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Organometallic uranium(IV) fluoride complexes: preparation using protonolysis chemistry and reactivity with trimethylsilyl reagents†

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Reaction of the uranium alkyl complex $(C_5Me_5)_2UMe_2$ (1) with $Et_3N\cdot 3HF$ in toluene in the presence of a donor ligand (pyridine or trimethylphosphine oxide) results in gas evolution and the formation of the uranium(IV) difluoride complexes $(C_5Me_5)_2UF_2(L)$ (L = NC₅H₅ (2), Me₃P=O (3)). Similarly, reaction of $(C_5Me_5)_2U[\kappa^2-(C,N)-CH_2Si(CH_3)_2N(SiMe_3)]$ (5) with $Et_3N\cdot 3HF$ in toluene gives the uranium(IV) amide-fluoride complex $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (6). The fluoride complex $(C_5Me_5)_2UF_2(NC_5H_3)$ (2) shows versatile reaction chemistry with a variety of trimethylsilyl reagents and demonstrates that the U–F bond provides an attractive synthetic strategy for accessing new functional groups that are not available from alkoxide or chloride complexes.

Introduction

Although organometallic fluoride complexes are well known for the transition metals¹⁻⁴ and main group metals,⁵⁻⁷ they are still rare for the actinides.⁸ To date, less than 25 organometallic fluoride complexes containing actinide metals have been reported with the majority featuring uranium as the metal center.⁹⁻²⁸ Progress in the field has been hampered by a lack of general synthetic routes to actinide-fluorides. Early work focused on the synthesis of $(C_5H_5)_3An$ -F (An = Th, U, Np) complexes, but many of these accounts are missing synthetic details and characterization data.^{8,19} Generally speaking, the early synthetic approaches are not attractive and tend to be inconsistent with variable yields.

In recent years, reliable strategies for the preparation of well-defined metallocene uranium(III, IV, and V) fluorides have been developed. For the metallocene Cp'₃U–F class of compounds, Andersen and co-workers exploited redox chemistry and showed that (Me₃SiC₅H₄)₃U reacts with AgF, COF₂ or Ph₃CF to form (Me₃SiC₅H₄)₃U–F in good yields.¹⁹ Atom-abstraction chemistry can also be used to access this class of compounds, and (MeC₅H₄)₃U('Bu) reacts with several fluorocarbons to give (MeC₅H₄)₃UF in high yields.^{18,19}

Similar advances have been made for bent metallocene uranium fluorides. For example, Andersen and co-workers demonstrated that the uranium(IV) difluoride complexes $(1,3-^{1}Bu_2C_5H_3)_2UF_2^{21}$ [{1,3-(Me_3Si)_2C_5H_3}_2UF(\mu-F)]_2^{21} and (1,2,4-^{1}Bu_3C_5H_2)_2UF_2^{24} can be prepared in high yields by reaction of BF₃·OEt₂ with the corresponding Cp'_2UX₂ (X = NMe₂, OMe or Me) complexes. Both Andersen and Lappert have reported that the uranium(III) fluorides [(1,3-R_2C_5H_3)_2UF]_2 (R = 'Bu or SiMe_3) are accessible in high yields by reduction of the corresponding uranium(IV) difluoride complexes.

alkoxide or chloride complexes.

Results and discussion

Synthesis and characterization of uranium fluoride complexes

that the uranium(v)-imido fluorides $(C_5Me_5)_2U(=NAr)(F)$ (Ar = 2,4,6-'Bu₃-C₆H₂, 2,6-'Pr₂-C₆H₃) can be prepared by oxidation of

