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Synthesis of low-valent uranium fluorides by C–F bond activation⁺

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The uranium(III) alkyl, Tp*₂UCH₂Ph (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*₂UF₂, were isolated and characterized by ¹H, ¹³C, ¹¹B 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 UF₆ in the nuclear fuel cycle.⁸

An early discovery 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, $Cp^{Me}_{3}U(CMe_{3})$ ($Cp^{Me} = \eta^{5}$ -MeC₅H₄), with fluorinated substrates. Treating $Cp^{Me}_{3}U(CMe_{3})$ with two equivalents of hexafluorobenzene in toluene at ambient temperature produced the uranium(rv) fluoride, $Cp^{Me}_{3}UF$, and the C–C coupled product, $C_{6}F_{5}CMe_{3}$.⁹ Inspired by this significant result, we sought to determine if similar C–F bond scission would be possible with the trivalent uranium alkyl, $Tp*_{2}UCH_{2}Ph$ (**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, ¹³C, and ¹¹B NMR spectroscopies, X-ray crystallography, and electronic absorption spectroscopy, while the

organic products have been confirmed using multinuclear NMR spectroscopy and mass spectrometry.

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-*Tp* CH₃ 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 (X = Cl, Br, I) series reported by Takats and co-workers,^{10,11} the product was assigned as Tp*₂UF (**1-F**, 94%). Analysis of the



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Fig. 1 Molecular structures of **1-F** (left) and **1-F**₂ (right), with ellipsoids displayed at 30% probability level. Selected 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-F**₂ 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-F**₂: 89.7(3)°.

organics by ¹H and ¹⁹F 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 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 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(m) = 0.96 Å, U(m) = 1.03 Å). Monomeric 1-F is reminiscent of the symmetric U(III) dimer, $[Cp''_2UF]_2$ ($Cp'' = 1,3-(Me_3Si)_2\eta^5-C_5H_3$), 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



Scheme 1 Synthesis of $1-F_2$ from 1-Bz and pentafluorobenzene. 1-F is produced via two competing pathways. Tetrafluorobenzyne is trapped by anthracene to form 1,2,3,4-tetrafluorotriptycene.

in the formation of **1-F** and the C–C coupled product, 1,2,3,4,5pentafluoro-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, 1,2,4,5tetrafluoro-3-benzyl-benzene, isolated in low yield (27%).

An X-ray crystallographic analysis of $1-F_2$ was performed on light brown crystals grown by slow diffusion of a hexane/pentane (2:1) solution into a concentrated $1-F_2$ /THF solution at -35 °C. Refinement of the data confirmed the assignment of $1-F_2$ (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. $1-F_2$ 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,



Fig. 2 Electronic absorption spectra of 1-F (purple) and 1-F_2 (tan) recorded in THF at 23 °C. Solvent overtones between 1670–1750 nm have been removed.

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-F**₂ are shorter than those in Kiplinger's uranium(IV) difluoride Cp*₂UF₂(NC₅H₅) (U–F = 2.146 Å),²⁰ likely due to the steric demand of the pyridine ligand. The distances in **1-F**₂ are on the order of those in other neutral uranium(IV) complexes ([Cp″₂UF₂]₂,¹⁶ Cp*₂U(O-2,6-iPr₂-C₆H₃)(F),²¹ Cp₃UF,²² Cp*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 midintensity, 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 $1-F_2$, 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 $100 \text{ M}^{-1} \text{ cm}^{-1}$ 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 ($< 20 \text{ cm}^{-1} \text{ M}^{-1}$) 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 $1-F_2$ 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 $1-F_2$. During the reaction, the deprotonated pentafluorobenzene undergoes β -fluoride elimination to generate the benzyne intermediate, 3,4,5,6-tetrafluorobenzyne,²⁹ which can be trapped by repeating the reaction 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-tetrafluorobenzyne (*vide supra*). When the sample had turned dark blue, multinuclear NMR experiments showed **1-F**^{*}, **1-F**, and **1-F**₂ 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 $1-F_2$ 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 sp² hybridized C-F bonds have higher bond strengths than their sp³ hybridized counterparts. For instance, complex 1-Bz reacts rapidly with hexafluorobenzene (C-F bond strength = 154 kcal mol⁻¹), but not at all with α, α, α -trifluorotoluene or perfluorohexane (C-F bond strengths < 125 kcal mol⁻¹).^{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



Fig. 3 ¹⁹F 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***, $Tp*_2U(C_6F_5)$.

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 and benzyl group noted, despite the low reduction potential and high reactivity towards substrates such as perfluorodecalin.

Another interesting observation made during the course of these studies was that **1-F** activates the sp³ 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-F**₂ at ambient temperature. Conversely, **1-F** cannot activate the C–F bonds of perfluorobenzene or pentafluorobenzene, as indicated by negligible conversion to **1-F**₂ after 24 h 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.

In summation, the uranium(m) 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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