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Review

Organometallic fluorides of the lanthanide and actinide elements

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Abstract

A brief survey of the preparation, and chemical and structural properties of organolanthanide and actinide fluoride complexes is given. © 1997 Elsevier Science S.A.

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1. Introduction

Organometallic fluoride complexes of the transition metals (i.e. compounds exhibiting a carbon–metal–fluorine moiety) have gained interest in recent years.

For example, such compounds play an important role in the breaking of C–F bonds in perfluoroalkenes and arenes. This area of chemistry has recently been covered in reviews by Crabtree et al. [1] and Richmond et al. [2]. Furthermore, new synthetic routes to organometallic fluorides have been developed recently and thus made a number of previously unknown complexes accessible [3]. Trimethyltin fluoride was effectively used as a fluorinating agent for complexes of the *d*-transition metals [4].

In contrast, synthetic strategies to organolanthanide and actinide fluoride complexes are still rare. Up to now, only 22 organometallic fluorides of the *f*-transition metals are known (see Tables 1 and 2). Interestingly, the stabilization of these complexes has relied on η^5-coordinating cyclopentadienyl ligands only, or its substituted analogues. Simple alkyl or aryl compounds have not so far been prepared due to the electronically unsaturated character of these systems.

In this short review, the synthetic and chemical features of organolanthanide and actinide fluoride complexes will be discussed. Attention should also be drawn to some structural aspects. A characteristic feature of organometallic fluoride complexes is the tendency to form fluorine bridges between two or more metal atoms which can led to unexpected and unprecedented molecular structures.

Table 1
Organometallic fluorides of the lanthanide elements

No.	Compound	Ref.
1	$Cp^*{}_2YbF\cdot Et_2O$	[9]
2	$Cp^*{}_2YbF\cdot THF$	[9]
3	$(MeC_5H_4)_2YbF\cdot THF$	[9]
4	$Cp^*{}_2EuF\cdot Et_2O$	[9]
5	$Cp^*{}_2SmF\cdot Et_2O$	[9]
6	$Cp^*{}_6Yb_5(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu_2\text{-}F)_6$	[9]
7	$Cp^*{}_6Yb_4(\mu_2\text{-}F)_4$	[11]
8	$Cp^*{}_4Yb_2(\mu_2\text{-}F)$	[12]
9	$[({}^tBuC_5H_4)_2Sm(\mu_2\text{-}F)]_3$	[13]

Table 2
Organometallic fluorides of the actinide elements

No.	Compound	Ref.
10	Cp_3UF	[16,22]
11	Cp_3ThF	[17]
12	Cp_3NpF	[19,20]
13	$Cp_3UF\cdot Cp_3Yb$	[26]
14	$Cp_3UF\cdot Cp_3U$	[26]
15	$(C_9H_7)_3UF$	[16]
16	$(MeC_5H_4)_3UF$	[27,28]
17	$\{(Me_3Si)C_5H_4\}_3UF$	[15]
18	$(MeC_5H_4)_3UF\cdot(MeC_5H_4)_3U$	[15]
19	$[\{(Me_3Si)_2C_5H_3\}_2U(\mu_2\text{-}F)(\mu\text{-}BF_4)]_2$	[29]
20	$\{(Me_3Si)_2C_5H_3\}_2U(F)(BF_4)$	[29]
21	$[\{(Me_3Si)_2C_5H_3\}_2UF_2]_n$	[29]
22	$[\{(Me_3Si)_2C_5H_3\}_2UF]_n$	[30]

However, the coverage of this review is not intended to be exhaustive, but overviews this highly specialized area to date. It is part in a series of review articles on organometallic fluorides [5].

Abbreviations: Cp, cyclopentadienyl; Cp', substituted cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Ln, lanthanide element; An, actinide element; R, organic group; R_F, perfluorinated organic group

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2. Organometallic fluorides of the lanthanide elements

A number of excellent review articles covering organolanthanide cyclopentadienyl complexes have appeared in the recent years [6]. Clearly the +3 oxidation state dominates this area of chemistry. Relatively few divalent organolanthanoid halides are known [7] and no simple organolathanide(II) fluoride (Cp'LnF) has ever been isolated. However, divalent Cp'LnF fragments were definitely identified in mixed-valence Ln(II/III) complexes.

