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Fluorinating Reagents | *Very Important Paper* |

Synthesis of Actinide Fluoride Complexes Using Trimethyltin Fluoride as a Mild and Selective Fluorinating Reagent

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Abstract: Trimethyltin fluoride (Me_3SnF) is a mild and selective reagent for the installation of actinide fluoride bonds as demonstrated by the room temperature synthesis of a variety of organometallic and inorganic thorium(IV), uranium(IV), and uranium(V) fluoride complexes {$(1,2,4\text{-}t\mathrm{Bu}_3C_5H_2)_2ThF_2$, $(C_5Me_5)_2U(F)(O\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)$, $U(F)(O\text{-}2,6\text{-}t\mathrm{Bu}_2C_6H_3)_3$, $U(F)[N(SiMe_3)_2]_3$, $(C_5Me_5)_2UF_2(L)$ (L = O=PMe$_3$, O=PPh$_3$, O=PCy$_3$), and $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)$} from their corresponding chloride, bromide, and iodide analogues. From these reactions, the new $(C_5Me_5)_2UF_2(L)$ (L = O=PPh$_3$, O=PCy$_3$) uranium fluoride complexes were isolated and characterized by NMR spectroscopy and X-ray crystallography.

Introduction

Actinide fluorine chemistry has been studied since the Manhattan project, where volatile separations of uranium isotopes were sought.[1] As the most volatile uranium compound, UF_6 was selected for isotope separations using the gaseous diffusion method; however, using UF_6 was complicated by its high reactivity and due to problems associated with its handling. Nevertheless, a major consequence of the gaseous diffusion process has been the accumulation of a significant amount of depleted UF_6.[2] As such, understanding the chemistry of the U–F bond has important implications for evaluating technologies for the storage, disposal, or re-use of depleted UF_6.

Despite the obvious experimental challenges, there is considerable interest in developing methods for the preparation of stable inorganic and organometallic actinide fluoride complexes as these molecules may provide crucial information regarding the poorly understood chemistry of actinide fluorides. In fact, there are only a couple of early accounts that report well-characterized reactivity of UF_6 with MeOH and Me_3SiOMe to give $(MeO)UF_5$[3] and $U(OMe)_6$,[4] respectively. Even in the presence of trace water, UF_6 reacts to form HF and uranium oxides, making the study of UF_6 and its chemistry challenging.[5] Over the past decade, this has changed. Techniques for handling and characterizing air- and water-sensitive materials have vastly improved, enabling a variety of new approaches for synthesizing molecular organometallic compounds containing actinide fluoride bonds.

Archetypal methods for synthesizing organometallic uranium fluoride compounds have evolved from redox chemistry with inorganic [$AgBF_4$,[6] AgF,[7] $AgPF_6$,[8] CuF_2,[9] HgF_2,[10] PF_3,[7,11] $(Ph_3P)AuCF_3$[12]] and organic (C_6H_5F,[10] Me_3SiCF_3,[13] COF_2,[7] PhCOF,[14] Ph_3CF[7]) fluoride reagents. In the area of thorium chemistry, thorium bipyridyl metallocene complexes react with AgF to give thorium fluoride derivatives.[15] The reduction of metallocene difluoride complexes has also proved to be a practical method for preparing trivalent fluorides.[6a,6b,16] Boron trifluoride ($BF_3{\cdot}OEt_2$) has been used as a fluoride exchange reagent to yield uranium fluorides upon reactions with metallocene uranium alkoxide,[17] alkyl,[17,18] and amide[17] complexes. Fluoride atom abstraction from aromatic and aliphatic fluorocarbons by $(MeC_5H_4)_3U(t\mathrm{Bu})$ has also been shown to give $(MeC_5H_4)_3UF$ in high yields.[7,19] Similarly, the uranium(III) alkyl $Tp^*{}_2UCH_2Ph$ activates C–F bonds on a variety of fluorinated substrates to yield $Tp^*{}_2UF$ and $Tp^*{}_2UF_2$ [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate].[20] Finally, protonolysis chemistry between uranium alkyl compounds using $NEt_3{\cdot}3HF$[21] and NH_4F[22] has been employed to afford uranium fluoride complexes.

Generally speaking, these existing routes to actinide fluoride complexes are limited and substrate specific. We have been investigating new methods for the synthesis of thorium and uranium fluoride complexes to explore their chemistry and sought to use trimethyltin fluoride (Me_3SnF) as a fluorinating reagent. Roesky and co-workers pioneered the use of Me_3SnF as a reagent for the metathesis of chlorides to the corresponding fluorides.[23] Although this compound forms a polymeric chain-like structure of tin and fluorine atoms in the solid state,[24] it has been shown to react with metal chlorides to generate metal fluorides and volatile trimethyltin chloride.[23b,23c,25] Specifically, Me_3SnF has been used to prepare a variety of alkaline-earth

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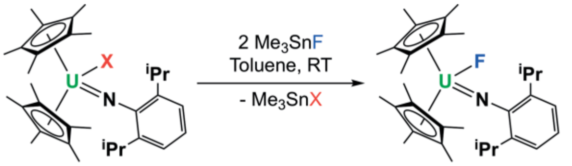
(Mg,[26] Ca,[27] Sr[28]), early (Sc,[29] Y,[29] Ti,[23a,29,30] Zr,[23a,30h,31] Hf,[23a,31b–31e] V,[32] Nb,[33] Ta[34]), mid (W[30j,35]), and late (Fe,[36] Co,[37] Zn[38]) transition-metal, main-group (Al,[39] Ga,[39g] Si,[23c,40] Ge,[41] Sb,[42] P[23b,43]) and lanthanide-metal (Sm,[44] Ho,[29] Er[29]) organometallic and inorganic fluoride complexes.

