giumanini and A.G. Giumanini, J. Org. Chem., 31 (1966) 2047.
33 L.A. Simonyan, N.P. Gambaryan and I.L. Knunyants, Zh. Vses. Khim. Ova, 11 (1966) 467. [Chem. Abstr., 65 (1966) 18489c.]
34 W.S. Cripps and C.J. Willis, Can. J. Chem., 53 (1975) 817.
35 R. Filler and H.H. Kang, J. Org. Chem., 40 (1975) 1173.
36 J.M. Birchall and R.N. Haszeldine, J. Chem. Soc., (1959) 3653.
37 M.S. Gordon and J.A. Pople, J. Chem. Phys., 49 (1968) 4643.
38 J.F. Olsen and J.M. Howell, Theor. Chim. Acta, 47 (1978) 39.
39 J.S. Francisco, Spectrochim. Acta, Part A, 40 (1984) 923.
40 F. Grein, Can. J. Chem., 63 (1985) 1988.
41 M.M. Heaton and D. Mills, Int. J. Quantum Chem., 28 (1985) 163.
42 Interatomic Distances, Chemical Society Special Publication No. 11, London, 1958.
43 A. Yokozeki and S.H. Bauer, J. Phys. Chem., 79 (1975) 155.
44 C.D. Montgomery, N.C. Payne and C.J. Willis, Inorg. Chem., 26 (1987) 519.
45 F. Swarts, Bull. Soc. Chim. Belg., 38 (1929) 99.
46 (a) A.L. Henne and R.L. Pelley, J. Am. Chem. Soc., 74 (1952) 1426.
(b) A.L. Henne and W.C. Francis, J. Am. Chem. Soc., 75 (1953) 991.
47 R.D. Chambers, Fluorine in Organic Chemistry, Wiley, New York, 1973, p. 71.
48 J.R. Gandler and W.P. Jencks, J. Am. Chem. Soc., 104 (1982) 1937.
49 E.M. Arnett and K.G. Venkatasubramaniam, J. Org. Chem., 48 (1983) 1569.
50 I.S. Chang and C.J. Willis, Can. J. Chem., 55 (1977) 2465.
51 R.L. Clair and T.B. McMahon, Int. J. Mass Spectrom. Ion Phys., 33 (1980) 21.
52 J.W. Larson and T.B. McMahon, J. Am. Chem. Soc., 105 (1983) 2944.
53 R.E. Banks and J.C. Tatlow, in R.E. Banks, D.W.A. Sharp and J.C. Tatlow (Eds.), Fluorine, The First Hundred Years, Elsevier, New York, 1986, p. 249.
54 K.F. Purcell, J.A. Stikeleather and S.D. Bunk, J. Am. Chem. Soc., 91 (1969) 4019.
55 A.D. Sherry and K.F. Purcell, J. Am. Chem. Soc., 94 (1972) 1853.
56 R.M. Guidry and R.S. Drago, J. Am. Chem. Soc., 95 (1973) 759.
57 A. Kivenen and J. Murto, Suom. Kemilstil. B, 42 (1969) 190.
58 (a) A. Kivenen, J. Murto, J. Korppi-Tommola and R. Kuopio, Acta Chem. Scand., 26 (1972) 904.
(b) J. Murto, A. Kivinen, J. Korppi-Tommola, R. Viitala and J. Hyömäki, Acta Chem. Scand., 27 (1973) 107.
59 O. Schrems, H.M. Oberhoffer and W.A.P. Luck, J. Mol. Struct., 80 (1982) 129.
60 O. Schrems, H.M. Oberhoffer and W.A.P. Luck, J. Phys. Chem., 88 (1984) 4335.
61 J. Chojnowski and W.W. Brandt, J. Am. Chem. Soc., 90 (1968) 1384.
62 R.K. Thomas, Proc. Roy. Soc. London, Ser. A, 322 (1971) 137.
63 L. Schriver and A. Burneau, J. Chem. Soc., Faraday Trans., (1985) 503.
64 A. Fratiello, R.E. Schuster, G.A. Vidulich, J. Bragin and D. Liu, J. Am. Chem. Soc., 95 (1973) 631.
65 R.S. Porter and G.H. Cady, J. Am. Chem. Soc., 79 (1957) 5628.
66 (a) R.A. De Marco, D.A. Couch and J.M. Shreeve, J. Org. Chem., 37 (1972) 3332.
(b) A. Majid and J.M. Shreeve, J. Org. Chem., 38 (1973) 4028.

