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Synthesis of Low-Valent Uranium Fluorides by C-F Bond Activation†

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The uranium(III) alkyl, $\text{Tp}^*_2\text{UCH}_2\text{Ph}$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate), activates C-F bonds on a variety of fluorinated substrates. From these reactions two new uranium containing products, Tp^*_2UF and Tp^*_2UF_2 , were isolated and characterized by ^1H , ^{13}C NMR, infrared and electronic absorption spectroscopies, as well as X-ray crystallography. Formation of the uranium(III) or uranium(IV) product was found to be substrate dependent.

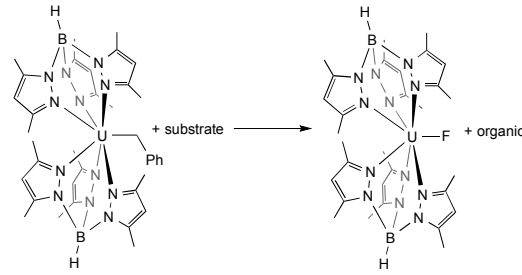
C-F bond activation is currently an active area of research due to its utility in a variety of synthetic applications.¹⁻⁴ While this process has been accomplished using alkaline earth,⁵ main group⁶ and transition metals,⁷ less is known about the ability of *f*-block elements to activate the relatively inert carbon-fluorine bond. As such, the collective knowledge regarding the structural details of complexes containing U-F bonds, especially those in low oxidation states, is limited. Much of the literature primarily describes uranium(VI) derivatives due to the utility of UF_6 in the nuclear fuel cycle.⁸

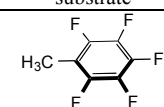
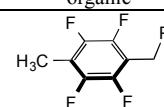
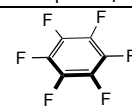
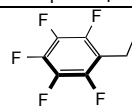
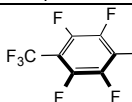
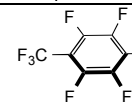
An early finding in the field of actinide mediated C-F bond activation was reported by Andersen and coworkers, who described the reactivity of the tetravalent uranium alkyl, $(\eta^5\text{-MeC}_5\text{H}_4)_3\text{U}(\text{CMe}_3)$, with fluorinated substrates. Treating $(\eta^5\text{-MeC}_5\text{H}_4)_3\text{U}(\text{CMe}_3)$ with two equivalents of hexafluorobenzene in toluene at ambient temperature produced the uranium(IV) fluoride, $(\eta^5\text{-MeC}_5\text{H}_4)_3\text{UF}$, and the C-C coupled product, $\text{C}_6\text{F}_5\text{CMe}_3$.⁹ Inspired by this significant result, we sought to determine if similar C-F bond scission would be possible with the trivalent uranium alkyl, $\text{Tp}^*_2\text{UCH}_2\text{Ph}$ (**1-Bz**). Herein, we report the reactivity of **1-Bz** with fluorinated substrates, which results in both C-F bond activation and new low-valent uranium fluoride complexes. These uranium fluorides have been characterized using ^1H NMR spectroscopy, X-ray crystallography, and electronic absorption spectroscopy, while the organic products have been confirmed using multinuclear NMR spectroscopy and mass spectrometry.

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Our studies commenced by treating a THF solution of **1-Bz** with one equivalent of 2,3,4,5,6-pentafluorotoluene at ambient temperature, which resulted in the isolation of a dark brown solid following work-up (Table 1, entry 1a). The ^1H NMR spectrum showed three paramagnetically shifted and broadened resonances ranging from -8.54 to 6.91 ppm, indicating equivalent Tp^* ligands in solution, similar to **1-Bz**. Resonances for the *endo*- and *exo*- $\text{Tp}^* \text{CH}_3$ protons are visible at -8.54 (18H) and -2.41 ppm (18H), respectively. A characteristic singlet appears at 6.91 ppm (6H) for the pyrazole *CH* protons. Given the spectroscopic similarity to the Tp^*_2UX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) series reported by Takats and co-workers,^{10, 11} the product was assigned as Tp^*_2UF (**1-F**, 94%). Analysis of the organics by ^1H and ^{19}F NMR spectroscopy showed resonances consistent with formation of 2,3,5,6-tetrafluoro-4-benzyl-toluene, which was isolated in high yield (90%) (Table 1, entry 1a). This product is

Table 1. Reactivity of **1-Bz** with fluorinated substrates to form **1-F**.


Entry	substrate	organic	Yield
1a			90%
1b			94%
1c			93%

consistent with C-F bond activation at the *para* position of the substrate, followed by C-C bond formation.