In this contribution, we demonstrate for the first time the use of Me_3SnF in halide exchange reactions with a suite of organometallic and inorganic actinide chloride, bromide, and iodide complexes as a mild route for the synthesis of thorium and uranium fluoride complexes. We further show that this methodology does not seem to be limited by metal (thorium vs. uranium), oxidation state [uranium(IV) vs. uranium(V)] or ligand platform (metallocene vs. non-metallocene).

Results and Discussion

Known uranium(V) imido halide complexes were chosen to initially examine the ability of Me_3SnF to serve as a fluorinating reagent for the preparation of organometallic actinide fluorides. As shown in Equation (1), $(C_5Me_5)_2U(X)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ [X = Cl (**1**), Br (**2**), I (**3**)],[9a,9b] reacts with 2 equiv. of Me_3SnF to afford $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**).[12] The resulting Me_3SnX (X = Cl, Br, I) byproduct is easily removed under reduced pressure, and the uranium(V) fluoride (**4**) is obtained in excellent yields (79–98 %) following work up. If desired, the Me_3SnX (X = Cl, Br, I) can be subsequently converted back into Me_3SnF by reaction with aqueous KF solution.[24,36,45] When the reactions are monitored by ^1H NMR spectroscopy in [D$_6$]benzene, resonances corresponding to the uranium(V) imido halide complex (**4**), in addition to singlets at δ = 0.29, 0.40, and 0.48, are observed for Me_3SnX (X = Cl, Br, and I), respectively, consistent with a halide exchange reaction.[46] Previously, complex **4** was synthesized by the oxidation of $(C_5Me_5)_2U(=N\text{-}2,6\text{-}iPr_2C_6H_3)(THF)$ with excess CuF_2,[9b] whereas the current procedure is redox-neutral.



(1)

X = Cl (**1**), Br (**2**), I (**3**)

4

Structurally characterized pentavalent uranium fluoride complexes are rare. Brown, crystalline blocks of **4** were grown by slow evaporation of a saturated toluene solution at ambient temperature and analyzed. Single-crystal X-ray diffraction confirmed the existence of the U–F bond in complex **4** (Figure 1). The molecular structure features a typical bent-metallocene framework with the fluoride and imido ligands in the metallocene wedge. The U(1)–F(1) [2.1280(17) Å], U(1)–N(1) [1.981(2) Å], and U–C$_{Cent}$ [2.453(3), 2.453(3) Å, cent = cyclopentadienyl centroid] bond lengths of complex **4** are all comparable to those reported for the structurally related uranium(V) imido fluoride complex $(C_5Me_5)_2U(F)(=N\text{-}2,4,6\text{-}tBu_3C_6H_2)$ [U–F = 2.122(5) Å, U–N = 1.965(8) Å, U–C$_{Cent}$ = 2.453(3), 2.453(3) Å].[9b] The U(1)–N(1)–C(21) [170.0(2)°], F(1)–U(1)–N(1) [106.60(8)°], and C$_{Cent}$–U–C$_{Cent}$ [143.0(1)°] bond angles of **4** are also comparable to those observed for $(C_5Me_5)_2U(F)(=N\text{-}2,4,6\text{-}tBu_3C_6H_2)$ [U–N–C$_{Ar}$ = 171.0(7)°, F–U–N = 97.0(3)°, and C$_{Cent}$–U–C$_{Cent}$ = 132.1(2)°].[9b] These values are also in agreement with those observed for the chloride, bromide, and iodide analogues of $(C_5Me_5)_2U(X)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$.[9b]

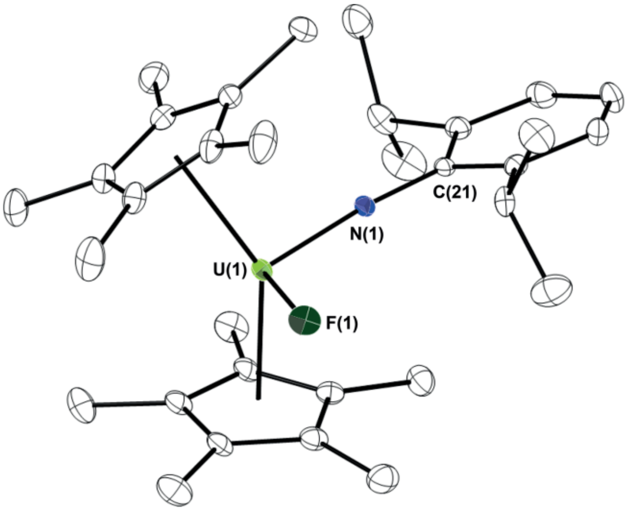
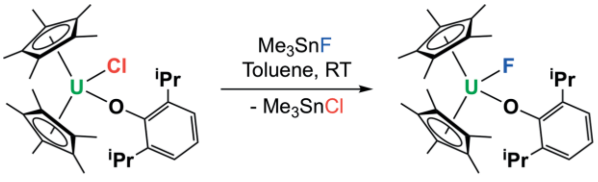