67 M.E. Redwood and C.J. Willis, Can. J. Chem., 45 (1967) 389.
68 A.G. Pittman and D.L. Sharp, J. Org. Chem., 31 (1966) 957.
69 (a) J.M. Shreeve, Adv. Inorg. Chem., 26 (1983) 119.
(b) M. Lustig and J.M. Shreeve, Adv. Fluorine Chem., 7 (1973) 175.
70 L.A. Harmon and R.J. Lagow, J. Chem. Soc., Perkin Trans., (1979) 2675.
71 W. Mahler, Inorg. Chem., 18 (1979) 352.
72 M.E. Redwood and C.J. Willis, Can. J. Chem., 43 (1965) 1893.
73 W.B. Farnham, B.E. Smart, W.J. Middleton, J.C. Calabrese and D.A. Dixon, J. Am. Chem. Soc., 107 (1985) 4565.
74 J.W. Larson and T.B. McMahon, J. Am. Chem. Soc., 107 (1985) 766.
75 T.C. Waddington, Adv. Inorg. Radiochem., 1 (1959) 158.
76 D.S. Kaganyuk, Zh. Neorg. Khim., 23 (1978) 2003.
77 L. Lawlor and J. Passmore, Inorg. Chem., 18 (1979) 2923.
78 T.B. McMahon and C.J. Northcutt, Can. J. Chem., 56 (1978) 1069.
79 K.O. Christe, E.C. Curtis and C.J. Schack, Spectrochim. Acta, Part A, 31 (1975) 1035.
80 B.S. Ault, J. Phys. Chem., 84 (1980) 3448.
81 J.S. Francisco and I.H. Williams, Chem. Phys., 98 (1985) 105.
82 M. Wechsberg and G.H. Cady, J. Am. Chem. Soc., 73 (1953) 4432.
83 D.D. DesMarteau, Inorg. Chem., 11 (1972) 193.
84 F. Hohorst and D.D. DesMarteau, Inorg. Chem., 13 (1974) 715.
85 L.R. Anderson and W.B. Fox, J. Am. Chem. Soc., 89 (1967) 4313.
86 D.D. DesMarteau, Inorg. Chem., 9 (1970) 2179.
87 F.P. Diodati and L.S. Bartell, J. Mol. Struct., 8 (1971) 395.
88 H. Oberhammer, T. Mahmood and J.M. Shreeve, J. Mol. Struct., 117 (1984) 311.
89 A.H. Lowrey, C. George, P. D'Antonio and J. Karle, J. Mol. Struct., 63 (1980) 243.
90 C.J. Marsden, D.D. DesMarteau and L.S. Bartell, Inorg. Chem., 16 (1977) 2359.
91 C.J. Marsden, L.S. Bartell and F.P. Diodati, J. Mol. Struct., 39 (1977) 253.
92 J.F. Olsen, J. Mol. Struct., 49 (1978) 361.
93 C. Glidewell, J. Mol. Struct., 67 (1980) 35.
94 L.C. Duncan and G.H. Cady, Inorg. Chem., 3 (1964) 850.
95 F.A. Hohorst, D.D. DesMarteau, L.R. Anderson, D.E. Gould and W.B. Fox, J. Am. Chem. Soc., 95 (1973) 3866.
96 T. Kitazume and J.M. Shreeve, Inorg. Chem., 17 (1978) 2173.
97 J.M. Shreeve, L.C. Duncan and G.H. Cady, Inorg. Chem., 4 (1965) 1516.
98 W.H. Hale and S.M. Williamson, Inorg. Chem., 4 (1965) 1342.
99 A. Sekiya and D.D. DesMarteau, J. Org. Chem., 44 (1979) 1131.
100 Q.-C. Mir, R.W. Shreeve and J.M. Shreeve, Phosphorus Sulfur, 8 (1980) 331.
101 D.E. Young, L.R. Anderson and W.B. Fox, Inorg. Chem., 10 (1971) 2810.
102 R.D. Chambers, H.C. Clark and C.J. Willis, J. Am. Chem. Soc., 82 (1960) 5298.
103 G.M. Tyul'ga, V.A. Gubanov, D.S. Rondarev, R.M. Ryuzanova and I.M. Dolgopol'skii, Zh. Org. Khim., 16 (1980) 300.
104 J.T. Hill, J. Fluorine Chem., 9 (1977) 97.
105 P.N. Kapoor and R.C. Mehrotra, Chem. Ind. (London), (1966) 1034.
106 D.C. Bradley and C.E. Holloway, J. Chem. Soc. A, (1969) 282.
107 R.C. Paul, P.K. Gupta, M. Gulati and S.L. Chadha, Inorg. Nucl. Chem. Lett., 13 (1977) 665.
108 R.C. Paul, P. Sharma, H. Singh, P.K. Gupta and S.L. Chadha, Indian J. Chem., Sect. A, 15 (1977) 653.
109 R.C. Paul, P. Sharma, P.K. Gupta and S.L. Chadha, Inorg. Chim. Acta, 20 (1976) 7.
110 R. Choukron and D. Gervais, Synth. React. Inorg. Met.–Org. Chem., 8 (1978) 137.