Divalent R_FLnF (Ln = Sm, Yb) species, and more complex organometallic compounds, have been detected as decomposition products in the reaction of samarium or ytterbium metal with bis(perfluoroaryl)mercury [8].

Given the insolubility of rare earth fluorides, even in polar solvents, it is not surprising that reaction of LnF_3 with organo alkali reagents does not generally yield the desired organolanthanide(III) fluoride. However, trivalent organolanthanide fluorides are accessible via oxidation of divalent Cp'_2Ln compounds either by fluorine abstraction from perfluoroolefins, or by reaction with metal fluorides. The latter method invariably leads to fluorine bridged mixed-valence Ln(II/III) complexes. Table 1 summarizes the known organometallic fluorides of the lanthanides.

In 1990, Watson et al. [9] reported on the activation of C–F bonds by divalent lanthanide reagents. Lanthanide complexes of the type $Cp'_2M \cdot L$ (M = Yb, Eu, Sm; L = Et_2O, THF) react with perfluoro-2,4-dimethyl-3-ethylpent-2-ene (C_9F_{18}) or perfluoro-2,3-dimethylpent-2-ene (C_7F_{14}) to form the corresponding trivalent lanthanide monofluorides **1–5** as diethyl ether or THF adducts (Scheme 1).

Fluorine atom abstraction occurs preferentially from the allylic positions of the perfluoroolefin with conversion to perfluoro dienes (>90% yield). It is likely that species of the type $Cp'_2M \cdots R_F$, where a fluorine atom on R_F acts as a weak Lewis base, coordinating the divalent Lewis acidic Cp'_2M, are transient intermediates in the fluorine abstraction process [9].

Two factors, namely the tendency of the divalent species to be oxidized and the strength of the resulting metal–fluorine bond, are thought to be the driving forces in these reactions. While the mechanism of C–F activation has been dealt with elsewhere [1,2], it is worth mentioning here that oxidative addition of alkyl and aryl chlorides, bromides and iodides to $Cp^*_2Yb \cdot Et_2O$ is well established [10].

The molecular structures of **1** and **2** were determined by single-crystal X-ray analysis. These red–orange compounds are monomeric in the solid state, containing a terminal fluorine ligand and a coordinated diethyl ether or THF molecule. No significant differences were found between the Cp^*_2YbF cores in the crystal structures of **1** and **2**. However, compounds **1** and **2** provide the first examples for terminal lanthanide–fluorine bond distances (2.02 Å (**1**) and 2.03 Å (**2**), respectively).

$$Cp'_2Ln \cdot L \xrightarrow{R_F} Cp'_2LnF \cdot L$$

1: Cp' = Cp*, Ln = Yb, L = Et_2O
2: Cp' = Cp*, Ln = Yb, L = THF
3: Cp' = (MeC_5H_4), Ln = Yb, L = THF
4: Cp' = Cp*, Ln = Eu, L = Et_2O
5: Cp' = Cp*, Ln = Sm, L = Et_2O
R_F = C_9F_{18}, C_7F_{14}

Scheme 1.

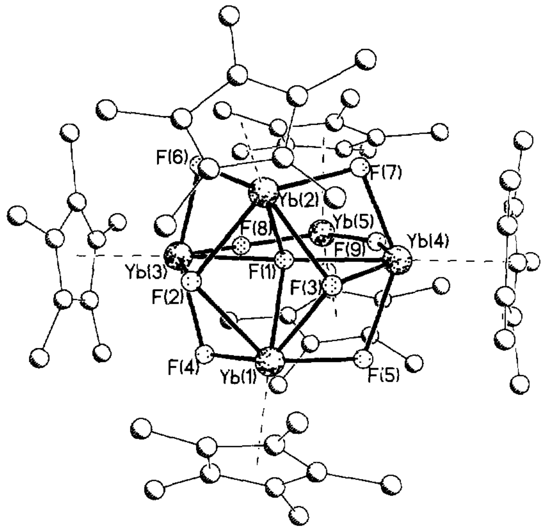


Fig. 1. Molecular structure of compound **6**.