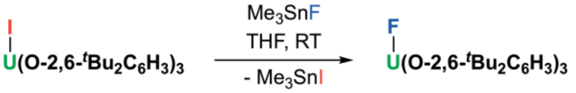
Figure 1. Molecular structure of $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**) with thermal ellipsoids projected at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

To understand the generality of this fluorination method, the reactivity of Me_3SnF with tetravalent uranium metallocene and non-metallocene ligand frameworks was tested. Reaction of Me_3SnF with the uranium(IV) aryloxide–chloride complex, $(C_5Me_5)_2U(Cl)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (**5**),[47] proceeds smoothly at room temperature to afford Me_3SnCl and the corresponding uranium(IV) fluoride complex $(C_5Me_5)_2U(F)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (**6**)[12] in 93 % yield [Equation (2)]. Likewise, treatment of the uranium(IV) tris(aryloxide) iodide and tris(amide) chloride complexes, $U(I)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (**7**)[48] and $U(Cl)[N(SiMe_3)_2]_3$ (**9**),[49] with Me_3SnF forms $U(F)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (**8**)[50] and $U(F)[N(SiMe_3)_2]_3$ (**10**)[51] in 53 % and 93 % yields, respectively [Equations (3) and (4)]. Previously, all three complexes, **6**, **8**, and **10**, were prepared by redox or fluoride-atom abstraction oxidative methods.



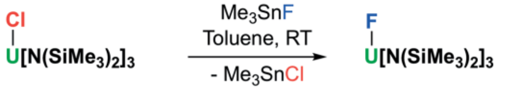
(2)

5 **6**



$$U(I)(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3 \xrightarrow[\text{- }Me_3SnI]{Me_3SnF,\ \text{THF, RT}} U(F)(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3 \quad (3)$$

7 **8**

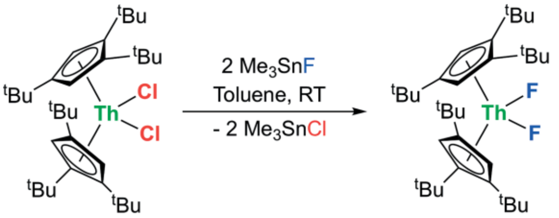


$$U(Cl)[N(SiMe_3)_2]_3 \xrightarrow[\text{- }Me_3SnCl]{Me_3SnF,\ \text{Toluene, RT}} U(F)[N(SiMe_3)_2]_3 \quad (4)$$

9 **10**

One interesting observation made during the course of these studies was that the liberated Me_3SnCl and Me_3SnI in reactions 2–4 can react with the uranium aryloxide and amide ancillary linkages in $(C_5Me_5)_2U(F)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (**6**), $U(F)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (**8**) and $U(F)[N(SiMe_3)_2]_3$ (**10**) to form the corresponding trimethyltin derivatives $Me_3Sn(O\text{-}2,6\text{-}iPr_2C_6H_3)$ [$\delta_{[D6]benzene}$ = 0.25 ($SnCH_3$), 1.27 (iPr-CH_3), 3.38 (iPr-CH), 6.93 (p-Ar–H), 7.12 (m-Ar–H)], $Me_3Sn(O\text{-}2,6\text{-}tBu_2C_6H_3)$ [$\delta_{[D6]benzene}$ = 0.32 ($SnCH_3$), 1.49 (tBu-CH_3), 6.90 (p-Ar–H), 7.35 (m-Ar–H)], and $Me_3SnN(SiMe_3)_2$ [$\delta_{[D6]benzene}$ = 0.21 ($SiCH_3$), 0.25 ($SnCH_3$)], respectively, which were identified by monitoring the reactions by ^1H NMR spectroscopy.[46] We found that this side reaction is circumvented by immediately placing the reactions under reduced pressure after the Me_3SnF is added such that volatile Me_3SnX (X = Cl, Br, I) compounds are removed as they are formed.

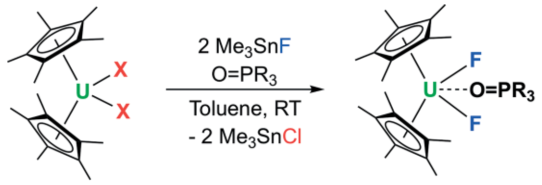
Finally, additional studies were carried out to see if the Me_3SnF chemistry could be applied to not only the installation of multiple fluoride bonds, but also as a fluorinating reagent at actinide metal centers other than uranium. Indeed, the metallocene thorium(IV) dichloride complex $(1,2,4\text{-}tBu_3C_5H_2)_2ThCl_2$ (**11**)[52] reacts cleanly with 2 equiv. of Me_3SnF, yielding $(1,2,4\text{-}tBu_3C_5H_2)_2ThF_2$ (**12**, 90 %)[15b] [Equation (5)]. Previously, complex **12** was prepared by oxidation of the bipyridyl thorium metallocene complex, $(1,2,4\text{-}tBu_3C_5H_2)_2Th(bipy)$ (bipy = 2,2′-bipyridine) using AgF.[15b]