111 M. Basso Bert and D. Gervais, J. Organomet. Chem., 165 (1979) 209.
112 P.C. Wales and H. Weigold, J. Organomet. Chem., 24 (1970) 413.
113 S.L. Chadha, V. Sharma and K. Uppal, Indian J. Chem., Sect. A, 25 (1986) 625.
114 R. Choukron and D. Gervais, Inorg. Chim. Acta, 27 (1978) 163.
115 R. Choukron, A. Dia and D. Gervais, Inorg. Chim. Acta, 34 (1979) 187.
116 L. Hubert-Pfalzgraf and J.G. Riess, Inorg. Chim. Acta, 41 (1980) 111.
117 S.L. Chadha and L. Mohini, Indian J. Chem., Sect. A, 21 (1982) 317.
118 S.A. Kegley, V. Sharma, J.H. Freudenberger, R.G. Bergman, S.P. Nolan and C.D. Hoff, J. Am. Chem. Soc., 109 (1987) 6563.
119 (a) L.B. Handy, J. Fluorine Chem., 7 (1976) 641.
(b) F.E. Brinckman, R.B. Johannesen, R.B. Hammerschmidt and L.B. Handy, J. Fluorine Chem., 6 (1975) 427.
120 S.L. Chadra, V. Sharma and A. Sharma, J. Chem. Soc., Dalton Trans., (1987) 1253.
121 R.G. Jones, E. Bindschandler, G. Karmas, G.A. Martin, J.R. Thirtle, F.A. Yoeman and H. Gilman, J. Am. Chem. Soc., 78 (1956) 4289.
122 D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Metal Alkoxides, Academic Press, London, 1978, p. 299.
123 R.C. Mehrotra and J. Singh, Inorg. Chem., 23 (1984) 1047.
124 R.C. Mehrotra, R.R. Goyal and N.C. Jain, Synth. React. Inorg. Met.-Org. Chem., 11 (1984) 345.
125 R.C. Mehrotra and J. Singh, Z. Anorg. Allg. Chem., 512 (1984) 221.
126 (a) R.C. Mehrotra and J. Singh, J. Coord. Chem., 13 (1984) 273.
(b) R.C. Mehrotra and J. Singh, Can. J. Chem., 62 (1984) 1003.
127 T. Ueshima, S. Tomita and T. Saegusa, Bull. Chem. Soc. Jpn., 41 (1968) 1194.
128 R.C. Paul, P. Sharma, L. Subbiah, H. Singh and S.C. Chadha, J. Inorg. Nucl. Chem., 38 (1976) 169.
129 J.S. Skelcey, J.E. Rumminger and K.O. Groves, U.S. Patent 3 494 946, 1970.
130 T. Kitazume and N. Ishikawa, Bull. Chem. Soc. Jpn., 53 (1980) 2064.
131 T.A. Kovacina, R.A. DeMarco, W.B. Fox, D.E. Young and L.R. Anderson, Inorg. Nucl. Chem. Lett., 10 (1974) 763.
132 R.C. Kumar, S.A. Kinkead and J.M. Shreeve, Inorg. Chem., 23 (1984) 3112.
133 S.A. Kinkead, R.C. Kumar and J.M. Shreeve, J. Am. Chem. Soc., 106 (1984) 7496.
134 D.B. Denney, D.Z. Denney, P.J. Hammond and Y.F. Hsu, J. Am. Chem. Soc., 103 (1981) 2340.
135 (a) G.W. Fraser and G. Meikle, J. Chem. Soc., Perkin Trans., (1975) 312.
(b) G.W. Fraser and G. Meikle, J. Chem. Soc., Dalton Trans., (1977) 1985.
136 D.B. Denney, D.Z. Denney, P.J. Hammond and Y.-P. Yang, J. Am. Chem. Soc., 103 (1981) 1785.
137 B.E. Smart, W.B. Farnham, W.J. Middleton and D.A. Dixon, Abstr. Centennial Fluorine Conf., Paris, France, 1986; J. Fluorine Chem., 35 (1987) 27.
138 A.J. Pittman, D.L. Sharp and R.E. Lundin, J. Polym. Sci., 4 (1966) 2637.
139 E.W. Abel, D.J. Walker and J.N. Wingfield, Inorg. Nucl. Chem. Lett., 5 (1969) 139.
140 V.A. Gubanov, G.M. Tyul'ga, I.G. Solodkaya and M.A. Sherman, Zh. Org. Khim., 20 (1984) 493, and references cited therein.
141 C. Wakselman and J. Leroy, J. Fluorine Chem., 12 (1978) 101.
142 R.E.A. Dear, W.B. Fox, R.J. Fredericks, E.E. Gilbert and D.K. Huggins, Inorg. Chem., 9 (1970) 2590.
143 H.J. Koetzsch, Chem. Ber., 99 (1966) 1143.
144 P.N. Kapoor, R.N. Kapoor and R.C. Mehrotra, Chem. Ind. (London), (1968) 1314.

