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Novel synthesis using inorganic fluorides ☆

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Abstract

Recent work on the preparation of low-valent organo-transition-metal fluoro complexes is summarised. Research into the reactivity of these species indicates that synthetic chemistry can be undertaken at the metal centre, the fluoride ligand or at other coordinated ligands, and points to the value of further investigation into this area.

Keywords: Synthesis; Inorganic fluorides; Review; Low-valent organo-transition-metal fluoro complexes

1. Introduction

Although it is well established that combinations of soft metals with hard ligands yield interesting and often unusual synthetic chemistries, many with potential catalytic applications [1], the chemistry of potentially the most promising combination, organo-transition-metal fluoro complexes, has been only cursorily explored. A recent review [2] highlights less than 200 verified examples of fluoro-organometallic species and describes the use of only one of these in a further synthetic reaction. The application of two relatively new reagents, TASF {tris(dimethylamino)sulphurtrimethylsilyldifluoride} [3] and Olah's reagent {py·HF} [4] to organometallic systems and our own success with the oxidative fluorination of low-valent metal centres have demonstrated that organo-transition-metal fluoride complexes are not esoteric oddities and offer considerable hope for the future. Furthermore, research into the reactivity of these complexes has, very recently, been successfully initiated [5–7]. These studies indicate that synthetic chemistry can indeed be undertaken at either the metal centre, the fluoride ligand or the other coordinated ligands in a predictable manner dependent on the metal centre. The use of such systems for synthesis has not yet been exploited. However, by analogy with metal hydride species, low-valent metal fluorides should be key reagents for the introduction of fluoride and, as a consequence of the extreme electronic properties of the fluoride ligand, may be anticipated to offer unusual chemistry at the other ligands.

The present paper aims to summarise current progress, in particular work which we have been associated with at Leicester, and tries to place the work within an overall framework.

2. Transition-metal carbonyl fluorides

Early preparative work and single-crystal X-ray structure determinations [8–12] on transition-metal carbonyl fluorides in Leicester established this class of compounds on a firm footing, and led to the proposal of a rationale for their existence [13]. They consist of certain, specific configurations which contain particularly stable units consisting of low-valent species containing carbonyl and fluoride ligands or combinations of units containing a low-valent metal with attached carbonyls, or carbonyls and fluorines, together with a fully fluorinated metal species. The basic metal carbonyl fluoride units are shown in Table 1.

Recently, using high-field NMR spectroscopies and solution EXAFS, a new range of novel transition-metal carbonyl fluorides and transition-metal carbonyl phosphine fluorides prepared by fluorination of appropriate metal(0) complexes with XeF_2 have been prepared [7,14,15], e.g. Figs. 1 and 2, some of which compare with the earlier predictions.

3. Acyl fluoride transition-metal fluoride complexes

Five-coordinate transition-metal carbonyl complexes may be readily oxidised with XeF_2. This was first demonstrated in 1988 in collaboration with Ebsworth and his coworkers in

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Table 1
Basic units in carbonyl fluoride systems

Triad	Cr	Mn	Fe	Co	Ni/Cu
d^{10}					$Cu^{I}(CO)F$
d^{8}				$-F-M^{I}(CO)_2F-$	$Ni^{II}(CO)_2F_2$
d^{6}	$M^{0}(CO)_5F^-$	$M^{I}(CO)_5F$	$-F-M^{II}(CO)_3F_2^-$	$M^{II}(CO)_3F_3$	
d^{4}	$-F-M^{II}(CO)_4F_2^-$				
d^{2}	$M^{III}(CO)_3F_3$				

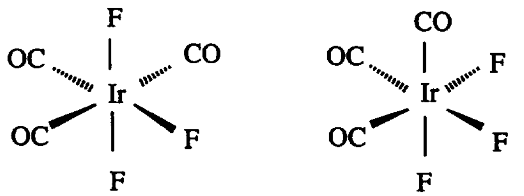

Fig. 1. *mer* and *fac* isomers of $Ir(CO)_3F_3$.