the corresponding uranium(IV) imido precursors with CuF₂.^{26,29}

A consequence of this scarcity is that very little is known about

the U-F bond or its chemistry. In fact, there are only a few

early accounts that report well-characterized reactions of UF₆

with MeOH and Me₃Si-OMe to give (MeO)UF₅³⁰ and U(OMe)₆,³¹

respectively. Recently, we observed that the uranium(IV) fluoride

complex (C₅Me₅)₂U(O-2,6-^{*i*}Pr₂C₆H₃)(F) reacts with Me₃Si-CF₃,

to give Me₃Si–F quantitatively and regenerate $(C_5Me_5)_2U(O-2,6-$

 ${}^{i}Pr_{2}C_{6}H_{3})(F)$ ²⁸ Evidence suggested that the generated U-CF₃

moiety is unstable and undergoes α -F elimnation to give the

Given these initial results, we have been investigating new

methods for the synthesis of organometallic uranium fluoride

complexes to explore the chemistry of the U-F bond. In this

contribution, we demonstrate that protonolysis chemistry with

Et₃N·3HF can be used to prepare metallocene uranium(IV) diflu-

oride and monofluoride complexes and that these new complexes

react with Me₃Si-X reagents. In addition, we describe parallel

studies with uranium(IV) alkoxide and chloride complexes and

show that the U-F bond provides an attractive synthetic strategy

for accessing new functional groups that are not available from

observed fluoride complex and presumably difluorocarbene.

As shown in Scheme 1, reaction of $(C_5Me_5)_2UMe_2$ (1)³² in toluene with 2 equiv of HF from Et₃N·3HF results in gas evolution, consistent with the generation of methane, and the formation of a yellow solution. From this solution, depending on the donor ligand added, $(C_5Me_5)_2UF_2(NC_5H_5)$ (2) or $(C_5Me_5)_2UF_2(O=PMe_3)$ (3) can be isolated as a green-brown or yellow-green solid, respectively, in 65% or 50% yield.

Complexes 2 and 3 represent a new class of monometallic uranium difluoride complexes that feature the $(C_5Me_5)_2U$ framework. Due to the basicity of the fluoride ligand, a characteristic

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[†] Electronic supplementary information (ESI) available: NMR spectra for fluoride complexes **2**, **3**, and **6**. CCDC reference numbers 763865 and 763866. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001911a



Scheme 1

feature of organometallic fluoride complexes is the tendency to form fluoride bridges between two or more metal atoms. Indeed, most of the structurally characterized metallocene difluoride complexes are dimeric with fluoride bridges. The exceptions are $(1,3-{}^{\prime}Bu_{2}C_{5}H_{3})_{2}UF_{2}$,²¹ and $(1,2,4-{}^{\prime}Bu_{3}C_{5}H_{2})_{2}UF_{2}$,²⁴ which employ bulky cyclopentadienyl ligands. In the present systems, the added donor ligands, pyridine (NC_5H_5) and trimethylphosphine oxide $(Me_3P=O)$, help to sterically saturate the uranium metal center and prevent dimer formation in both the solid-state (vide infra) and solution. The ¹H NMR spectrum of 2 in C_6D_6 is simple and consists of a single resonance at δ –2.41 for the C₅Me₅ protons. Consistent with reversible coordination to the uranium metal center, the resonances for the pyridine ligand are not visible. The trimethylphosphine oxide ligand has a stronger interaction with the paramagnetic uranium(IV) metal center in complex 3. Thus, addition of Me₃P=O to a C_6D_6 solution of the pyridine adduct 2 gives complex 3 with release of free pyridine (δ 8.53, 7.10, and 6.77). The ¹H NMR spectrum of $(C_5Me_5)_2UF_2(O=PMe_3)$ (3) in C_6D_6 shows a singlet at δ -2.46 for the C_5Me_5 protons and a doublet at δ -17.87 corresponding to the methyl groups on the coordinated Me₃P=O ligand. Complex 3 also gives a multiplet in the ³¹P NMR spectrum at δ –34.76. Presumably because they are directly bound to the paramagnetic U^{IV} center, resonances were not seen for the terminal fluoride ligands in ¹⁹F NMR spectra for either complex 2 or 3.

