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UI_4(1,4-dioxane)$_2$, [UCl_4(1,4-dioxane)]$_2$, and UI_3(1,4-dioxane)$_{1.5}$: Stable and Versatile Starting Materials for Low- and High-Valent Uranium Chemistry

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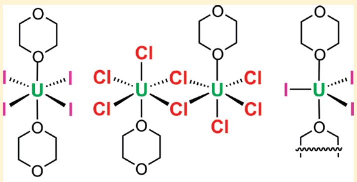
S Supporting Information

ABSTRACT: The uranium(III) and uranium(IV) iodide complexes UI_3(1,4-dioxane)$_{1.5}$ and UI_4(1,4-dioxane)$_2$ have been easily prepared in high yield by reacting uranium turnings with a 1,4-dioxane solution of iodine under mild conditions. The two complexes exhibit outstanding thermal stability and are excellent precursors to a variety of uranium(III), uranium(IV), and uranium(VI) alkoxide, amide, organometallic, and halide compounds, including a safe, room-temperature synthesis of [UCl_4(1,4-dioxane)]$_2$, which is a useful synthetic alternative to UCl_4.



Stable and Versatile Starting Materials for UI_4, UCl_4, and UI_3 Chemistry

INTRODUCTION

Uranium molecular chemistry has become a valuable tool for understanding the behavior and properties of the light actinides in a variety of applications ranging from environmental and aqueous processing to advanced materials for nuclear fuel cycles.[1,2] Inexpensive, easy, and safe access to a wide range of uranium halide starting materials is vital for continued developments in the field.

To date, $UI_3(THF)_4$[3,4] and UCl_4[5−9] have served as the most popular starting materials for synthetic uranium(III) and uranium(IV) chemistry. However, difficulties exist with the syntheses of both compounds. For example, the preparation of UCl_4 requires high temperature (140−700 °C) combinations of uranium oxides (UO_2, UO_3, or U_3O_8) and chlorinating reagents (CCl_4, S_2Cl_2, or $Cl_2C{=}C(Cl)\text{-}CCl_3$).[5−9] From this collection, the method of choice for the synthesis of UCl_4 has been the reaction of $UO_3 \cdot 2H_2O$ (or U_3O_8) with hot (190 °C) hexachloropropene, a highly toxic chemical, and special precautions must be taken to avoid uncontrolled radical reactions.[9] Another high-temperature route requires heating UH_3 with NH_4Cl at 300 °C for 30 h to initially generate $(NH_4)_2UCl_6$, which is then heated at 350 °C under high vacuum to ultimately give UCl_4.[10] The synthesis of $UI_3(THF)_4$ needs to be performed in the presence of HgI_2 at temperatures slightly below 10 °C and is usually low-yielding because of the formation of unwanted byproducts caused by the ring-opening of THF. In addition, $UI_3(THF)_4$ is thermally sensitive and must be stored at low temperature.[4]

Efforts to circumvent these issues with $UI_3(THF)_4$ and UCl_4 have appeared in modern accounts that focus on the development of new uranium(III) and uranium(IV) halide starting materials. For instance, syntheses of bare UI_3 have been developed, but they necessitate harsh conditions and/or the use of special equipment.[11−15] Reports of Lewis base adducts of UI_4 have also appeared, but many of these compounds also possess limited thermal stability or contain unsaturated ligands that are incompatible with strong nucleophiles.[16−20]

An important advance to the field was recently provided by Arnold and co-workers, who demonstrated that sonication of uranium turnings with iodine in diethyl ether gives UI_3 or $UI_4(OEt_2)_2$, depending on the stoichiometry.[21] In related work, Hayton and co-workers reported that UH_3 could be used to access $UI_4(OEt_2)_2$ in high yields by oxidation with iodine; similar oxidations with silver reagents afforded $UX_4(DME)_2$ (X = Br, Cl, OTf).[22] However, UH_3 must be prepared by reaction of uranium metal with 1 atm hydrogen at 225 °C, and both of these $UI_4(OEt_2)_2$ synthetic routes require special equipment or materials that are not available at all institutions.