To determine if **1-F** exists as a monomer or dimer in the solid state, analysis by X-ray crystallography was employed. Dark green blocks of **1-F** grown by cooling a concentrated THF/pentane/benzene (10/1/0.5) solution to -35 °C were analyzed. Refinement of the data revealed a seven coordinate uranium monomer with a monocapped octahedral geometry (Fig. 1, left). The U-N bond lengths, ranging from 2.542(4) to 2.739(3) Å, are in agreement with typical U-N bond lengths seen for bis-Tp* supported uranium(III) species.¹²⁻¹⁴ As expected, the terminal U-F distance of 2.156(3) Å is shorter than the analogous U-X distances reported for Tp*₂UCl (2.698 Å) and Tp*₂UI (3.220 Å). To the best of our knowledge, this complex represents the first crystallographically characterized terminal uranium(III) fluoride. The molecular structure

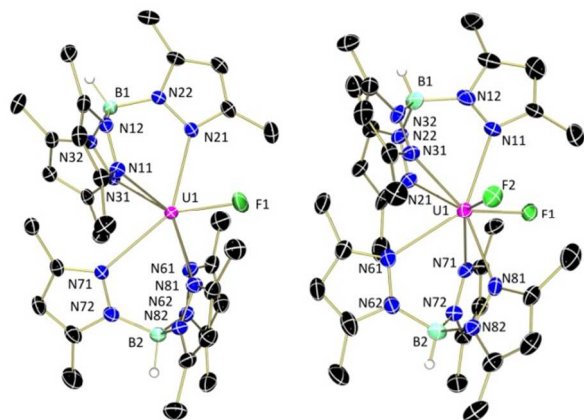


Fig. 1 Molecular structures of **1-F** (left) and **1-F₂** (right), with ellipsoids displayed at 30% probability level. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity. Select bond distances for **1-F** in Å: U1-F1 = 2.156(3), U1-N11 = 2.552(3), U1-N21 = 2.640(4), U1-N31 = 2.644(3), U1-N61 = 2.542(4), U1-N71 = 2.739(3), U1-N81 = 2.604(4). Select bond distances for **1-F₂** in Å: U1-F1 = 2.090(6), U1-F2 = 2.086(6), U1-N11 = 2.596(10), U1-N21 = 2.678(9), U1-N31 = 2.545(9), U1-N61 = 2.677(9), U1-N71 = 2.582(9), U1-N81 = 2.615(10). F-U-F angle for **1-F₂**: 89.7(3)^o

of **1-F** is similar to that reported by Takats for Tp*₂SmF, which has a Sm-F distance of 2.090 Å.¹⁵ The difference in M-F bond length is on the order of the difference between the ionic radii of the two metals (Sm(III) = 0.96 Å, U(III) = 1.03 Å). Monomeric **1-F** is reminiscent of the symmetric U(III) dimer, [Cp*₂UF]₂ (Cp* = 1,3-(Me₃Si)₂C₅H₃), reported by Andersen, which contains two bridging fluorine atoms.¹⁶ However, the terminal U-F bond of **1-F** is shorter (0.175 Å) than the shortest of the four bridging U-F bonds (2.331(3) Å) reported for [Cp*₂UF]₂. The monomeric nature of **1-F** versus the dimeric [Cp*₂UF]₂ is likely due to the greater steric demand of the Tp* ancillary ligand over the Cp-based system.¹⁷

In order to understand the generality of the C-F bond activation and C-C coupling reactions, the reactivity of **1-Bz** with additional fluorinated substrates was tested. Treating **1-Bz** with one equivalent of hexafluorobenzene under the same reaction conditions resulted in the formation of **1-F** and the C-C coupled product, 1,2,3,4,5-pentafluoro-6-benzyl-benzene, in high yields (94%) (Table 1, entry 1b). Similar reactivity was observed for **1-Bz** with perfluorotoluene, which once again produced **1-F** (89%) and the product from C-C coupling, 1,2,4,5-tetrafluoro-6-benzyl-3-(trifluoromethyl)benzene, in 93% yield (Table 1, entry 1c). Interestingly, no reaction was observed for *α,α,α*-trifluorotoluene or perfluorohexane, even after heating to 55 °C; only degradation of **1-Bz** was noted.