145 K.S. Mazdiyasni, B.J. Schaper and L.M. Brown, Inorg. Chem., 10 (1971) 889.
146 A. Merbach and J.P. Carrard, Helv. Chim. Acta, 54 (1971) 2771.
147 K.S. Mazdiyazni and B.J. Schaper, J. Less-Common Met., 30 (1973) 105.
148 T. Blackmore, M.I. Bruce, P.J. Davidson, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc. A, (1970) 3153.
149 R.A. Anderson, Inorg. Nucl. Chem. Lett., 15 (1979) 57.
150 P.G. Eller and P.J. Vergamini, Inorg. Chem., 22 (1983) 3184.
151 D.G. Karraker and J.A. Stone, Inorg. Chem., 18 (1979) 2205.
152 J.H. Freudenberger and R.R. Schrock, Organometallics, 5 (1986) 1411.
153 J.H. Freudenberger, R.R. Schrock, M.R. Churchill, A.L. Rheingold and J.W. Ziller, Organometallics, 3 (1984) 1563.
154 M.W. Churchill and J.W. Ziller, J. Organomet. Chem., 286 (1985) 27.
155 L.G. McCullough, R.R. Schrock, J.C. Dewan and J.C. Murdzek, J. Am. Chem. Soc., 107 (1985) 5987.
156 H. Strutz, J.C. Dewan and R.R. Schrock, J. Am. Chem. Soc., 107 (1985) 5999.
157 H. Hacklin and G.V. Roeschenthaler, Chem.-Ztg., 108 (1984) 291.
158 J.P. Laussac, Org. Magn. Reson., 12 (1979) 237.
159 J.P. Laussac, R. Enjalbert, J. Galy and J.F. Laurent, J. Coord. Chem., 12 (1983) 133.
160 D. Dakternieks, G.V. Roeschenthaler and R. Schmutzler, J. Fluorine Chem., 11 (1978) 387; 12 (1978) 413.
161 T. Kubota and T. Tanaka, Nippon Kagaku Kaishi, (1985) 2140; (Chem. Abstr., 105 (1986) 226, 756).
162 D.B. Denney, D.Z. Denney, P.J. Hammond, L.T. Liu and Y.P. Yang, J. Org. Chem., 48 (1983) 2159.
163 D. Dakternieks and G.V. Roeschenthaler, Z. Anorg. Allg. Chem., 504 (1983) 135.
164 R. Francke, D. Dakternieks, R.W. Gable, B. Hoskins and G.V. Roeschenthaler, Chem. Ber., 118 (1985) 922.
165 E. Evangelidou-Tsolis, F. Ramirez, J.F. Pilot and C.P. Smith, Phosphorus, 4 (1974) 109.
166 E. Evangelidou-Tsolis and F. Ramirez, Phosphorus, 4 (1974) 121.
167 (a) H. Kischkel and G.V. Roeschenthaler, Chem. Ber., 118 (1985) 4842.
(b) G.V. Roeschenthaler, Angew. Chem., 89 (1977) 900.
168 J.M. Canich, G.L. Gard, and J.M. Shreeve, Inorg. Chem., 23 (1984) 441.
169 D.K. Huggins and W.B. Fox, U.S. Patent 3 631 081, 1971.
170 R.A. Anderson and G.E. Coates, J. Chem. Soc., Dalton Trans., (1975) 1244.
171 R.A. Anderson, Inorg. Chem., 18 (1979) 209.
172 D.A. Johnson, J.C. Taylor and A.B. Waugh, Inorg. Nucl. Chem. Lett., 15 (1979) 205.
173 D.A. Johnson, J.C. Taylor and A.B. Waugh, J. Inorg. Nucl. Chem., 42 (1980) 1271.
174 L.G. McCullough and R.R. Schrock, J. Am. Chem. Soc., 106 (1984) 4067.
175 J.A.M. Canich, M.E. Lerchen, G.L. Gard and J.M. Shreeve, Inorg. Chem., 25 (1986) 3030.
176 Q.-C. Mir and J.M. Shreeve, J. Am. Chem. Soc., 101 (1979) 3961.
177 Q.-C. Mir, K.A. Laurence, R.W. Shreeve, D.P. Babb and J.M. Shreeve, J. Am. Chem. Soc., 101 (1979) 5949.
178 G.L. Gard and J.M. Shreeve, J. Am. Chem. Soc., 104 (1982) 5566.
179 D.E. Gould, L.T. Ratcliffe, L.R. Anderson and W.B. Fox, Chem. Commun., (1970) 216.
180 N. Walker and D.D. DesMarteau, J. Fluorine Chem., 5 (1975) 127.
181 S.-L. Yu and D.D. DesMarteau, Inorg. Chem., 17 (1978) 2484.
182 D.E. Young and W.B. Fox, Inorg. Nucl. Chem. Lett., 7 (1971) 1033.
183 R.A. Bekker, G.G. Melikyan, B.L. Dyatkin and I.L. Knunyants, Dokl. Akad. Nauk SSSR, 221 (1975) 1333.