Recently, we discovered that $ThCl_4$(1,4-dioxane)$_2$ could be prepared under mild conditions from $ThCl_4(H_2O)_4$, HCl, and Me_3SiCl in 1,4-dioxane.[23] A useful attribute of 1,4-dioxane is that unlike THF it does not readily undergo ring-opening. Additionally, it is a weak donor ligand and is easily displaced by stronger donor ligands such as 1,2-dimethoxyethane (DME) and THF to access $ThCl_4(DME)_2$ and $ThCl_4(THF)_{3.5}$, respectively. Herein, we show that 1,4-dioxane can also be used to prepare two new uranium(III) and uranium(IV) iodide synthons, UI_3(1,4-dioxane)$_{1.5}$ and UI_4(1,4-dioxane)$_2$. Of particular note is that these complexes are stable above ambient temperature and are useful precursors to a variety of alkoxide, amide, organometallic, and halide compounds, including a safe, room-temperature synthesis of [UCl_4(1,4-dioxane)]$_2$, which is a practical synthetic alternative to UCl_4.

RESULTS AND DISCUSSION

Reaction of uranium turnings with 2.05 equiv of iodine in 1,4-dioxane at room temperature for 7 days affords the uranium(IV)

Received: February 1, 2011
Published: March 21, 2011

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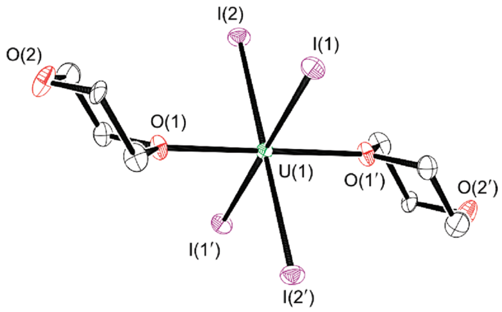


Figure 1. Molecular structure of $UI_4(1,4\text{-dioxane})_2$ (**1**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U(1)−I(1), 2.9637(11); U(1)−I(2), 2.9588(10); U(1)−O(1), 2.333(6); I(1)−U(1)−I(2), 90.31(3); I(1)−U(1)−O(1), 89.53(15); I(2)−U(1)−O(1), 89.74(16); O(1)−U(1)−O(1′), 179.999(1).

complex $UI_4(1,4\text{-dioxane})_2$ (**1**) as a red-orange solid in 95% isolated yield (eq 1). Shorter reaction times (18 h) can be achieved with mild heat (50 °C). Importantly, the synthesis of **1** can be easily performed on multigram scales and does not require the purification of iodine by sublimation or the activation of the uranium turnings by sonication or HgI_2.

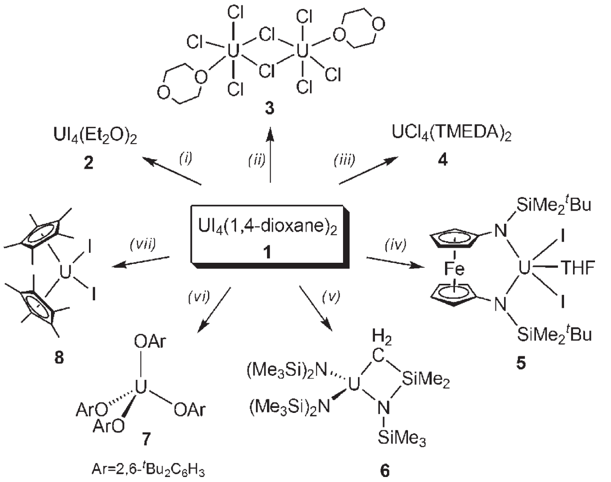
$$U^0 + 2.05I_2 \xrightarrow[\text{rt, 7 days or 50 °C, 18h}]{\text{1,4-dioxane}} \underset{\mathbf{1}}{UI_4(1,4\text{-dioxane})_2} \qquad (1)$$

Complex **1** was fully characterized by a combination of ^1H NMR spectroscopy, elemental analysis, and X-ray crystallography. The ^1H NMR spectrum of **1** at ambient temperature in C_6D_6 is simple and exhibits a broad singlet at δ 3.32 ppm, which is consistent with reversible coordination of the 1,4-dioxane to the uranium metal center.