A complicating feature of fluorine atom abstraction in the reaction of $Cp^*_2Yb \cdot Et_2O$ with C_9F_{18} is the formation of secondary products. The red ytterbium cluster $Cp^*_6Yb_5(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu_2\text{-}F)_6$ (**6**) (Fig. 1) has been prepared from the further reaction of $Cp^*_2YbF \cdot Et_2O$ with perfluoroolefins. The fluoro organic byproduct was identified as the highly unsaturated C_9F_{14} perfluoro triene [9].

In the solid state, pentanuclear **6** is composed of one Cp^*_2YbF (Yb(5)) and four Cp^*YbF_2 units (Yb(1)–Yb(4)) with fairly symmetrical μ_2-, μ_3- and μ_4-fluorine bridges. All ytterbium atoms are trivalent. From the X-ray data of **6**, the averaged Yb–F distances are 2.20 Å for a fluorine atom bridging between two ytterbium atoms and 2.37 Å for a fluorine atom bridging between three or four ytterbium atoms, respectively.

Unlike the completely trivalent Yb cluster **6**, oxidation of Cp^*_2Yb with AgF in toluene affords the tetranuclear mixed-valence Yb(II/III) complex $Cp^*_6Yb_4(\mu_2\text{-}F)_4$ (**7**), even in the presence of a four-fold excess of AgF. X-ray structural analysis of **7** (Fig. 2) shows a regularly arranged cyclic set of two divalent Cp^*YbF (Yb(1) and Yb(1A)) and two trivalent Cp^*_2YbF fragments (Yb(2) and Yb(2A)) connected by four nearly linear μ_2-fluorine bridges [11].

While the coordination of the trivalent ytterbium atoms is a distorted tetrahedron, the formal divalent metals show a trigonal planar environment. The averaged Yb–F bond distances are 2.13 Å (Yb(III)–F) and 2.22 Å (Yb(II)–F), respectively.

The Yb(II/III) mixed-valence formulation, with non-interacting spins, has been confirmed by variable-temperature magnetic susceptibility measurements [11].

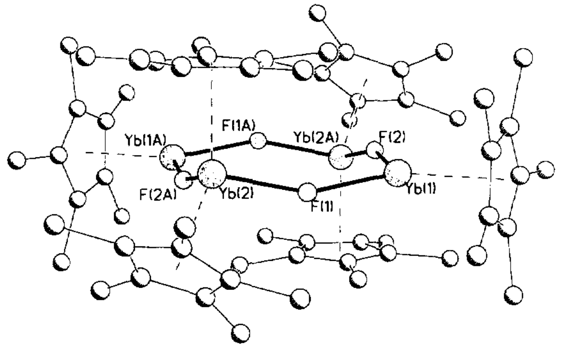


Fig. 2. Molecular structure of compound **7**.

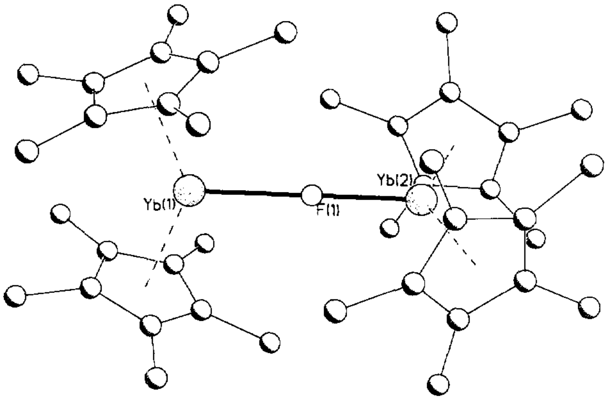


Fig. 3. Molecular structure of compound **8**.