184 R.A. Bekker, G.G. Melikyan, B.L. Dyatkin and I.L. Knunyants, Zh. Org. Khim., 12 (1976) 1379.

185 (a) C.J. Schaverein, J.C. Dewan and R.R. Schrock, J. Am. Chem. Soc., 108 (1986) 2771.
(b) J.S. Murdzek and R.R. Schrock, Organometallics, 6 (1987) 1373.

186 H.C. Clark and A.L. Pickard, J. Organomet. Chem., 8 (1967) 427.

187 M. Allan and C.J. Willis, J. Am. Chem. Soc., 90 (1968) 5343.

188 D.M. Barnhart and E.C. Lingafelter, Cryst. Struct. Commun., 11 (1973) 733.

189 W.R. Cullen, L.D. Hall, J.T. Price and J. Spendjian, Can. J. Chem., 53 (1975) 366.

190 H.D. Empsall, M. Green and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 96.

191 R.T. Boeré and C.J. Willis, Inorg. Chem., 24 (1985) 1059.

192 C.J. Willis, J. Chem. Soc., Chem. Commun., (1972) 944.

193 P.F. Bramman, T. Lund, J.B. Raynor and C.J. Willis, J. Chem. Soc., Dalton Trans., (1975) 45.

194 A. Jezierski and J.B. Raynor, J. Chem. Soc., Dalton Trans., (1981) 1.

195 D.M.T. Chan, W.C. Fultz, W.A. Nugent, D.C. Roe and T.H. Tulip, J. Am. Chem. Soc., 107 (1985) 251.

196 E. Kupke, E. Liepins, I. Urtane, G. Zelcans and E. Lukevics, J. Organomet. Chem., 279 (1985) 343.

197 G.W. Astrologes and J.C. Martin, J. Am. Chem. Soc., 98 (1976) 2895.

198 B.W. Davies, N.C. Payne, and C.J. Willis, unpublished results.

199 See ref. 165 and citations therein.

200 (a) S.A. Bone and S. Trippett, Tetrahedron Lett., 19 (1975) 1583.
(b) S.A. Bone, S. Trippett and P.J. Whittle, J. Chem. Soc., Perkin Trans. 1, (1974) 2125.
(c) S. Antczak, S.A. Bone, J. Brierley and S. Trippett, J. Chem. Soc., Perkin Trans. 1, (1977) 278.