Dark red, X-ray quality crystals of $UI_4(1,4\text{-dioxane})_2$ (**1**) were obtained from a toluene/1,4-dioxane (90:10) solution at −30 °C. The molecular structure of **1** is presented in Figure 1 and features octahedral geometry about the U(IV) metal center with *trans*-bound 1,4-dioxane molecules and four equatorial iodide ligands. There is an inversion center at uranium, and no deviation of the iodide ligands from the equatorial plane is observed. The U−I bond distances of 2.9637(11) and 2.9588(10) Å lie at the short end of the range observed for the handful of structurally characterized Lewis base adducts of UI_4 (e.g., $UI_4(N{\equiv}CPh)_4$, U−I = 3.027(1) Å;[20] $UI_4(py)_3$, U−I = 2.9558(4)−3.0438(4) Å;[19] $UI_4[O{=}C(NMe_2)_2]_4$, U−I = 2.996(3), 3.027(3) Å;[16] $UI_4(Et_2O)_2$, U−I = 2.9614(6) Å).[21] Presumably, this is due to the weaker donor strength of 1,4-dioxane. To the best of our knowledge, complex **1** represents the first structurally characterized 1,4-dioxane complex of an actinide ion. Consistent with the weaker donor strength of 1,4-dioxane, the U−O bond length of 2.333(6) Å is comparable to those observed for the diethyl ether complex $UI_4(Et_2O)_2$ (**2**) (2.366(8) Å)[21] and much longer than those reported for the *N,N,N′,N′*-tetramethylurea complex $UI_4[O{=}C(NMe_2)_2]_4$ (2.20(3), 2.17(3) Å).[16]

$UI_4(1,4\text{-dioxane})_2$ (**1**) exhibits significantly increased thermal stability compared to the related $UI_4(THF)_4$ and $UI_4(Et_2O)_2$ (**2**) systems. In fact, due to its thermal instability, $UI_4(THF)_4$ cannot be isolated.[18,24] However, it can be generated in situ at room temperature from $UI_4(N{\equiv}CMe)_4$ in THF solution but undergoes rapid ring-opening of THF.[18] The diethyl ether complex $UI_4(Et_2O)_2$ (**2**) is also thermally sensitive and undergoes loss of diethyl ether above room temperature.[21,22,25] Furthermore, $UI_4(Et_2O)_2$ (**2**) reacts with the surface of glass vials to yield $[H(OEt_2)_2][UI_5(OEt_2)]$.[25] In contrast, $UI_4(1,4\text{-dioxane})_2$ (**1**) is stable in 1,4-dioxane or toluene solution for 12 h at 80 °C without degradation and can be stored at room temperature under an inert atmosphere for at least two weeks. We attribute this greater stability to not only the higher boiling point of 1,4-dioxane, which limits loss of the coordinating ligand,[26] but also the lower susceptibility of coordinated 1,4-dioxane toward metal-mediated nucleophilic attack.

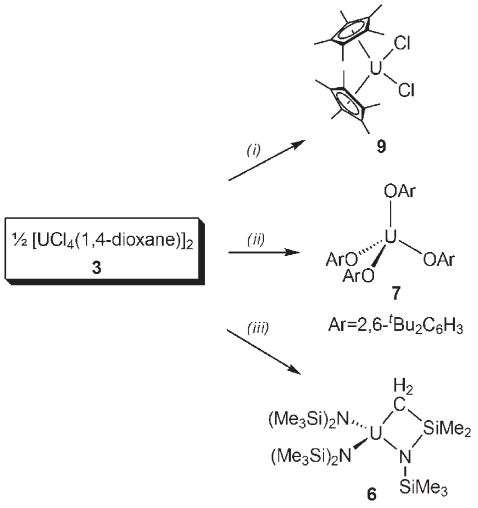
Scheme 1[a]



[a] Reagents and conditions: (i) Et_2O, rt, 1 h, 71% yield; (ii) 4 equiv HCl (4.0 M/1,4-dioxane), 1,4-dioxane, rt, 10 min, 86% yield; (iii) (1) 2.2 equiv TMEDA, toluene, rt, 18 h; (2) 5 equiv HCl (4.0 M/1,4-dioxane), rt, 4 h; (3) 5 equiv TMEDA, rt, 1 h, 91% yield; (iv) $[K_2(OEt_2)_2]fc[NSi(^tBu)Me_2]_2$, THF, −35 °C→rt, 1 h, 61% yield; (v) 4 equiv $K[N(SiMe_3)_2]$, toluene, 110 °C, 15 h, 70% yield; (vi) 4.1 equiv $K(O\text{-}2,6\text{-}^tBu_2C_6H_3)$, THF, rt, 12 h, 64% yield; (vii) 2 equiv $K(C_5Me_5)$, toluene, 110 °C, 18 h, 65% yield.