11 **12**

(5)

As shown in Equation (6), similar chemistry was observed for uranium. Reaction of the uranium(IV) dichloride and dibromide complexes $(C_5Me_5)_2UX_2$ [X = Cl (**13**),[53] Br (**14**)[47]] in the presence of phosphine oxides afforded the monometallic difluoride uranium(IV) complexes $(C_5Me_5)_2UF_2(O{=}PR_3)$ [R = CH_3 (**15**, 97–99 %);[21] R = Ph (**16**, 70–99 %); R = Cy (**17**, 71–77 %)]. Due to the basicity of the fluoride ligand, a characteristic feature of organometallic fluoride complexes is the tendency to form fluoride bridges between two or more metal atoms. However, the added phosphine oxide donor ligands help to sterically saturate the uranium metal center and prevent dimer formation in both the solution and solid state.



(6)

X = Cl (**13**), Br (**14**)

R = Me (**15**), Ph (**16**), Cy (**17**)

Earlier work by our group showed that monometallic uranium difluoride complex **15** could be prepared by protonolysis of $(C_5Me_5)_2UMe_2$ with $Et_3N{\cdot}3HF$ in the presence of trimethylphosphine oxide.[21] Halide exchange using Me_3SnF not only offers a higher yielding and more streamlined route to **15**, but also enables access to the triphenylphosphine oxide (**16**) and tricyclohexylphosphine oxide (**17**) derivatives.

Complexes **16** and **17** represent new members to this small but growing class of low-valent uranium fluorides. Similar to complex **15**, ^{19}F NMR resonances were not visible for the terminal fluoride ligands in either complex **16** or **17**. The ^1H NMR spectrum for $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**) in [D_6]benzene is sim-

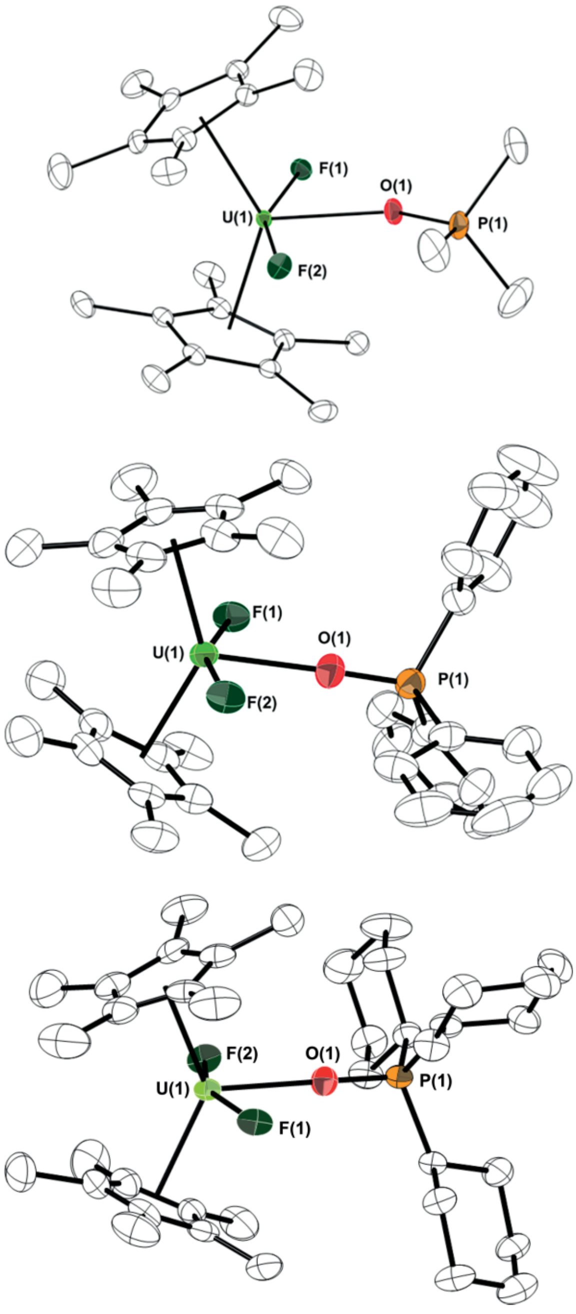


Figure 2. Molecular structures of $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**), $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**), and $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) with thermal ellipsoids projected at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

ple and shows a singlet at δ = –2.47 ppm for the C_5Me_5 protons and broad resonances at δ = 6.74 (*m*-Ar–*H*), 4.62 (*p*-Ar–*H*), and 2.60 (*o*-Ar–*H*) corresponding to the phenyl groups on the coordinated $Ph_3P{=}O$ ligand. The ^1H NMR spectrum for $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) in [D$_6$]benzene is a bit more complicated with a singlet at δ = –1.81 ppm for the C_5Me_5 protons and several broad resonances corresponding to the protons of inequivalent cyclohexyl groups on the coordinated $Cy_3P{=}O$ ligand. Finally, complexes $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**), $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**) and $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) in [D$_6$]benzene all display signals in their $^{31}P\{^1H\}$ NMR spectra at δ = –34.76, –9.38, and 14.87, respectively.