201 G.V. Roeschenthaler, K. Sauerbrey and R. Schmutzler, Chem. Ber., 111 (1978) 3105.

202 G.V. Roeschenthaler, R. Bohlen and W. Storzer, Z. Anorg. Allg. Chem., 507 (1983) 93.

203 G.V. Roeschenthaler, K. Sauerbrey, J.A. Gibson and R. Schmutzler, Z. Anorg. Allg. Chem., 450 (1979) 79.

204 W. Storzer, D. Schomburg and G.V. Roeschenthaler, Z. Naturforsch., Teil B, 36 (1981) 1071.

205 G.V. Roeschenthaler and W. Storzer, Z. Naturforsch., Teil B, 37 (1982) 281.

206 G.V. Roeschenthaler, G. Volker, R. Bohlen and D. Schomburg, Z. Naturforsch., Teil B, 40 (1985) 1593.

207 U. von Allwoerden, I. Tseggai and G.V. Roeschenthaler, Phosphorus Sulfur, 21 (1984) 177.

208 R. Francke, R. Di Giacomo, D. Dakternieks and G.V. Roeschenthaler, Z. Anorg. Allg. Chem., 519 (1984) 141.

209 D. Schomburg, W. Storzer, R. Bohlen, W. Kuhn and G.V. Roeschenthaler, Chem. Ber., 116 (1983) 3301.

210 W.S. Sheldrick, J.A. Gibson and G.V. Roeschenthaler, Z. Naturforsch., Teil B, 33 (1978) 1102.

211 (a) J.H. Prager and P.H. Ogden, J. Org. Chem., 33 (1968) 2100.
(b) P.H. Ogden and G.C. Nicholson, Tetrahedron Lett., (1968) 3553.

212 H.W. Roesky, J. Lucas, K. Keller, K.S. Dhathathreyan, M. Moltemeyer and G.S. Sheldrick, Chem. Ber., 118 (1985) 2659.

213 A.F. Janzen and C.J. Willis, Can. J. Chem., 44 (1966) 745.

214 C.M. Mitchell and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 102.

215 P.J. Hayward and C.J. Nyman, J. Am. Chem. Soc., 93 (1971) 617.

216 M. Green, S.K. Shaksooki and F.G.A. Stone, J. Chem. Soc. A, (1971) 2828.

217 P. Bradford, R. Hynes, N.C. Payne and C.J. Willis, unpublished results.
218 A. Modinos and P. Woodward, J. Chem. Soc., Dalton Trans., (1975) 2134.
219 W.B. Beaulieu, G.D. Mercer and D.M. Roundhill, J. Am. Chem. Soc., 100 (1978) 1147.
220 L.R. Anderson, C.T. Ratcliffe, D.E. Young and W.B. Fox, J. Fluorine Chem., 7 (1976) 481.
221 L.R. Anderson, C.T. Ratcliffe, D.E. Young and W.B. Fox, J. Fluorine Chem., 7 (1976) 491.
222 W.S. Cripps and C.J. Willis, Can. J. Chem., 53 (1975) 817.
223 J. Dedinas, J. Am. Chem. Soc., 95 (1973) 7172.
224 K.C. Hodges, D. Schomburg, J.-V. Weiss and R. Schmutzler, J. Am. Chem. Soc., 99 (1977) 6096.
225 L.A. Motnyak, A.I. Burmakov, B.V. Kunshenko, V.P. Sass, L.A. Alekseeva and L.M. Yagupol'skii, Zh. Org. Chem., 17 (1981) 728.
226 R.S. Nyholm and B.R. Hollebone, J. Chem. Soc. A, (1971) 332.
227 S.T. Lin, R.N. Narske and K.J. Klabunde, Organometallics, 4 (1985) 571.
228 J.F. Harrod and K.R. Taylor, Inorg. Chem., 14 (1975) 1541.
229 W. Beck, K. Stetter, S. Tadros and K. Schwarzhaus, Chem. Ber., 100 (1967) 3944.
230 F.E. Brinckman, R.B. Johannesen and L.B. Handy, J. Fluorine Chem., 1 (1972) 493.
231 A. Majid, D.W.A. Sharp, J.M. Winfield and I. Hanley, J. Chem. Soc., Dalton Trans., (1973) 1876.
232 H.J. Abel, H. Rabeneck and H. Schaefer, Z. Anorg. Allg. Chem., 415 (1975) 241.
233 J. Fornies, M. Green, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 1006.
234 M.K. Cooper and D.W. Yaniuk, J. Organomet. Chem., 164 (1979) 211.
235 M.K. Cooper, N.J. Hair and D.W. Yaniuk, J. Organomet. Chem., 150 (1978) 157.
236 M.R. Churchill, J.C. Fettinger, W.M. Rees and J.D. Atwood, J. Organomet. Chem., 308 (1986) 361.
237 J.G. Noltes and J. Boersma, J. Organomet. Chem., 12 (1968) 425.
238 L.F. Sytsma and R.J. Kline, J. Organomet. Chem., 54 (1973) 15.
239 (a) M.G. Hogben and W.A.G. Graham, J. Am. Chem. Soc., 91 (1969) 283.
(b) M.G. Hogben, R.S. Gay, A.J. Oliver, J.A.C. Thompson and W.A.G. Graham, J. Am. Chem. Soc., 91 (1969) 291.
240 F. Ramirez and J.F. Maracek, Int. J. Methods Synth. Org. Chem., (1979) 71.
241 A. Meller and C.P. Graebe, Chem. Ber., 118 (1985) 2020.
242 D.S. Ross and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1972) 34.
243 J.I. Darragh, S.F. Hossain and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1975) 218.
244 M.I. Kabachnik, L.S. Zakarov, I.Yu. Kudryavtsev, A.P. Kharchenko, G.P. Tataurov and L.I. Korobeinikoa, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 896.
245 C. MacDonald, A.J. Tomlinson and C.J. Willis, Can. J. Chem., 49 (1971) 2578.
246 K.G. Magers, C.G. Smith and D.T. Sawyer, Inorg. Chem., 17 (1978) 515.
247 M.H. Chisholm and L.A. Rankel, Inorg. Chem., 16 (1977) 2177.
248 M.M. Walczak, P.K. Leavitt and P.K. Thiel, J. Am. Chem. Soc., 109 (1987) 5621.
249 J. Browning, C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1969) 20.
250 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1969) 3019.
251 A. Greco, M. Green, S.K. Shaksooki and F.G.A. Stone, J. Chem. Soc. D, (1970) 1374.
252 R. Countryman and B.R. Penfold, J. Cryst. Mol. Struct., 2 (1972) 281.
253 B. Clarke, M. Green, R.B.L. Osborne and F.G.A. Stone, J. Chem. Soc. A, (1968) 167.
254 F.G.A. Stone, G.A. Francis, J. Browning and M. Green, J. Chem. Soc. A, (1971) 453.
255 C.H. Davies, C.H. Game, M. Green and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1974) 357.