Additional studies were carried out using non-perfluorinated aromatic substrates. Treating a dark green solution of **1-Bz** with one equivalent of pentafluorobenzene produced an immediate color change to dark purple, indicative of **1-F** formation (Scheme 1). However, continued stirring caused additional colour changes to dark blue, followed by translucent light brown, which persisted upon standing. Removal of the volatiles *in vacuo* yielded a tan solid. The ¹H NMR spectrum of the new uranium species had three paramagnetically shifted resonances ranging from -7.61 to 19.31 ppm, indicative of C_{2v} symmetry. Resonances for the *endo*- and *exo*-Tp* CH₃ protons appeared at -7.61 (18H) and 19.31 ppm (18H), respectively. The pyrazole CH resonance was visible at 6.87 ppm (6H), which led to the hypothesis that two C-F bond activation events occurred to form Tp*₂UF₂ (**1-F₂**, 77%). The ¹H and ¹⁹F NMR spectra of the isolated organic product showed formation of the C-C coupled product, 3-benzyl-1,2,4,5-tetrafluorobenzene, isolated in low yield (27%).

An X-ray crystallographic analysis of **1-F₂** was performed on light brown crystals grown by slow diffusion of a hexane/pentane (2:1) solution into a concentrated **1-F₂**/THF solution at -35 °C. Refinement of the data confirmed the assignment of **1-F₂** (Fig. 1, right). As in the case of **1-F**, the U-N bond lengths were typical for Tp*₂U complexes, ranging from 2.545(9) to 2.678(9) Å. **1-F₂** represents the only example of a crystallographically characterized bis-Tp* supported uranium complex with two additional ligands completing the coordination sphere. The two fluoride ligands prove to be small enough to allow for symmetric Tp* ligands in the solution phase, while the larger chlorides of Tp*₂UCl₂ impart asymmetry in the solution ¹H NMR spectrum.¹⁸ The U-F bond lengths of 2.090(6) and 2.086(6) Å are shorter than those of **1-F**, reflecting the difference in the ionic radii of the U(III) and U(IV) centers (~0.1 Å).¹⁹ The U-F bond lengths in **1-F₂** are shorter than those in Kiplinger's uranium(IV) difluoride Cp*₂UF₂(NC₅H₃) (U-F = 2.146 Å),²⁰ likely due to the steric demand of the pyridine ligand. The distances in **1-F₂** are on the order of those in other neutral uranium(IV) complexes ([[1,3-(Me₃-Si)₂C₅H₃]₂UF₂]₂,¹⁶ (C₅Me₃)₂U(O-2,6-*i*Pr₂-C₆H₃)(F),²¹ (C₅H₃)₃UF,²² (C₅Me₃)₃UF,²³) which range from 2.073 – 2.429 Å.

Further characterization of the unique tri- and tetravalent uranium fluorides was accomplished using electronic absorption spectroscopy (Fig. 2). Data were collected in THF at ambient temperature in the range of 300-2100 nm. For **1-F**, low- to mid-intensity, color-producing *d-f* transitions can be seen in the visible and near IR regions of the spectrum, as is typical for uranium(III) species.^{24, 25} In contrast, the visible region of the spectrum for **1-F₂**, which features a uranium(IV) center, shows much less intense bands, consistent with the light brown color. The near-infrared regions of electronic absorption spectra show characteristic features for uranium(III) and uranium(IV) ions, confirming the valency. In the case of **1-F**, this part of the spectrum shows *f-f* transitions with molar absorptivities up to 100 M⁻¹cm⁻¹ in the range of 1100-1400 nm and 1900-2100 nm, which is commonly observed for other uranium(III) ions.^{26, 27} The corresponding region for **1-F₂** shows much weaker (<20 cm⁻¹M⁻¹) Laporte-forbidden *f-f* transitions, as is typically observed for uranium(IV) species with an *f²* electronic configuration.^{24, 25, 28}

The reaction to generate **1-F₂** from pentafluorobenzene and **1-Bz** was repeated in a sealed NMR tube (THF-*d*₈) to confirm formation of volatile organic products. Analysis by ¹H NMR spectroscopy showed the presence of toluene, indicating protonation of the U-C bond in **1-Bz** with concurrent formation of **1-F₂**. During the reaction, the deprotonated pentafluorobenzene undergoes β-fluoride elimination to generate the benzyne intermediate, 3,4,5,6-tetrafluorobenzene,²⁹ which can be trapped by repeating the reaction