The molecular structures of **15**–**17** are given in Figure 2. All three complexes display bent metallocene structures with the phosphine oxide coordinated to the uranium(IV) metal center between two fluoride ligands within the wedge. The terminal U–F bond lengths are 2.1285(12) and 2.1292(12) Å for $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**), 2.1223(32) and 2.1325(28) Å for $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**), and 2.1277(17) and 2.1246(17) Å for $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**). Although these values are similar to that observed in the structurally related $(C_5Me_5)_2UF_2(py)$ [U–F = 2.146(5) Å],[21] they are significantly longer than those reported for the other known uranium(IV) terminal fluoride complexes $(1,2,4\text{-}tBu_3C_5H_2)_2UF_2$ [U–F = 2.081(5) Å],[18] $(1,3\text{-}tBu_2C_5H_3)_2UF_2$ [U–F = 2.086(5) Å[17]], and $Tp^*{}_2UF_2$ ([U–F = 2.086(6), 2.090(6) Å]. This observation is consistent with comparatively more electron-rich uranium metal centers in complexes **15**–**17** due to the additional electron density provided by the phosphine oxide ligands.

Conclusions

We have shown that trimethyltin fluoride (Me_3SnF) serves as a mild and selective reagent for the installation of actinide fluoride bonds. The halide exchange reaction with actinide chloride, bromide, and iodide complexes affords the corresponding fluorides as demonstrated by the synthesis of a variety of organometallic and inorganic thorium and uranium fluoride complexes. As this chemistry does not seem to be limited by actinide metal, oxidation state, or ligand platform, we expect that this protocol will provide a general means for introducing fluoride ligands on actinide metal centers.

Experimental Section

General Considerations: Unless otherwise noted, all reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (Ar or N_2) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer at ambient temperature. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities.[54] $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85 % H_3PO_4 solution. IR spectra were obtained using a Thermo Scientific Nicolet iS5 FT–IR spectrometer, using a Golden Gate Diamond ATR (ZnSe lenses) with a reaction anvil (neat solid samples). Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 50S K/J thermocouple using capillary tubes flame-sealed under N_2; values are uncorrected. Elemental Analyses were performed by ALS Environmental (Tucson, AZ) or Atlantic Microlab, Inc. (Norcross, GA).

Materials: Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Brockmann I, Aldrich), and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous, dried with KH for 48 h, passed through a column of activated alumina, and stored over activated 3 Å molecular sieves prior to use. $(C_5Me_5)_2U(X)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (X = Cl, Br, I),[9a,9b] $(C_5Me_5)_2U(Cl)(O\text{-}2,6\text{-}iPr_2C_6H_3)$,[47] $U(I)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$,[55] $U(Cl)[N(SiMe_3)_2]$,[49] $(C_5Me_5)_2UCl_2$,[53] $(C_5Me_5)_2UBr_2$,[47] $(1,2,4\text{-}tBu_3C_5H_2)_2ThCl_2$,[52] and Me_3SnF[36] were prepared according to literature procedures.

Synthesis of $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (4)

Method A: From $(C_5Me_5)_2U(Cl)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (1): A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2U(Cl)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**1**, 0.300 g, 0.418 mmol), Me_3SnF (0.153 g, 0.836 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 4 h and then the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (15 mL) and filtered through a Celite-padded coarse-porosity fritted filter. All volatiles were removed from the brown filtrate to give $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**) as a brown solid (0.266 g, 0.378 mmol, 90 %). The ^1H NMR spectrum collected in [D$_6$]benzene was consistent with data previously reported for complex **4**.[9b] ^1H NMR ([D$_6$]benzene, 298 K): δ = 69.65 (s, 1 H, *CH*Me$_2$), 26.08 (s, 1 H, $\nu_{1/2}$ = 69 Hz, Ar–H), 16.76 (s, 1 H, $\nu_{1/2}$ = 28 Hz, Ar–H), 15.39 (s, 6 H, $\nu_{1/2}$ = 66 Hz, CH*Me*$_2$), 3.93 (s, 30 H, $\nu_{1/2}$ = 107 Hz, C$_5$*Me*$_5$), –10.11 (s, 6 H, $\nu_{1/2}$ = 48 Hz, CH*Me*$_2$), –15.93 (s, 1 H, $\nu_{1/2}$ = 133 Hz, Ar–H), –34.99 (s, 1 H, C*H*Me$_2$) ppm. ***Method B: From $(C_5Me_5)_2U(Br)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (2):*** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2U(Br)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**2**, 0.220 g, 0.289 mmol), Me_3SnF (0.106 g, 0.578 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 4 h and then the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (15 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The brown filtrate was collected and volatiles were removed under reduced pressure to give $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**) as a brown solid (0.155 g, 0.221 mmol, 76 %). ***Method C: From $(C_5Me_5)_2U(I)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (3):*** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2U(I)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**3**, 0.300 g, 0.371 mmol), Me_3SnF (0.136 g, 0.742 mmol), and toluene (5 mL). The reaction mixture was stirred at ambient temperature for 4 h and then the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane (15 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The brown filtrate was collected and volatiles were removed under reduced pressure to give $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**) as a brown solid (0.260 g, 0.370 mmol, 99 %). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated toluene solution at ambient temperature.