256 J. Browning, H.D. Empsall, M. Green and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1973) 381.
257 V.A. Mukhedar and A.J. Mukhedar, J. Inorg. Nucl. Chem., 43 (1981) 2801.
258 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1970) 3161.
259 W.J. Bland, R.D.W. Kemmitt and R.D. Moore, J. Chem. Soc., Dalton Trans., (1973) 1292.
260 J. Fornies, M. Green, A. Laguna, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 1515.
261 M. Green, J.A.K. Howard, A. Laguna, L.E. Smart, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 278.
262 N.M. Boag, J. Browning, C. Crocker, P.L. Goggin, R.J. Goodfellow, M. Murray and J.L. Spencer, J. Chem. Res. (S) (1978) 228.
263 L.E. Smart, J. Browning, M. Green, A. Laguna, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 1777.
264 J. Clemens, M. Green and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1973) 375.
265 M. Cooke and M. Green, J. Chem. Soc. A, (1969) 651.
266 R. Burt, M. Cooke and M. Green, J. Chem. Soc. A, (1970) 2975.
267 M. Cooke, M. Green and T.A. Kuc, J. Chem. Soc. A, (1971) 1200.
268 A. Bond and M. Green, J. Chem. Soc., Dalton Trans., (1972) 763.
269 M. Green and B. Lewis, J. Chem. Soc., Dalton Trans., (1975) 1137.
270 M.I. Bruce, B.L. Goodall, D.N. Sharrocks and F.G.A. Stone, J. Organomet. Chem., 39 (1972) 139.
271 J.W.L. Martin and C.J. Willis, Can. J. Chem., 55 (1977) 2459.
272 J.W.L. Martin and C.J. Willis, Can. J. Chem., 56 (1978) 2966.
273 J.W.L. Martin, N.C. Payne and C.J. Willis, Inorg. Chem., 17 (1978) 3478.
274 D.L. Barber, S.J. Loeb, J.W.L. Martin, N.C. Payne and C.J. Willis, Inorg. Chem., 20 (1981) 272.
275 J.H. Timmons, J.W.L. Martin, A.E. Martell, P. Rudolf, A. Clearfield, J.H. Arner, S.J. Loeb and C.J. Willis, Inorg. Chem., 19 (1980) 3553.
276 S.J. Loeb, J.F. Richardson and C.J. Willis, Inorg. Chem., 22 (1983) 2736.
277 S.J. Loeb, J.W.L. Martin and C.J. Willis, Can. J. Chem., 56 (1978) 2369.
278 E. Konefal, S.J. Loeb, D.W. Stephan and C.J. Willis, Inorg. Chem., 23 (1984) 538.
279 E. Konefal, S.J. Loeb, D.W. Stephan and C.J. Willis, Inorg. Chim. Acta, 115 (1986) 147.
280 S.J. Loeb, D.W. Stephan and C.J. Willis, Inorg. Chem., 23 (1984) 1509.
281 S.J. Loeb, J.W.L. Martin and C.J. Willis, Inorg. Chem., 18 (1979) 3160.
282 J.H. Timmons, J.W.L. Martin, A.E. Martell, P. Rudolf, A. Clearfield, S.J. Loeb and C.J. Willis, Inorg. Chem., 20 (1981) 181.
283 S.J. Loeb and C.J. Willis, Inorg. Chem., 20 (1981) 2791.
284 R.T. Boeré, C.D. Montgomery, N.C. Payne and C.J. Willis, Inorg. Chem., 24 (1985) 3680.
285 C.D. Montgomery, N.C. Payne and C.J. Willis, Inorg. Chim. Acta, 117 (1986) 103.
286 C. MacDonald and C.J. Willis, Can. J. Chem., 51 (1973) 732.
287 J.T. Price, A.J. Tomlinson and C.J. Willis, Can. J. Chem., 50 (1972) 939.
288 Q.-C. Mir and J.M. Shreeve, Inorg. Chem., 19 (1980) 1510.
289 R.T. Boeré, W.M. Brown, D.W. Stephan and C.J. Willis, Inorg. Chem., 24 (1985) 593.
290 R.T. Boeré and C.J. Willis, Can. J. Chem., 63 (1985) 3530.
291 R.T. Boeré and C.J. Willis, Can. J. Chem., 64 (1986) 492.
292 R.T. Boeré, N.C. Payne and C.J. Willis, Can. J. Chem., 64 (1986) 1474.
293 R.T. Boeré, D.W. Esser, C.J. Willis, D.W. Stephan and T.W. Obal, Can. J. Chem., 65 (1987) 798.