From the same reaction, however, besides red compound **7** another product of brown color was obtained which was shown to be the dinuclear complex $Cp^*_4Yb_2(\mu_2\text{-}F)$ (**8**) [12]. A different synthetic approach to **7** and **8** involves the reaction of hexafluorobenzene (C_6F_6) and Cp^*_2Yb in hexane, with cleavage of a C–F bond. Similar C–F bond activation has been observed for other fluoroaromatics and fluoroalkenes but not for C_2F_6 or CF_3CH_3.

The molecular structure of **8** was confirmed by X-ray diffraction studies (Fig. 3). The Yb(II)···F–Yb(III) angle was found to be linear. The bridging fluorine is asymmetric (Yb–F 2.08 and 2.34 Å, respectively), allowing assignment of Yb(2) as Yb(III) and Yb(1) as Yb(II).

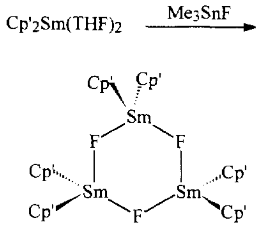
Dinuclear compound **8** may be correctly viewed as a donor–acceptor complex where the lone pair on fluorine in Cp^*_2YbF acts as the Lewis base and Cp^*_2Yb as the corresponding Lewis acid.

Since thermal rearrangement of **8** leads to **7** (Scheme 2) where a decrease in the Cp*:Yb ratio from 2:1 to 1:1 indicates relief of steric crowding about the metal, it has been suggested that **7** is the thermodynamically more stable product [12].

Very recently, Schumann et al. prepared the trimeric organosamarium fluoride $[(^tBuC_5H_4)_2Sm(\mu_2\text{-}F)]_3$ (**9**) [13] according to Scheme 3. In this reaction, trimethyltin fluoride serves as the fluorinating agent in addition to oxidizing the divalent samarium compound. The molecular structure of **9** consists of an almost planar six-membered ring with alternating Sm and F atoms. The average value of the Sm–F distances found is 2.24 Å.

$$\underset{\mathbf{8}}{4\,Cp^*_4Yb_2F} \longrightarrow \underset{\mathbf{7}}{Cp^*_6Yb_4F_4} + 4\,Cp^*_2Yb + 2\,\text{"}Cp^*\text{"}$$

Scheme 2.



9: Cp' = ($^tBuC_5H_4$)

Scheme 3.

3. Organometallic fluorides of the actinide elements

The organoactinide fluorides are commonly found in the +4 oxidation state and most obey the general formula Cp'_3AnF. Much of the work concerning organoactinide elements has been conducted by Kanellakopulos et al., and a review which appeared in 1972 summarizes early efforts in this field [14]. A more specialized article by Weydert and Andersen in 1994 reviews properties of organouranium(IV) fluorides and describes new synthetic strategies for Cp'_3UF complexes [15]. A complete list of organoactinide fluorides is given in Table 2.

Unfortunately, many of the organoactinide fluoride complexes are only briefly mentioned in the literature without experimental details or spectroscopic characterization.

In 1965, the parent compound Cp_3UF (**10**) was prepared in 17% yield from Cp_3UBr using NaF as fluorinating agent. The green compound can be purified by vacuum sublimation at 170°C [16].

Pale yellow Cp_3ThF (**11**) has been prepared in 70% yield from the reaction of thorium tetrafluoride with alkali cyclopentadienide (1:3 molar ratio) [17]. Mass spectrometric investigations of Cp_3UF (**10**) and Cp_3ThF (**11**) show that they are monomeric in the vapor phase [18].

Green Cp_3NpF (**12**) is prepared via reaction of NpF_3 and Cp_2Be [19]. Isotopically pure $Cp_3^{239}NpF$ has been isolated by β-conversion of $Cp_3^{239}UF$ [20]. The temperature dependence of the magnetic susceptibility of **12** has been reported [21].