Single crystals of complex 2 suitable for X-ray diffraction were obtained from a THF/(Me₃Si)₂O solution at -30 °C. The molecular structure is shown in Fig. 1 and reveals a typical bent-metallocene framework with the two fluoride ligands and coordinated pyridine contained within the metallocene wedge. The coordinated pyridine is sandwiched between the two fluoride ligands with $F-U-F = 151.1(3)^{\circ}$ and $F-U-N = 75.58(14)^{\circ}$. At 2.146(5) Å, the U-F bond distance observed in 2 falls in the range of bond distances observed for the handful of other structurally characterized U^{IV} terminal fluoride complexes $(e.g., [\{1,3-(Me_3Si)_2C_5H_3\}_2UF(\mu-F)]_2, U-F = 2.073(5) \text{ Å};^{21}(1,2,4 ^{\prime}Bu_{3}C_{5}H_{2}u_{2}UF_{2}, U-F = 2.081(5) \text{ Å}, ^{24}(1,3-^{\prime}Bu_{2}C_{5}H_{3})_{2}UF_{2}, U-F =$ 2.086(2) Å;²¹ (C₅H₅)₃U-F, U-F = 2.106(12) Å;¹³ (C₅Me₅)₂U(O- $2,6-Pr_2C_6H_3)(F), U-F = 2.108(6) \text{ Å};^{28} (C_5Me_5)_3U-F, U-F =$ 2.43(2) Å).²³ Likewise, the U–N_{pyridine} bond distance (2.581(8) Å) is comparable to those observed for other U^{IV}-pyridine coordination complexes (e.g., U(OTf)₃(OH)(py)₄, U–N = 2.579(3)-2.616(3) Å;³³ $(C_8H_8)UCl_2(py)_2$, U-N = 2.639(5), 2.644(6) Å;³⁴ UI₄(py)₄, U- $N = 2.586(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ Å};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{SPh})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ U}(\text{Ph})_4(\text{py})_3, \text{ U-N} = 2.563(5) - 2.634(5) \text{ A};^{35} \text{ U}(\text{Ph})_4(\text{Ph})_4(\text{Ph})_4(\text{Ph})_4(\text{Ph})_5(\text{Ph}$ 2.629(5) Å).36

The fluoride complexes are air- and water-sensitive compounds and the presence of adventitious water during crystallization can lead to the formation of an interesting bimetallic uranium(IV)



Fig. 1 Molecular structure of $(C_5Me_5)_2UF_2(NC_5H_5)$ (2) with thermal ellipsoids projected at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): U(1)–F(1), 2.146(5); U(1)–N(1), 2.581(8); F(1)–U(1)–F(1), 151.1(3); F(1)–U(1)–N(1), 75.58(14).

fluoride bridging oxo complex, $[(C_5Me_5)_2UF]_2(\mu-O)$ (4). The formation of this complex is easily detected by ¹H NMR spectroscopy in C_6D_6 , which shows two singlets at δ 3.62 and -1.17 for the two distinct C_5Me_5 groups. Unfortunately, all efforts to rationally synthesize $[(C_5Me_5)_2UF]_2(\mu-O)$ (4) were unsuccessful.

The structure of complex 4 is given in Fig. 2 and shows molecular C₂ symmetry with the rotational axis perpendicular to the U-O-U axis. Each U^{IV} ion adopts a pseudotetrahedral geometry with a fluoride ligand and the bridging oxo ligand contained within the metallocene wedge. The two U-F bonds are twisted 83.2° with respect to each other across the U-O-U axis. The U-F bond distances (2.121(2), 2.123(2) Å) compare well with those observed in complex 2. Not surprisingly, there is less steric crowding in $[(C_5Me_5)_2UF]_2(\mu-O)$ (4) compared to reported tris(cyclopentadienyl)uranium μ -oxo structures. Thus, the U-O-U bond angle of 163.96(15)° is bent compared to the linear bridges found in [(Me₃SiC₅H₄)₃U]₂(µ-O)³⁷ and $[(C_5H_5)_3U]_2(\mu$ -O),³⁸ with the U–O bond distances of 2.118(3) Å and 2.124(3) Å being comparable to those reported for $[(Me_3SiC_5H_4)_3U]_2(\mu-O)$ (2.1053(2) Å),³⁷ $[(C_5H_5)_3U]_2(\mu-O)$ (2.0881(4) Å),³⁸ and $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{U}(\mu-\text{O})]_3$ (2.05(1)–2.12(1) Å).³⁹



Fig. 2 Molecular structure of $[(C_5Me_5)_2 UF]_2(\mu-O)$ (4) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): U(1)–F(1), 2.121(2); U(1)–O(1), 2.118(3); U(2)–F(2), 2.123(2); U(2)–O(1), 2.124(3); F(1)–U(1)–O(1), 99.72(10); F(2)–U(2)–O(1), 99.09(10); U(1)–O(1)–U(2), 163.96(15); U(1) ··· U(2), 4.201.