Synthesis of $(C_5Me_5)_2U(F)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (6): A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2U(Cl)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (**5**, 0.100 g, 0.139 mmol), Me_3SnF (0.025 g, 0.139 mmol), and toluene (5 mL). The reaction mixture was immediately placed under reduced pressure until dry. The reaction mixture was then charged with a second equivalent of Me_3SnF (0.025 g, 0.139 mmol) in toluene (5 mL), and subsequently placed under reduced pressure until dry. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2U(F)(O\text{-}2,6\text{-}iPr_2C_6H_3)$ (**6**) as a red solid (0.091 g, 0.129 mmol, 93 %). The ^1H NMR spectrum collected in $[D_6]$benzene was consistent with data previously reported for complex **6**.[12] ^1H NMR ($[D_6]$benzene, 298 K): δ = 6.75 (d, 1 H, $^3J_{H,H}$ = 8 Hz, *m*-Ar–*H*), 6.30 (t, 1 H, $^3J_{H,H}$ = 8 Hz, *p*-Ar–*H*), 4.13 (d, 1 H, $^3J_{H,H}$ = 8 Hz, *m*-Ar–*H*), 3.19 (s, 30 H, C_5Me_5), –1.71 (s, 6 H, $CHMe_2$), –10.25 (s, 1 H, $CHMe_2$), –11.45 (s, 6 H, $CHMe_2$), –45.33 (s, 1 H, $CHMe_2$) ppm.

Synthesis of $U(F)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (8): A 20-mL scintillation vial was charged with a stir bar, $U(I)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (**7**, 0.084 g, 0.085 mmol), Me_3SnF (0.016 g, 0.085 mmol), and THF (5 mL). The reaction mixture immediately placed under reduced pressure until dry. The resulting residue was triturated with $(Me_3Si)_2O$ (3 mL). Insoluble solids were collected on a coarse-porosity fritted filter, washed with $(Me_3Si)_2O$ (0.5 mL), and dried under reduced pressure to give $U(F)(O\text{-}2,6\text{-}tBu_2C_6H_3)_3$ (**8**) as a yellow solid (0.040 g, 0.046 mmol, 54 %). The ^1H NMR spectrum collected in $[D_6]$benzene was consistent with data previously reported for complex **8**.[50] ^1H NMR ($[D_6]$benzene, 298 K): δ = 15.97 (s, 6 H, $\nu_{1/2}$ = 43 Hz, *m*-Ar–*H*), 12.43 (s, 3 H, $\nu_{1/2}$ = 28 Hz, *p*-Ar–*H*), –4.54 (s, 54 H, $\nu_{1/2}$ = 62 Hz, CMe_3) ppm.

Synthesis of $U(F)[N(SiMe_3)_2]_3$ (10): A 20-mL scintillation vial was charged with a stir bar, $U(Cl)[N(SiMe_3)_2]_3$ (**9**, 0.100 g, 0.133 mmol), Me_3SnF (0.027 g, 0.146 mmol), and toluene (3 mL). The reaction mixture was immediately placed under reduced pressure until dry. The resulting residue was dissolved in hexane (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The purple filtrate was collected and volatiles were removed under reduced pressure to give $U(F)[N(SiMe_3)_2]_3$ (**10**) as a purple solid (0.095 g, 0.129 mmol, 98 %). The ^1H NMR spectrum collected in $[D_6]$benzene was consistent with data previously reported for complex **10**.[51] ^1H NMR ($[D_6]$benzene, 298 K): δ = –4.57 (s, 36 H, $\nu_{1/2}$ = 479 Hz, $SiMe_3$) ppm.

Synthesis of $(1,2,4\text{-}tBu_3C_5H_2)ThF_2$ (12): A 20-mL scintillation vial was charged with a stir bar, $(1,2,4\text{-}tBu_3C_5H_2)_2ThCl_2$ (**11**, 0.085 g, 0.110 mmol), Me_3SnF (0.040 g, 0.220 mmol, 2 equiv.), and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles were removed under reduced pressure to give $(1,2,4\text{-}tBu_3C_5H_2)_2ThF_2$ (**12**) as a white solid (0.073 g, 0.100 mmol, 90 %). The ^1H NMR spectrum collected in $[D_6]$benzene was consistent with data previously reported for complex **12**.[15b] ^1H NMR ($[D_6]$benzene, 298 K): δ = 6.35 (s, 4 H, C*H*), 1.55 (s, 36 H, CMe_3), 1.37 (s, 18 H, CMe_3) ppm.