As outlined in Scheme 1, $UI_4(1,4\text{-dioxane})_2$ (**1**) is an excellent synthetic precursor to a wide range of U(IV) alkoxide, amide, organometallic, and halide complexes. Substitution of the 1,4-dioxane ligands by diethyl ether occurs by dissolving complex **1** in diethyl ether, to give $UI_4(OEt_2)_2$ (**2**)[21] in 71% isolated yield. This observation highlights the relative donor strength of diethyl ether versus 1,4-dioxane toward uranium(IV) and indicates that $UI_4(1,4\text{-dioxane})_2$ (**1**) should be a useful U(IV) starting material. Indeed, reaction of $UI_4(1,4\text{-dioxane})_2$ (**1**) with anhydrous HCl (4.0 M/1,4-dioxane) smoothly converts **1** to the chloride-bridged uranium dimer complex $[UCl_4(1,4\text{-dioxane})]_2$ (**3**). Complex **3** is insoluble in 1,4-dioxane and precipitates from the reaction mixture, granting a simple workup and 86% isolated yield. Likewise, treatment of complex **1** with *N,N′*-tetramethylethylenediamine (TMEDA), followed by anhydrous HCl (4.0 M/1,4-dioxane), gives the known $UCl_4(TMEDA)_2$ (**4**)[27] in 91% yield. Salt metathesis chemistry provides access to amide, alkoxide, and organometallic compounds, as illustrated by the synthesis of $fc[NSi(^tBu)Me_2]_2UI_2(THF)$ (**5**),[28] $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ (**6**),[29,30] $U(O\text{-}2,6\text{-}^tBu_2C_6H_3)_4$ (**7**),[31−33] and $(C_5Me_5)_2UI_2$ (**8**).[34−36]

As typified by the syntheses of complexes **5** and **8**, $UI_4(1,4\text{-dioxane})_2$ (**1**) provides a more efficient and atom-economical way to access uranium(IV) iodide compounds. For example, Scheme 2[a]



[a] Reagents and conditions: (i) 2 equiv $(C_5Me_5)MgCl(THF)$, toluene, 110 °C, 15 h, 70% yield; (ii) 4.3 equiv $K(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$, toluene, 70 °C, 15 h, 65% yield; (iii) 4 equiv $Na[N(SiMe_3)_2]$, toluene, 110 °C, 15 h, 80% yield.

while complex **5** has been synthesized by a disproportionation reaction that takes place over 16 h upon mixing $UI_3(THF)_4$ with $[K_2(OEt_2)_2]fc[NSi({}^tBu)Me_2]_2$,[28] the reaction between UI_4(1,4-dioxane)$_2$ (**1**) and $[K_2(OEt_2)_2]fc[NSi({}^tBu)Me_2]_2$ affords complex **5** in 1 h. Moreover, the primary routes to complex **8** have involved multistep syntheses starting from either UCl_4 or $UI_3(THF)_4$ and culminating with a halogen exchange reaction between $(C_5Me_5)_2UCl_2$ and Me_3SiI[34,35] or by oxidation of $(C_5Me_5)_2UI(THF)$ with CuI_2,[36] respectively. Using UI_4(1,4-dioxane)$_2$ (**1**) and 2 equiv of $K(C_5Me_5)$, complex **8** can be easily prepared in one step in 65% isolated yield.

The high-yielding room-temperature synthesis of $[UCl_4$(1,4-dioxane)$]_2$ (**3**) deserves additional comment, as it represents a considerable advance over the existing preparative routes to UCl_4. As noted above, the method of choice for the synthesis of UCl_4 has been the high-temperature (190 °C) radical reaction between $UO_3 \cdot 2H_2O$ (or U_3O_8) and hexachloropropene.[5,9] From a synthetic standpoint, complex **3** is equivalent to UCl_4 (Scheme 2), which makes it potentially a more appealing starting material. For example, $1/2[UCl_4$(1,4-dioxane)$]_2$ (**3**) reacts with 2 equiv of $(C_5Me_5)MgCl(THF)$ to give the known dichloride complex $(C_5Me_5)_2UCl_2$ (**9**).[37] Likewise, reaction of $1/2[UCl_4$(1,4-dioxane)$]_2$ (**3**) with 4 equiv of $K[O\text{-}2,6\text{-}{}^tBu_2C_6H_3]$ or $Na[N(SiMe_3)_2]$ correspondingly gives $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_4$ (**7**)[31,33] and $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ (**6**).[29,30]