Extension of the Et₃N·3HF protonolysis chemistry to uranium metallacycles provides an entry into mixed-ligand uranium fluoride complexes. As shown in Scheme 2, reaction of Et₃N·3HF with the uranium metallocycle $(C_5Me_5)_2U[\kappa^2-(C,N)-$ CH₂Si(CH₃)₂N(SiMe₃)] (**5**)⁴⁰ gives the monometallic mixed-ligand



uranium amide-fluoride complex $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (6). This reaction is challenging to control, even at low temperatures, and the formation of complex 6 is accompanied by additional products. However, the ¹H NMR spectrum of $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (6) in C_6D_6 is consistent with that obtained for 6 by oxidation of $(C_5Me_5)_2 U[N(SiMe_3)_2]$ with CuF₂, and consists of a singlet at δ 5.95 for the C₅Me₅ protons, with the local symmetry of the N(SiMe₃)₂ ligand disrupted due to the presence of a U····H-C agostic⁴¹ interaction that is maintained in solution between the methyl groups and the uranium center. The ¹H NMR spectrum of 6 thus shows three different $SiMe_3$ environments: the freely rotating SiMe₃ group appears as a singlet at δ –0.78, while the other SiMe₃ group is held in a rigid conformation giving rise to two signals at δ –0.33 for the SiMe₂ protons and δ –58.26 for the agostic SiMe group. The structurally related and characterized uranium(IV) iodide derivative $(C_5Me_5)_2 U[N(SiMe_3)_2](I)$ displays a similar ¹H NMR spectrum.⁴⁰

Reaction chemistry with trimethylsilyl reagents

Reaction of the known uranium fluoride complex 7 with azidotrimethylsilane (Me_3Si-N_3) at room temperature for 12 h cleanly affords the known uranium(IV) azide (8) along with elimination of Me_3Si-F (Scheme 3).



Complex **8** has been previously prepared by gold-based oxidative functionalization of the trivalent uranium compound $(C_5Me_5)_2U(O-2,6-iPr_2C_6H_3)$ (THF) using $(Ph_3P)Au-N_3$.²⁸ In marked contrast, the uranium(IV) mixed aryloxide-chloride complex $(C_5Me_5)_2U(O-2,6-iPr_2C_6H_3)$ (Cl) (9) does not show any reaction with Me₃Si-N₃.

Similarly, the uranium difluoride complex **2** also demonstrates interesting and distinct chemistry with a variety of trimethylsilyl reagents (Scheme 4). For example, reaction of $(C_5Me_5)_2UF_2(NC_5H_5)$ (2) with excess trimethylsilyl cyanide (Me₃Si-CN) results in a color change from yellow-green to red, to yield the known uranium(IV) dicyanide complex **10**. Complex **10** was originally prepared by Ephritikhine and co-workers by reaction of $(C_5Me_5)_2UI_2$ or $(C_5Me_5)_2U(OTf)_2$ with KCN for use in the synthesis of linear metallocene complexs.⁴²



Scheme 4

The uranium difluoride complex **2** also reacts with excess Me_3Si-N_3 , which provides a convenient method for accessing the dark red trimetallic azide species $[(C_5Me_5)_2U(N_3))(\mu-N_3)]_3$ (11). As reported by Evans and co-workers, this unusual multimetallic structure was originally accessed from the reaction between $(C_5Me_5)_2UCl_2$ (12) and NaN_3 .⁴³ Again, neither the corresponding uranium(IV) dichloride $(C_5Me_5)_2UCl_2$ (12) or the bis(aryloxide) $(C_5Me_5)_2UCPl_2$ (13)⁴⁴ complexes display any productive reactivity towards Me_3Si-CN or Me_3Si-N_3 , even under forcing conditions (110 °C, 12h). In fact, the aryloxide complex 13 decomposes under these reaction conditions.

Interestingly, the Me₃Si–F elimination chemistry is only observed using the pyridine adduct $(C_5Me_5)_2UF_2(NC_5H_5)(2)$ and not the trimethylphosphine oxide complex $(C_5Me_5)_2UF_2(O=PMe_3)$ (3). Presumably, this is due to the tighter binding of the Me₃P=O ligand to the uranium(IV) metal center compared to the softer pyridine, as noted in the ¹H NMR studies for both difluoride complexes.