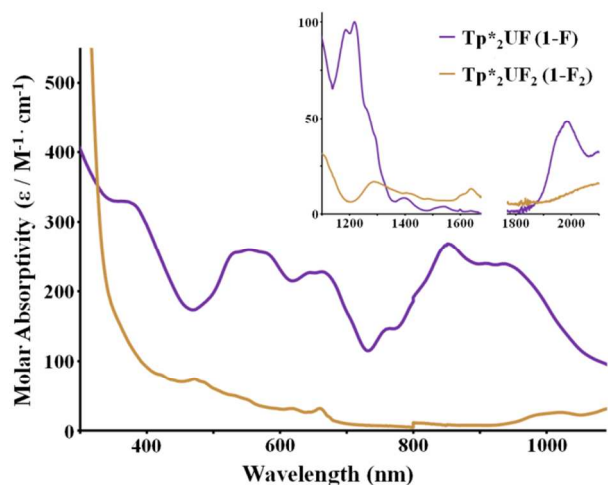


Fig. 2 Electronic absorption spectra of **1-F** (purple) and **1-F₂** (tan) recorded in THF at 23 °C. Solvent overtones between 1600 – 1800 nm have been removed.

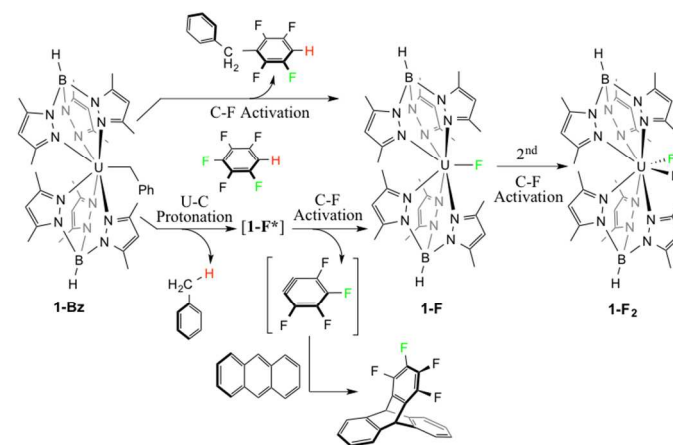
in the presence of an excess of anthracene to successfully form 1,2,3,4-tetrafluorotriptycene. This was confirmed by ¹H and ¹⁹F NMR spectroscopy and mass spectrometry (Scheme 1). Thus, benzyne dissociation occurs readily, as seen by the paucity of benzyne coordinated uranium complexes.^{30, 31} Concomitant formation of 1,2,4,5-tetrafluoro-3-benzyl-benzene and the substituted benzyne supported the hypothesis that two reaction pathways were occurring for the initial C-F activation. Interestingly, ¹⁹F NMR spectroscopy showed unreacted substrate (>60%) remained in the NMR tube experiment despite complete conversion to **1-F₂**. Using a sub-stoichiometric amount (0.25 equiv) of pentafluorobenzene again resulted in full conversion to **1-F₂**, albeit at a slower rate. Thus, multiple C-F activation events occur at each substrate molecule.

Monitoring the reaction between **1-Bz** and pentafluorobenzene by ¹H, ¹¹B, and ¹⁹F NMR spectroscopy showed complete conversion of **1-Bz** to a mixture of **1-F** and an intermediate species (**1-F***) within fifteen minutes. The *in situ* ¹H NMR spectrum of **1-F*** shows 7 broad resonances (-32.13 to 12.58 ppm), as well as a new signal at 4.83 ppm in the ¹¹B NMR spectrum. Two broad resonances in the ¹⁹F spectrum at -141.64 ppm and -236.63, and a triplet at -143.81 ppm support a rotating perfluorophenyl group in **1-F***. Based on this characterization, we hypothesize **1-F*** is Tp*₂U(C₆F₅). This is consistent with the observed extrusion of toluene during the reaction, and β-fluoride elimination from **1-F*** to give both **1-F** and 3,4,5,6-tetrafluorobenzene (*vide supra*). When the sample had turned dark blue, multinuclear NMR experiments showed **1-F***, **1-F**, and **1-F₂** were present in solution.

The reaction of **1-Bz** with 2,3,5,6-tetrafluorotoluene proceeds through the analogous blue phase, and monitoring the reaction by ¹⁹F NMR spectroscopy shows the presence of an intermediate analogous to **1-F*** with two broad resonances at -126.97 and -241.82 ppm (Fig. 3). These data support the formation of an intermediate with a rotating tetrafluorotoluene ligand Tp*₂U(C₆F₄-*p*-Me), and by analogy, the proposed identity of **1-F***. Furthermore, reaction of **1-Bz** with perfluorodecalin or perfluorocyclohexene, which have no protons, proceeds directly to **1-F₂** with no visible or spectroscopic evidence to support formation of a **1-F***-analogue. Instead, **1-Bz** reacts quickly with these cyclic substrates, cleanly generating **1-F₂** in good yields (68, 74%, respectively) in one hour. In these cases, extrusion of bibenzyl was noted. Interestingly, full conversion to **1-**

F₂ was successful with sub-stoichiometric quantities of these substrates, once again supporting that multiple C-F activation events occur per substrate molecule.