An apparently better route to **10** (80% yield) involves a salt melt reaction between Cp_2Mg and UF_4 [16]. Alternatively, compound **10** is obtained in 41% yield from a proton transfer reaction between Cp_4U and NH_4F in THF [22].

A later study of the halide series Cp_3UX (X = F, Cl, Br, I) using NMR spectroscopy, molecular weight and magnetic susceptibility measurements, revealed that only Cp_3UF (**10**) has unusual properties. Unlike its homologues, **10** exhibits a strong tendency to appear in associated forms, both in solution and in the solid state [23,24].

X-ray structural analysis of **10**, however, showed that the crystal contains Cp_3UF monomers, having a short U–F bond distance of 2.11 Å and a long intermolecular UF· · ·U distance of 3.87 Å. Suspected dimer formation via uranium–fluorine–uranium bridging was not found. Interestingly, the long intermolecular UF· · ·U contact does bring the hydrogens of the cyclopentadienyl rings into close proximity to the fluorine in the adjacent Cp_3UF molecule, giving rise to weak intermolecular hydrogen bonding [25].

10 behaves as a Lewis acid towards bases and thus reacts with Cp_3M ($M = Yb$, U) to form 1:1 adducts. The adducts $Cp_3UF \cdot Cp_3Yb$ (**13**) and $Cp_3UF \cdot Cp_3U$ (**14**) are insoluble and only sparingly volatile above 350°C. The complexes were characterized by IR spectroscopy and mass spectrometry [26].

The only indenylactinide fluoride complex $(C_9H_7)_3UF$ (**15**) is available from the reaction of UCl_4 with $(C_9H_7)K$ and Teflon powder in benzene or alternatively from the fluorination of $(C_9H_7)_3UCl$ with NaF [16]. However, compound **15** is only briefly mentioned without detailed synthetic procedures. No yields or analytical data have been reported.

Reacting trivalent $(MeC_5H_4)_3U \cdot THF$ with PF_3, Andersen et al. intended to prepare a σ-donor phosphine complex. The product that was isolated, however, proved to be the uranium(IV) monofluoride $(MeC_5H_4)_3UF$ (**16**) [27]. This experiment lead Andersen and Weydert to develop new synthetic routes to Cp'_3UF complexes. The readily available base-free uranium(III) precursor $\{(Me_3Si)C_5H_4\}_3U$ reacts smoothly with AgF, COF_2 or Ph_3CF to form $\{(Me_3Si)C_5H_4\}_3UF$ (**17**) in high yields (Scheme 4) [15].

An insoluble material precipitates rapidly on reaction of $(MeC_5H_4)_3UF$ (**16**) with $(MeC_5H_4)_3U \cdot THF$ in toluene. The precipitate has the correct stoichiometry for a mixed-valence fluorine bridged compound $(MeC_5H_4)_3UF \cdot (MeC_5H_4)_3U$ (**18**) analogous to that described for $Cp_3UF \cdot Cp_3U$ (**14**). In the reaction of $\{(Me_3Si)C_5H_4\}_3UF$ (**17**) with $\{(Me_3Si)C_5H_4\}_3U$ no interaction between the two reactants is detected, as confirmed by ^1H-NMR spectroscopy. Increased steric bulk of the $(Me_3Si)C_5H_4$ ligands probably prevents the two metal centers approaching each other to form a fluorine bridged compound [15].

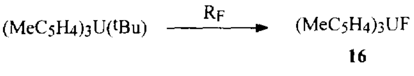
In 1993, Weydert et al. were successful in the activation of C–F bonds using organouranium(IV) complexes. $(MeC_5H_4)_3U(^tBu)$ reacts under mild conditions with hexafluorobenzene (C_6F_6), benzotrifluoride ($PhCF_3$), perfluoromethylcyclohexane (C_7F_{14}) or perfluorocyclohexane (C_6F_{12}) in the presence of hydrocarbon solvents to give $(MeC_5H_4)_3UF$ (**16**) in high yield (Scheme 5). The organic products of these reactions, identified and quantified by NMR spectroscopy, GC and GC–MS techniques are indicative of a radical reaction sequence [28].