Efforts were made to extend the Me₃Si–F elimination chemistry to the mixed amide-fluoride complex $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (6). However, no reaction was observed between 6 and Me₃Si– N₃ even under forcing conditions (110 °C, 12h). Since the azide complex $(C_5Me_5)_2U[N(SiMe_3)_2](N_3)$ is accessible using gold-based oxidative functionalization chemistry,²⁸ this observation suggests that the Me₃Si–F elimination is prevented by steric crowding at the metal center due to the bulky bis(trimethylsilyl)amide ligand.

Conclusions

The isolation of complexes $(C_3Me_5)_2UF_2(NC_5H_5)$ (2), $(C_5Me_5)_2UF_2(O=PMe_3)$ (3), and $(C_3Me_5)_2U[N(SiMe_3)_2](F)$ (6) demonstrate that uranium alkyl complexes and Et₃N·3HF provide an excellent entry point for accessing uranium fluoride complexes. In contrast to the corresponding chlorides and alkoxides, uranium fluoride complexes show versatile reaction chemistry with a variety of trimethylsilyl reagents to generate U–C and U–N linkages. This work shows that the U–F bond can be exploited for accessing new chemistry that is simply not available from classic alkoxide or chloride complexes. We are currently exploring the generality of this chemistry as well as investigating new methods for making uranium fluoride bonds.

Experimental

General considerations

Reactions and manipulations were performed at 20 °C in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train or using standard Schlenk techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer at ambient temperature. Chemical shifts for ¹H NMR spectra were referenced to solvent impurities and ³¹P NMR spectra were referenced to external phosphoric acid. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, Columbia Analytical Services, or Midwest Microlab LLC.

Materials

Except where otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Benzene- d_6 (Aldrich) and pyridine- d_5 (Cambridge) were purified by passage through activated alumina and were stored over activated 4 Å molecular sieves prior to use. Celite (Aldrich), alumina (Brockman I, Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves prior to use. $(C_5Me_5)_2UMe_2$ (1),³² $(C_5Me_5)_2U[\kappa^2 - (C,N) - CH_2Si(CH_3)_2N(SiMe_3)]$ (5),⁴⁰ $(C_5Me_5)_2U(O 2,6^{-i}Pr_2C_6H_3(F)$ (7),²⁸ $(C_5Me_5)_2U(O-2,6^{-i}Pr_2C_6H_3)(THF),^{45}$ $(C_5Me_5)_2U[N(SiMe_3)_2]$,⁴⁶ and $(C_5Me_5)_2UCl_2$ (12)³² were prepared according to literature procedures.

Caution: Depleted uranium (primary isotope ²³⁸U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47 × 10° years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α - and β -counting equipment.

Caution: Me_3Si-N_3 should always be handled with caution under anhydrous conditions, as hydrolysis can lead to formation of toxic HN_3 . Likewise, hydrolysis of Me_3Si-CN , can result in the formation of toxic HCN, and should be handled under anhydrous conditions under an inert atmosphere, or in a well ventilated hood. While we have not observed any explosive behavior with $(C_5Me_5)_2U(O-2,6^{-i}Pr_2C_6H_3)(N_3)$ (8) or $[(C_5Me_5)_2U(N_3)(\mu-N_3)]_3$ (11), all azide complexes are potentially shock sensitive and should be handled with great care using personal protection precautions.

Synthesis of $(C_5Me_5)_2UF_2(NC_5H_5)$ (2). A 125-mL side-arm flask equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (1) (1.13 g, 2.10 mmol) and toluene (35 mL). NEt₃·3HF (0.226 g, 1.40 mmol) was added with stirring by pipette as a solution in toluene (15 mL). Pyridine (0.332 g, 4.20 mmol) was then added, and the reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celitepadded coarse porosity fritted filter and volatiles were removed under reduced pressure to give **2** as a green-brown solid (0.85 g, 1.36 mmol, 65%). X-ray quality crystals of **2** were obtained by recrystallization from a concentrated THF/(Me₃Si)₂O solution at -37 °C. ¹H NMR (C₆D₆, 298 K): δ -2.41 (s, 30H, C₅Me₅).

Multiple attempts to obtain satisfactory elemental analysis have failed presumably because of the thermal sensitivity of **2**.