Under these conditions, **1-Bz** readily activates both *sp*² and *sp*³ hybridized C-F bonds, with the exception of those in the benzylic position of α,α,α-trifluorotoluene, or with linear fluorinated alkyls, such as perfluorohexane and 1-fluoropentane. This is notable given that *sp*² hybridized C-F bonds have higher bond strengths than their *sp*³ hybridized counterparts. For instance, complex **1-Bz** reacts rapidly with hexafluorobenzene (C-F bond strength = 154 kcal/mol), but not at all with α,α,α-trifluorotoluene or perfluorohexane (C-F bond strengths <125 kcal/mol).^{32, 33} An increase in the degree of fluorination in aromatic substrates facilitates the C-F bond activation by **1-Bz**, despite the fact that this results in increased C-F bond strengths. This observation is likely due to the decrease in reduction potential of the substrate that accompanies the increase in electron-withdrawing fluorine substituents.^{34, 35} Similar reactivity was noted by Andersen for the lanthanide complex Cp*₂Yb, which activates the C-F bonds of perfluorobenzene, but is inert towards perfluoroethane.³⁶ Of note for **1-Bz** is the qualitative positive correlation between the degree of fluorination of aromatic substrates and their reactivities. Analogously, a correlation between substrate electron affinity and substrate reactivity was also noted by Andersen; those substrates having higher electron affinities were more reactive than those having lower electron affinities. For **1-Bz**, only in the case of aromatic C-F bond activation was the corresponding C-C bond formation between the substrate molecule and benzyl group noted, despite the low reduction potential and high reactivity towards substrates such as perfluorodecalin.



Scheme 1. Synthesis of **1-F₂** from **1-Bz** and pentafluorobenzene. **1-F** is produced via two competing pathways. Tetrafluorobenzene is trapped by anthracene to form 1,2,3,4-tetrafluorotriptycene.

Another interesting observation made during the course of these studies was that **1-F** activates the *sp*³ hybridized C-F bonds in α,α,α-trifluorotoluene and perfluorohexane. These substrates do not react with **1-Bz** at 55 °C over long reaction times, but slowly convert **1-F** to **1-F₂** at ambient temperature. Conversely, **1-F** cannot activate the C-F bonds of perfluorobenzene or pentafluorobenzene, as indicated by negligible conversion to **1-F₂** after 24 hrs of stirring at ambient temperature. The lack of reactivity with these substrates is in sharp contrast to their reactivity with **1-Bz**, which activates both.

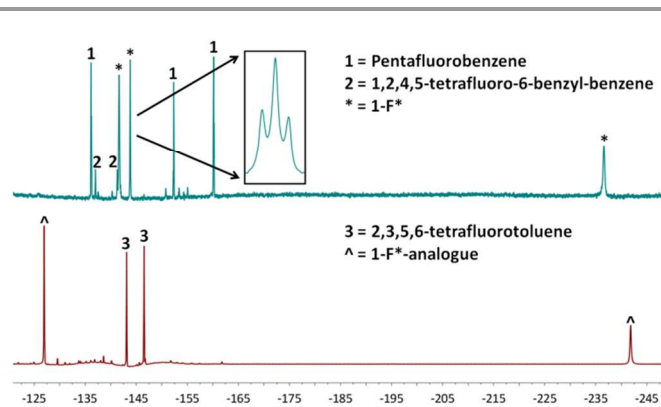


Fig. 3 ^{19}F NMR spectra (ppm) monitoring the reactions of **1-Bz** with pentafluorobenzene (top, 40 min. time point), and **1-Bz** with 2,3,5,6-tetrafluorotoluene (bottom, 60 min. time point) supporting the symmetry of the of the bound, fluorinated intermediate species. Inset shows the triplet resonance for the F at the *p*-position of **1-F***, $\text{Tp}^*\text{U}(\text{C}_6\text{F}_5)$.

In summation, the uranium(III) benzyl species, **1-Bz**, activates strong C-F bonds readily, while weaker C-F bonds remain intact. Through this process, two new low-valent uranium fluoride complexes were generated, **1-F** and **1-F₂**, and their formation was found to be substrate dependant. Isolation and characterization of **1-F** is significant, as this is the first example of a terminal trivalent uranium fluoride.

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Notes and references

† Electronic Supplementary Information (ESI) available: Experimental procedures, multinuclear NMR data, X-ray crystallographic data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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