The straightforward synthesis, stability, and favorable properties of UI_4(1,4-dioxane)$_2$ (**1**) and $[UCl_4$(1,4-dioxane)$]_2$ (**3**) prompted us to investigate the use of 1,4-dioxane as a supporting ligand for trivalent uranium. As given in eq 2, reaction of uranium turnings with 1.35 equiv of iodine in 1,4-dioxane at room temperature for 18 h affords the new uranium(III) complex UI_3(1,4-dioxane)$_{1.5}$ (**10**) as a blue-violet solid in 99% isolated yield. Complex **10** is remarkably robust and can also be prepared at 80 °C in comparable yields. As with complex **1**, the synthesis of UI_3(1,4-dioxane)$_{1.5}$ (**10**) can be easily performed on multigram scales and does not require the purification of iodine by sublimation or the activation of the uranium turnings by sonication or HgI_2. As such, this synthetic route to **10** represents a significant improvement over the synthesis of $UI_3(THF)_4$ (**11**),[3,4] which is prone to decomposition of the intermediate $UI_4(THF)_4$ by ring-opening of coordinated THF at room temperature.[4,18]

$$U^0 + 1.35I_2 \xrightarrow[\text{rt or 80 °C}\atop\text{18h}]{\text{1,4-dioxane}} \underset{\mathbf{10}}{UI_3(\text{1,4-dioxane})_{1.5}} \qquad (2)$$

It is interesting that the analogous synthesis in diethyl ether affords the adduct-free complex UI_3[21] and demonstrates the relative donor strength of diethyl ether versus 1,4-dioxane toward uranium(III). In contrast to UI_4(1,4-dioxane)$_2$ (**1**), the 1,4-dioxane ligands in **10** are not displaced by diethyl ether.

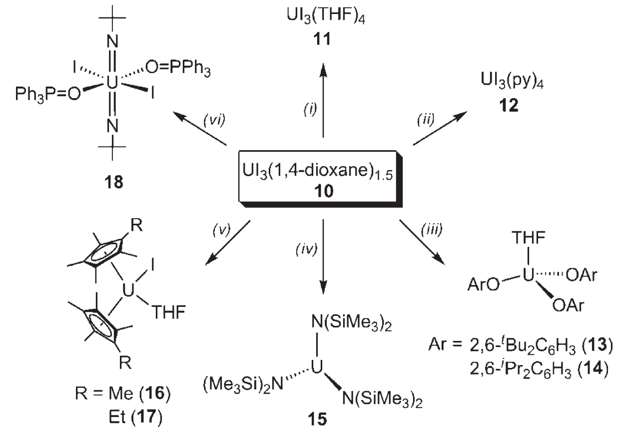
Similar to $UI_3(THF)_4$ (**11**) and related compounds, the formation of complex **10** initially involves the generation of a uranium(IV) intermediate, UI_4(1,4-dioxane)$_2$ (**1**), which appears as a red suspension within a few hours and is later reduced to blue-violet UI_3(1,4-dioxane)$_{1.5}$ (**10**). This was confirmed by the reaction of UI_4(1,4-dioxane)$_2$ (**1**) with uranium turnings in 1,4-dioxane at room temperature, which quantitatively gives UI_3(1,4-dioxane)$_{1.5}$ (**10**) (eq 3).

$$\underset{\mathbf{1}}{3UI_4(\text{1,4-dioxane})_2} + U^0 \xrightarrow[\text{rt, 48h}]{\text{1,4-dioxane}} \underset{\mathbf{10}}{4UI_3(\text{1,4-dioxane})_{1.5}} \qquad (3)$$

Since complex **10** is only slightly soluble in 1,4-dioxane and is insoluble in noncoordinating solvents (such as diethyl ether, benzene, toluene, or hexane), this precluded characterization by NMR spectroscopy and X-ray crystallography. However, the identity of the complex was unequivocally established by H, C, I, and U elemental analyses, ligand displacement by coordinating solvents (THF or pyridine), and reaction chemistry. On the basis of our recent work with $ThCl_4$(1,4-dioxane)$_2$, it is likely that the poor solubility of UI_3(1,4-dioxane)$_{1.5}$ (**10**) is due to an extended polymeric structure with bridging 1,4-dioxane ligands.[23]