Synthesis of $(C_5Me_5)_2UF_2(O=PMe_3)$ (3). A 125-mL side-arm flask equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (1) (2.5 g, 4.6 mmol) and toluene (40 mL). NEt₃·3HF (0.5 g, 3.09 mmol) was added with stirring as a solution in toluene (10 mL). Trimethylphosphine oxide (0.48 g, 4.6 mmol) was then added, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celitepadded coarse porosity fritted filter and the volatiles were removed under reduced pressure to give **3** as a yellow solid (1.47 g, 2.3 mmol, 50%). Analytically pure samples of **3** were obtained by recrystallization from a concentrated Et₂O solution at -30 °C. ¹H NMR (C₆D₆, 298 K): δ -2.46 (s, 30H, C₅Me₅), -17.87 (d, J =9 Hz, 9H, O=PMe₃). ³¹P NMR (C₆D₆, 298 K): δ -34.76. Anal. Calcd for C₂₃H₃₉F₂OPU (mol. wt. 638.55 g mol⁻¹): C, 43.26; H, 6.16. Found: C, 43.50; H, 5.49.

Synthesis of $(C_5Me_5)_2U[N(SiMe_3)_2](F)$ (6). A 125-mL sidearm flask equipped with a stir bar was charged with $(C_5Me_5)_2U[N(SiMe_3)_2]$ (0.400 g, 0.598 mmol) and toluene (50 mL). CuF₂ (0.304 g, 2.99 mmol) was added as a solid to the stirring solution resulting in an immediate color change from green-black to dark red. The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celitepadded coarse porosity fritted filter and the volatiles were removed under reduced presure to give **6** as dark red crystals (0.383 g, 0.557 mmol, 93%). ¹H NMR (C₆D₆, 298 K): δ 5.95 (s, 30H, C₅Me₅), -0.33 (s, 6H, SiMe₂), -0.78 (s, 9H, SiMe₃), -58.26 (s, 3H, SiMe). Anal. Calcd for C₂₆H₄₈FNSi₂U (mol. wt. 687.86 g mol⁻¹): C, 45.40; H, 7.03; N, 2.04. Found: C, 45.62; H, 7.11; N, 1.93.

Synthesis of $(C_5Me_5)_2U(O-2,6^{-j}Pr_2C_6H_3)(N_3)$ (8). A 20 mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2U(O-2,6^{-j}Pr_2C_6H_3)(F)$ (7) (0.050 g, 0.071 mmol) and ~ 2 mL of C_6D_6 . To this stirring solution was added an excess of Me₃Si–N₃ (0.040 g, 0.355 mmol) as a solution in ~ 0.5 mL C_6D_6 . Spectroscopic characterization matches literature data:²⁸ ¹H NMR (C_6D_6 , 298 K): δ 7.69 (1H, d, J = 8 Hz, m-Ar-H), 7.00 (d, J = 8 Hz, 1H, m-Ar-H), 6.59 (t, J = 8 Hz, 1H, p-Ar-H), 6.05 (s, 30H, C_5Me_5), -5.56 (d, J = 4 Hz, 6H, ¹Pr– CH_3), -13.18 (s, 6H, ¹Pr– CH_3), -32.60 (m, 1H, ¹Pr–CH).

Synthesis of $(C_5Me_5)_2U(O-2,6^{-i}Pr_2C_6H_3)(Cl)$ (9). A 125-mL side-arm flask equipped with a stir bar was charged with (C5Me5)2U(O-2,6-iPr2C6H3)(THF) (0.250 g, 0.330 mmol) and toluene (50 mL). CuCl (0.243 g, 1.65 mmol) was added, resulting in an immediate color change from green to red, and the reaction mixture was allowed to stir at room temperature. After 18 h, the reaction mixture was filtered through a Celite-padded coarse porosity fritted filter, and the volatiles were removed under reduced pressure. The red residue was extracted into hexane (50 mL) and filtered through a Celite-padded coarse porosity fritted filter. The filtrate was collected and the volatiles were removed under reduced pressure to give 9 as a dark red solid (0.204 g, 0.283 mmol, 86%). ¹H NMR (C₆D₆, 298 K): δ 8.47 (1H, d, J = 8 Hz, *m*-Ar-*H*), 8.38 (d, J = 7 Hz, 1H, *m*-Ar-H), 7.83 (s, 30H, C₅Me₅), 7.07 (t, J =8 Hz, 1H, p-Ar-H), -5.96 (s, 6H, 'Pr-CH₃), -12.31 (s, 6H, 'Pr-CH₃), -35.49 (m, 1H, ^{*i*}Pr-CH), -44.44 (m, 1H, ^{*i*}Pr-CH). Anal. Calcd for $C_{32}H_{47}CIOU$ (mol. wt. 721.20 g mol⁻¹): C, 53.29; H, 6.57. Found: C, 51.08; H, 6.22.