$$\{(Me_3Si)C_5H_4\}_3U + AgF \longrightarrow \mathbf{17} + Ag$$

$$2\ \{(Me_3Si)C_5H_4\}_3U + COF_2 \longrightarrow 2\ \mathbf{17} + CO$$

$$2\ \{(Me_3Si)C_5H_4\}_3U + 2\ Ph_3CF \longrightarrow 2\ \mathbf{17} + Ph_3CCPh_3$$

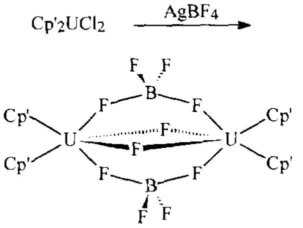
Scheme 4.



$$(MeC_5H_4)_3U(^tBu) \xrightarrow{R_F} \underset{\mathbf{16}}{(MeC_5H_4)_3UF}$$

$R_F = C_6F_6, PhCF_3, C_7F_{14}, C_6F_{12}$

Scheme 5.



19: $Cp' = \{(Me_3Si)_2C_5H_3\}$

Scheme 6.

The main driving force for this reaction is thermodynamic, with cleavage of a weak uranium–carbon bond and formation of a strong uranium–fluorine bond being the main contributory factors.

The reaction between $\{(Me_3Si)_2C_5H_3\}_2UCl_2$ or $\{(Me_3Si)_2C_5H_3\}_2U(CH_2R)_2$ ($R = SiMe_3$, Ph) and $AgBF_4$ in Et_2O yields orange–red crystals characterized as the dimeric complex $[\{(Me_3Si)_2C_5H_3\}_2U(\mu_2\text{-}F)(\mu\text{-}BF_4)]_2$ (**19**) [29] according to Scheme 6.

The molecular structure of **19** was confirmed by single-crystal X-ray analysis, showing two uranium centers related to each other by a pair of bridging bidentate BF_4^- groups and two bridging F^- ligands (mean U–FB 2.41 Å, mean U–FU 2.31 Å). The observation of very distinct terminal B–F distances in **19** (1.38 and 1.23 Å, respectively) is unusual.

The existence of a dynamic equilibrium between dimeric **19** and the monomer $\{(Me_3Si)_2C_5H_3\}_2U(F)(BF_4)$ (**20**) in $CDCl_3$ or $[D_8]$toluene was demonstrated by NMR spectroscopy. Evaluation of the ^1H- and ^{11}B-NMR experiments allowed calculation of the equilibrium constants for $\mathbf{19} \rightleftharpoons 2\ \mathbf{20}$. Appearance of a broad singlet in the ^{19}F-NMR spectrum, which is invariant in the temperature range −40 to 60°C, indicates fluoride lability in **19** and **20**, respectively. This signal has been attributed to rapid F^- exchange not only within the BF_4^- ligand but also between F^- and BF_4^-, with the time averaged chemical shifts for **19** and **20** being indistinguishable [29].

The polymeric uranocene difluoride $[\{(Me_3Si)_2C_5H_3\}_2UF_2]_n$ (**21**) forms on treatment of **19** with NMe_3 in THF, with abstraction of BF_3. Green compound **21** was identified in solution in a mixture along with BF_3 using ^1H-, ^{11}B- and ^{19}F-NMR techniques but spectroscopic data were not reported [29].

Green $[\{(Me_3Si)_2C_5H_3\}_2UF]_n$ (**22**) is the only organoactinide(III) fluoride mentioned in the literature. Reduction of $[\{(Me_3Si)_2C_5H_3)_2U(\mu_2\text{-}F)(\mu\text{-}BF_4)]_2$ (**19**) with sodium amalgam in toluene produces polymeric **22** in 75% yield. No details other than melting point and ^{1}H-NMR absorptions for the $SiMe_3$ groups have been reported [30].

Acknowledgements

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