Edinburgh [16], when the first iridium-fluoroacyl complex was prepared:

$$[Ir(CO)_3(PEt_3)_2]^+ + XeF_2 \longrightarrow [IrF(CO)_2(COF)(PEt_3)_2]^+ \quad (1)$$

It has since been shown in Edinburgh [6] that addition of Lewis acid abstracts fluoride ion from the acyl group:

$$[IrF(CO)_2(COF)(PEt_3)_2]^+ + BF_3 \longrightarrow [IrF(CO)_3(PEt_3)_2]^{2+} + BF_4^- \quad (2)$$

The ruthenium and osmium analogues *and* the intermediates in the reaction pathway have now been identified [17] and it has been shown conclusively that the carbon–fluorine bond formation in these electron-deficient cationic metal complexes is by nucleophilic attack of fluoride at the carbonyl. On warming [Ru (−20 °C), Os (50 °C)] these acyl fluorides eliminate CO. The reaction sequence for the osmium species is illustrated in Fig. 3.

4. Reactivity of main group fluorides with square-planar metal complexes

Xenon difluoride oxidatively fluorinates rhodium(I) and iridium(I) to yield octahedral complexes [18]:

$$IrCl(CO)(PEt_3)_2 + XeF_2 \longrightarrow IrClF_2(CO)(PEt_3)_2 + Xe \quad (3)$$

It has also been clearly demonstrated that other Main Group fluorides such as SF_4 and SeF_4 [19], and fluoride halides such as NF_2Cl [20] and CF_3Br [21], are also activated by these four-coordinate complexes to produce related six-coordinate species.

$$IrCl(CO)(PEt_3)_2 + NF_2Cl \longrightarrow IrCl_2(CO)(NF_2)(PEt_3)_2 \quad (4)$$

$$RhCl(CO)(PEt_3)_2 + CF_3Br \longrightarrow RhClBr(CO)(CF_3)(PEt_3)_2 \quad (5)$$

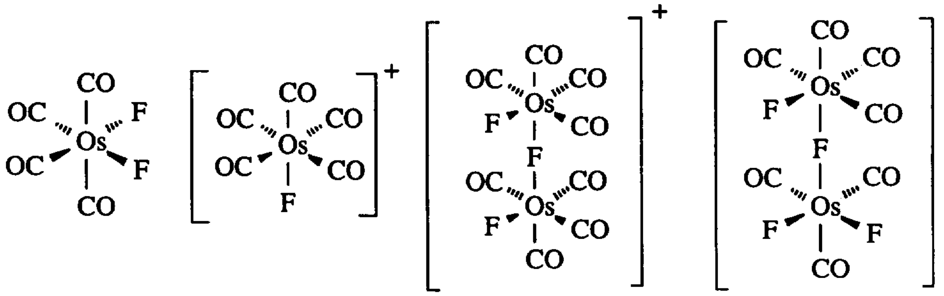

Fig. 2. Products of the oxidative fluorination of $[Os_3(CO)_{12}]$ with XeF_2 in HF.

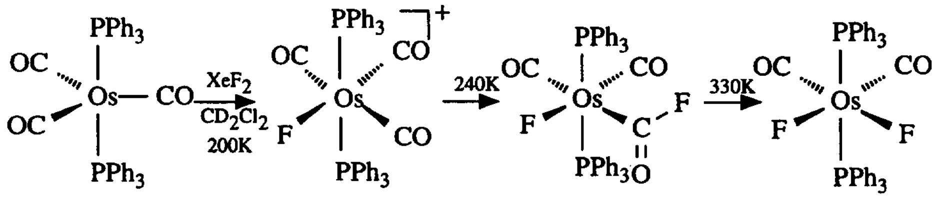

Fig. 3. Reaction of $Os(CO)_3(PPh_3)_2$ with XeF_2.