 $(C_5Me_5)_2U(CN)_2$ (10). A 20 mL scintillation vial equipped with a stir bar was charged with 2 (0.050 g, 0.080 mmol) and ~1.5 mL NC₅D₅. To this solution was added excess Me₃Si– CN (0.025 g, 0.252 mmol) dissolved in ~0.5 mL NC₅D₅. The reaction mixture was stirred at room temperature for 15 h, during which time the color changed from green-brown to dark red. Spectroscopic characterization matches literature data:^{42 1}H NMR (NC₅D₅, 298 K): δ 8.07 (s, 30H, C₅Me₅). Note: The presence of excess Me₃Si-CN leads to the formation of adducts of 10 (C₅Me₅)₂U(CN)₂(NCSiMe₃)_x, which appear as a broad singlet at δ 9.94.

[(C₅Me₅)₂U(N₃)(μ-N₃)]₃ (11). A 20 mL scintillation vial equipped with a stir bar was charged with 2 (0.047 g, 0.075 mmol) in ~1.5 mL C₆D₆. To this stirring solution was added excess Me₃Si–N₃ (0.085 g, 0.750 mmol) dissolved in ~0.5 mL C₆D₆. The reaction mixture was stirred at room temperature for 20 h, during which time the color changed from green-brown to dark red. Spectroscopic characterization matches literature data:⁴³ ¹H NMR (C₆D₆, 298 K): δ 0.62 (s, 30H, C₅Me₅).

X-ray crystallography

The crystal structures of 2 and 4 were determined similarly. Crystals were mounted in a nylon cryoloop using Paratone-N oil under an argon gas flow. The data were collected on a Bruker D8 APEX II charge-coupled-device (CCD) diffractometer, with a KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with a graphite monochromatized Mo-Ka Xray source ($\lambda = 0.71073$ Å), with MonoCap X-ray source optics. Hemispheres of data were collected using ω scans. Data collection and initial indexing and cell refinement were handled using APEX II software.⁴⁷ Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.48 The data were corrected for absorption using the SADABS program.⁴⁹ Decay of reflection intensity was monitored by analysis of redundant frames. The structures were solved using Direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Residual electron density originating from solvent contributions was removed using SQUEEZE/PLATON for 4.50 Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.⁵¹ Additional details regarding data collection and software versions are provided in the CIF files.

Crystal data for (C₅Me₅)₂UF₂(NC₅H₅) (2). C₂₅H₃₅F₂NU, M = 625.57, orthorhombic, space group *Pnma*, a = 18.7527(17) Å, b = 13.4677(13) Å, c = 9.4862(9) Å, V = 2395.8(4) Å³, Z = 4, $D_c = 1.734$ Mg m⁻³, $\mu = 6.801$ mm⁻¹, F(000) = 1208, T = 140(1) K, 21187 measured reflections, 2929 independent ($R_{int} = 0.0706$), $R_1 = 0.0537$, w $R_2 = 0.1052$ for $I > 2\sigma(I)$. CCDC 763865.

Crystal data for $[(C_5Me_5)_2UF]_2(\mu$ -O)-toluene (4-toluene). $C_{47}H_{68}F_2OU_2, M = 1163.07$, monoclinic, space group $P2_1/c, a = 27.007(3)$ Å, b = 9.6398(10) Å, c = 17.0651(17) Å, $\beta = 102.690(1)^\circ$, V = 4334.3(8) Å³, Z = 4, $D_c = 1.782$ Mg m⁻³, $\mu = 7.505$ mm⁻¹, F(000) = 2240, T = 120(1) K, 47738 measured reflections, 10298 independent ($R_{int} = 0.0590$), $R_1 = 0.0289$, w $R_2 = 0.0644$ for $I > 2\sigma(I)$. CCDC 763866.

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