294 (a) N.W. Alcock, A.W.G. Platt and P.G. Pringle, Inorg. Chim. Acta, 128 (1987) 215.
(b) N.W. Alcock, A.W.G. Platt and P.G. Pringle, J. Chem. Soc., Dalton Trans., (1987) 2273.

295 G.K. Anderson and R. Kumar, Inorg. Chem., 23 (1984) 4064.

296 M.U. Haque, J. Ahmed and W. Horne, Acta Crystallogr., C39 (1983) 1048.

297 D.W.T. Chan, personal communication.

298 B.R. Penfold, personal communication.

299 R.K. Brown, R.O. Day, S. Husebye and R.R. Holmes, Inorg. Chem., 17 (1978) 3276.

300 V.R. Polishchuk, M.Yu. Antipin, V.I. Bakhmutov, N.N. Bubnov, S.P. Solodovnikov, T.M. Timofeeva, Yu.T. Struchkov, B.L. Tumanskii and I.L. Knunyants, Dokl. Akad. Nauk SSSR, 249 (1979) 1125.

301 E.G. Janzen and J.L. Gerlock, J. Phys. Chem., 71 (1967) 4577.

302 B. Kamenar and C.K. Prout, J. Chem. Soc. A, (1970) 2379.

303 A.A. Pinkerton, D. Schwarzenbach, L. Hubert-Pfalzgraf and J.G. Riess, Inorg. Chem., 15 (1976) 1196.

304 L. Hubert-Pfalzgraf, A.A. Pinkerton and J.G. Riess, Inorg. Chem., 17 (1978) 663.

305 M.H. Chisholm, C.C. Kirkpatrick and J.C. Huffman, Inorg. Chem., 20 (1981) 871.

306 F.A. Cotton, D. DeMarco, B.W.S. Kolthammer and R.A. Walton, Inorg. Chem., 20 (1981) 3048.

307 M.H. Chisholm, J.C. Huffman and A.L. Raterman, Inorg. Chem., 22 (1983) 4100.

308 G.A. Siegel, R.A. Bartlett, D. Decker, M.O. Olmstead and P.R. Power, Inorg. Chem., 26 (1987) 1773.

309 L.B. Anderson, F.A. Cotton, D. DeMarco, A. Fang, W.H. Ilsley, B.W.S. Kolthammer and R.A. Walton, J. Am. Chem. Soc., 103 (1981) 5078.

310 S. Lincoln and S.A. Koch, Inorg. Chem., 25 (1986) 1594.

311 C.J. Willis, J. Chem. Soc., Chem. Commun., (1974) 117.