Synthesis of $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (15)

***Method A: From $(C_5Me_5)_2UCl_2$ (13)*:** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2UCl_2$ (**13**, 0.100 g, 0.172 mmol), $O{=}PMe_3$ (0.016 g, 0.172 mmol), Me_3SnF (0.063 g, 0.344 mmol) and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and volatiles were removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**) as a yellow solid (0.107 g, 0.167 mmol, 97 %). The ^1H NMR spectrum collected in $[D_6]$benzene was consistent with data previously reported for complex **15**.[21] ^1H NMR ($[D_6]$benzene, 298 K): δ = –2.22 (s, 30 H, $\nu_{1/2}$ = 32 Hz, C_5Me_5), –17.31 (d, 9 H, $^2J_{P\text{-}H}$ = 10 Hz, $O{=}PMe_3$). $^{31}P\{^1H\}$ NMR ($[D_6]$benzene, 298 K): δ = –34.76 ppm. IR (ATR-IR, 296 K, neat): $\tilde{\nu}$ = 2950, 2909, 2856, 1437, 1376, 1311, 1296, 1103, 944, 863, 779, 752, 737, 545 cm^{-1}. M.p. 227–229 °C. Single crystals suitable for X-ray diffraction were obtained by upon cooling a saturated toluene solution to –30 °C. ***Method B: From $(C_5Me_5)_2UBr_2$ (14)*:** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2UBr_2$ (**14**, 0.100 g, 0.150 mmol), $O{=}PMe_3$ (0.014 g, 0.150 mmol), Me_3SnF (0.027 g, 0.150 mmol) and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. A second equivalent of Me_3SnF (0.027 g, 0.150 mmol) and toluene (5 mL) were added and the reaction mixture was immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**) as a yellow solid (0.095 g, 0.149 mmol, 99 %).

Synthesis of $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (16)

***Method A: From $(C_5Me_5)_2UCl_2$ (13)*:** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me)_2UCl_2$ (**13**, 0.100 g, 0.172 mmol), $O{=}PPh_3$ (0.048 g, 0.172 mmol), Me_3SnF (0.032 g, 0.172 mmol), and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was charged with Me_3SnF (0.032 g, 0.172 mmol) and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL), filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**) as a yellow solid (0.099 g, 0.120 mmol, 70 %). ^1H NMR ($[D_6]$benzene, 298 K): δ = 6.74 (s, 6 H, $\nu_{1/2}$ = 16 Hz, *m*-Ar–*H*), 4.62 (s, 3 H, $\nu_{1/2}$ = 19 Hz, *p*-Ar–*H*), 2.60 (s, 6 H, $\nu_{1/2}$ = 37 Hz, *o*-Ar–*H*), –2.47 (s, 30 H, $\nu_{1/2}$ = 32 Hz, C_5Me_5) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]$benzene, 298 K): δ = –9.38 ppm. IR (ATR-IR, 296 K, neat): $\tilde{\nu}$ = 3058, 2901, 2854, 2721, 1486, 1436, 1376, 1147, 1120, 1089, 1072, 1027, 997, 896, 749, 723, 692, 535 cm^{-1}. M.p. 239–240 °C. Elemental analysis could not be obtained due to poor combustibility of the sample. Single crystals suitable for X-ray diffraction were obtained upon cooling a saturated toluene solution layered with hexane to –30 °C. ***Method B: From $(C_5Me_5)_2UBr_2$ (14)*:** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me)_2UBr_2$ (**14**, 0.100 g, 0.150 mmol), $O{=}PPh_3$ (0.042 g, 0.150 mmol), Me_3SnF (0.027 g, 0.150 mmol), and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was charged with Me_3SnF (0.027 g, 0.150 mmol) and toluene (5 mL). The reaction mixture immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**) as a yellow solid (0.123 g, 0.149 mmol, 99 %).

Synthesis of $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (17)

***Method A: From $(C_5Me_5)_2UCl_2$ (13)*:** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me)_2UCl_2$ (**13**, 0.200 g, 0.344 mmol), $O{=}PCy_3$ (0.102 g, 0.344 mmol), Me_3SnF (0.063 g, 0.344 mmol), and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was charged with Me_3SnF (0.063 g, 0.344 mmol) and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL), filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) as a yellow solid (0.224 g, 0.265 mmol, 77 %). ^1H NMR ($[D_6]$benzene, 298 K): δ = 7.97 (s, 6 H, $\nu_{1/2}$ = 51 Hz, Cy-*H*), 2.10–1.88 (m, 3 H, Cy-*H*), –1.15 (s, 3 H, $\nu_{1/2}$ = 20 Hz, Cy-*H*),

−1.81 (s, 30 H, $\nu_{1/2}$ = 34 Hz, C_5Me_5), −3.56 (s, 6 H, $\nu_{1/2}$ = 48 Hz, Cy-*H*), −6.36 (s, 6 H, $\nu_{1/2}$ = 33 Hz, Cy-*H*), −10.74 (s, 6 H, $\nu_{1/2}$ = 32 Hz, Cy-*H*), −32.42 (s, 3 H, $\nu_{1/2}$ = 36 Hz, Cy-*H*) ppm. $^{31}P\{^1H\}$ NMR ([D_6]-benzene, 298 K): δ = 14.87 ppm. IR (ATR-IR, 296 K, neat): $\tilde{\nu}$ = 2928, 2850, 2176, 1444, 1343, 1286, 1228, 1130, 1095, 1075, 1049, 1026, 1005, 987, 953, 762, 563 cm^{-1}. M.p. 260.5–262.5 °C. $C_{38}H_{63}F_2OPU$ (842.91): C, 54.15; H, 7.53; found C, 53.13; H, 7.64. Single crystals suitable for X-ray diffraction were obtained upon cooling a saturated toluene solution to −30 °C. ***Method B: From $(C_5Me_5)_2UBr_2$ (14):*** A 20-mL scintillation vial was charged with a stir bar, $(C_5Me)_2UBr_2$ (**14**, 0.100 g, 0.150 mmol), O=PCy_3 (0.044 g, 0.150 mmol), Me_3SnF (0.027 g, 0.150 mmol), and toluene (5 mL). The reaction mixture was immediately placed under vacuum until dry. The resulting residue was charged with Me_3SnF (0.027 g, 0.150 mmol) and toluene (5 mL). The reaction mixture immediately placed under vacuum until dry. The resulting residue was dissolved in toluene (5 mL), filtered through a Celite-padded coarse-porosity fritted filter. The yellow filtrate was collected and the volatiles removed under reduced pressure to give $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) as a yellow solid (0.089 g, 0.106 mmol, 71 %).