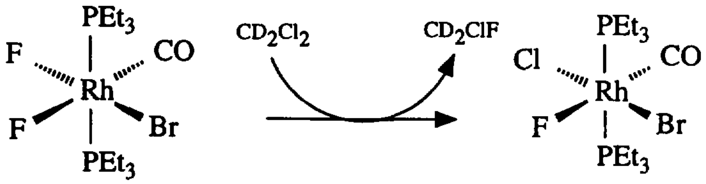

Fig. 4. Reaction of $Rh(CO)BrF_2(PEt_3)_2$ with CD_2Cl_2.

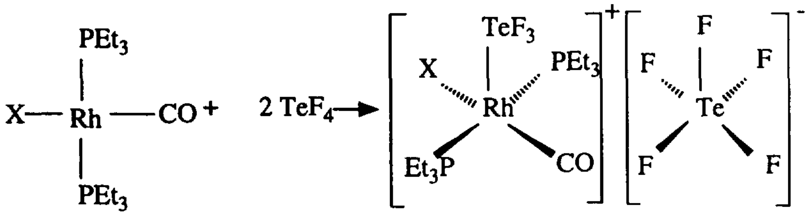

Fig. 5. Reaction of $Rh(CO)X(PEt_3)_2$ with TeF_4.

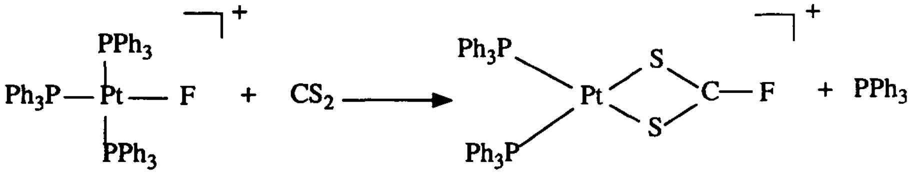

Fig. 6. Reaction of $[PtF(PPh_3)_3]^+$ with CS_2.

$$IrCl(CO)(PEt_3)_2 + MF_4 \longrightarrow IrClF(CO)(MF_3)(PEt_3)_2 \quad (M=S, Se) \qquad (6)$$

5. Reactivity of organometallic fluorides

Here, highly predictable synthetic chemistry, controlled by the strength of the metal–fluorine bond, has been observed. Strong metal–fluorine bonds allow reaction *either at the metal centre*, i.e. the addition of Lewis bases results in ligand substitution reactions [7,17]:

$$[Os(CO)_3F_2]_4 + PMe_3 \longrightarrow cis\text{–}trans\text{–}cis\text{-}Os(CO)_2(PMe_3)_2F_2 \qquad (7)$$

$$fac\text{-}Ir(CO)_3F_3 + PMe_3 \longrightarrow trans\text{–}fac\text{-}Ir(CO)(PMe_3)_2F_3 \qquad (8)$$

or at the other coordinated ligands, i.e. the addition of fluoride to cationic organometallic fluorides results in carbon–fluorine bond formation (see Section 3 above).

Weaker metal–fluorine bonds allow reaction *at the fluoride ligand*, either F–Cl exchange, at temperatures as low as −45 °C (see Fig. 4), or Lewis-acid abstraction of fluoride to form coordinatively unsaturated metal complexes [22] (see Fig. 5), or insertion of small organic molecules such as C_2F_4 or CS_2 into the metal–fluorine bond [23] (see Fig. 6).

6. Conclusions

It has been shown that inorganic fluorides react readily and predictably with organometallic species yielding low-valent transition-metal fluorides. The strengths of the metal–fluorine bonds are sufficiently predictable to allow synthetic chemistry at the metal centre, at the fluoride ligand or at the other coordinated ligands. Of particular importance is the observation that some metal centres promote carbon–fluorine bond formation. This suggests that low-valent transition-metal fluorine chemistry may be extensive but that in-depth investigations of synthetic routes and ligand compatibility is necessary.

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