X-ray Crystallography

Data for $(C_5Me_5)_2U(F)(=N\text{-}2,6\text{-}iPr_2C_6H_3)$ (**4**), $(C_5Me_5)_2UF_2(O{=}PMe_3)$ (**15**), and $(C_5Me_5)_2UF_2(O{=}PPh_3)$ (**16**) were collected on a Bruker Apex II diffractometer, with an APEX II CCD detector. Data for $(C_5Me_5)_2UF_2(O{=}PCy_3)$ (**17**) were collected on a Bruker D8 Quest diffractometer, with CMOS detector in shutterless mode. Data for $C_{32}H_{47}FNU$ (**4**): monoclinic, $P2_1/c$, a = 12.927(2) Å, b = 11.4779(18) Å, c = 19.746(3) Å, β = 91.802(2)°, V = 2928.4(8) Å^3, Z = 4, ϱ = 1.594 g/cm^3, μ = 5.569 Mo-K_α, T = 140 K, 2θ_{max} = 57.24°, min/max trans. = 0.2391/0.4022, total reflns = 31885, unique reflns = 6677, parameters = 330, $R_1(wR_2)$ [$I \geq 2\sigma(I)$] = 0.0230(0.0607). Data for $C_{26.5}H_{43}F_2OPU$ (**15**): monoclinic, $P2_1/c$, a = 15.017(3) Å, b = 10.962(2) Å, c = 16.779(3) Å, β = 90.1060(19)°, V = 2762.1(9) Å^3, Z = 4, ϱ = 1.646 g/cm^3, μ = 5.963 Mo-K_α, T = 140 K, 2θ_{max} = 57.52°, min/max trans. = 0.2513/0.5347, total reflns = 31594, unique reflns = 6750, parameters = 398, $R_1(wR_2)$ [$I \geq 2\sigma(I)$] = 0.0165(0.0408). Data for $C_{45}H_{53}F_2OPU$ (**16**): orthorhombic, $P2_12_12_1$, a = 10.9732(8) Å, b = 17.8607(13) Å, c = 20.5456(15) Å, β = 90.00°, V = 4026.7(5) Å^3, Z = 4, ϱ = 1.512 g/cm^3, μ = 4.112 Mo-K_α, T = 140 K, 2θ_{max} = 53.62°, min/max trans. = 0.4386/0.4935, total reflns = 40856, unique reflns = 9618, parameters = 398, $R_1(wR_2)$ [$I \geq 2\sigma(I)$] = 0.0301(0.0723). Data for $C_{45}H_{71}F_2OPU$ (**17**): monoclinic, $P2_1/n$, a = 10.4620(7) Å, b = 17.9494(13) Å, c = 22.8914(16) Å, β = 91.744(2)°, V = 4296.7(5) Å^3, Z = 4, ϱ = 1.445 g/cm^3, μ = 3.855 Mo-K_α, T = 140 K, 2θ_{max} = 62.54°, min/max trans. = 0.4116/0.5128, total reflns = 86771, unique reflns = 14049, parameters = 398, $R_1(wR_2)$ [$I \geq 2\sigma(I)$] = 0.0306(0.0954). The crystals were cooled with a Bruker KRYO-FLEX liquid nitrogen vapor-cooling device (**4**, **15**, **16**), or an Oxford Cryostream 700 (**17**). Hemispheres of data were collected with ω scans. Data collection, initial indexing and cell refinements were handled with APEX II software.[56] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out with Saint+ software.[57] The data were corrected for absorption with the SADABS program.[58] The structure was solved with direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Structure solution and refinement were performed with SHELXTL.[59] CCDC 1572453 (for **16**), 1572454 (for **4**), 1572455 (for **17**), and 1572456 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Fluorinating Reagents

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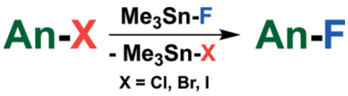
Synthesis of Actinide Fluoride Complexes Using Trimethyltin Fluoride as a Mild and Selective Fluorinating Reagent



$$\text{An-X} \xrightarrow[\text{- Me}_3\text{Sn-X}]{\text{Me}_3\text{Sn-F}} \text{An-F}$$

X = Cl, Br, I

Trimethyltin fluoride (Me_3SnF) is a mild and selective reagent for the installation of actinide fluoride bonds as demonstrated by the room temperature synthesis of a variety of organometallic and inorganic thorium and uranium from their corresponding chloride, bromide, and iodide analogues.

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