UI_3(1,4-dioxane)$_{1.5}$ (**10**) is a versatile reagent for low- and high-valent uranium chemistry, as it displays a wide range of reactivity, which is summarized in Scheme 3. The 1,4-dioxane ligands in complex **10** are readily displaced by other strong donors such as THF or pyridine to quantitatively access the known complexes $UI_3(THF)_4$ (**11**)[3] and $UI_3(py)_4$ (**12**),[4] respectively. Interestingly, the bidentate ligand DME is not able to displace the coordinated 1,4-dioxane from **10** to form the known adduct $UI_3(DME)_2$, even when heated to 75 °C for 2 h. The aryloxide and homoleptic amide complexes $U(OAr)_3(THF)$ (Ar = 2,6-${}^tBu_2C_6H_3$ (**13**);[38] 2,6-${}^iPr_2C_6H_3$ (**14**)[39]) and $U[N(SiMe_3)_2]_3$ (**15**)[3,4,21,40,41] are obtained in good yields by salt metathesis using 3 equiv of K(OAr) and $Na[N(SiMe_3)_2]$, respectively. Similarly, the monoiodide complexes $(C_5Me_4R)_2UI(THF)$ (R = Me (**16**),[42] Et (**17**)[43]) can be synthesized in high yield by reacting **10** with 2 equiv of $K(C_5Me_4R)$ (R = Me, Et). Finally, complex **10** reacts with *tert*-butylamine and iodine in THF, followed by $Ph_3P{=}O$ in toluene, to give the linear bis(imido) uranium(VI) complex **18** in 46% isolated yield.[44] This shows that the reactivity of UI_3(1,4-dioxane)$_{1.5}$ (**10**) is not limited to trivalent uranium and underscores its broad utility as a starting material for inorganic and organometallic uranium chemistry.

Scheme 3^a



^{a} Reagents and conditions: (i) THF, rt, 1 h, 98% yield; (ii) pyridine, rt, 4 h, 89% yield; (iii) 3 equiv KOAr (Ar = 2,6-^{t}Bu$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$), THF, rt, 1 h, 81−82% yield; (iv) 3 equiv Na[N(SiMe$_3$)$_2$], THF, rt, 1 h, 73% yield; (v) 2 equiv K(C$_5$Me$_4$R) (R = Me, Et), THF, rt, 18 h, 67−75% yield; (vi) (1) 6.8 equiv ^{t}BuNH$_2$, 1.5 equiv I$_2$, THF, rt, 10 min; (2) 2.3 equiv Ph$_3$P=O, rt, 15 h, 46% yield.

■ CONCLUSIONS

We have developed simple, safe, inexpensive, and high-yielding solution routes to UI$_4$(1,4-dioxane)$_2$ and UI$_3$(1,4-dioxane)$_{1.5}$, which possess exceptional thermal stability and are easy to prepare on a large scale. Furthermore, they are excellent starting materials to a wide range of uranium(III), uranium(IV), and uranium(VI) alkoxide, amide, organometallic, and halide compounds, including a safe, room-temperature synthesis of [UCl$_4$(1,4-dioxane)]$_2$, which has proved to be a useful synthetic alternative to UCl$_4$. We anticipate that these three new uranium compounds will become important reagents in synthetic actinide chemistry and enable future progress in uranium materials science and nuclear fuel cycle research.

■ EXPERIMENTAL SECTION

General Synthetic Considerations. Unless otherwise noted, all 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. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra were referenced to solvent impurities. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, Columbia Analytical Services (Tucson, AZ), or Midwest Microlab, LLC (Indianapolis, IN).

Note: Heating can be performed inside a ventilation hood using oil baths and thick-walled Schlenk tubes equipped with Teflon valves. However, we found it more convenient to heat reactions inside the glovebox using an IKA RCT Basic stirring hot plate equipped with an ETS-D5 thermocouple and ChemGlass reaction PIE-BLOCK hardware, which have a drilled thermowell for insertion of an electronic contact, thermometer.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. 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 48 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves prior to use. Benzene-*d*$_6$ (Aldrich), toluene-*d*$_8$ (Aldrich), and tetrahydrofuran-*d*$_8$ (Cambridge Isotope Laboratories) were purified by storage over activated 4 Å molecular sieves or sodium metal prior to use. ^{238}U turnings were obtained from Los Alamos National Laboratory and cleaned as described below. Iodine was purchased from Aldrich and used as received. [K$_2$(OEt$_2$)$_2$]fc[NSi(^{t}Bu)Me$_2$]$_2$[45] and K(C$_5$Me$_4$Et)[43] were prepared according to literature procedures.

Caution! *Depleted uranium (primary isotope* ^{238}*U) is a weak α-emitter (4.197 MeV) with a half-life of 4.47 × 10*^{9} *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.*

Oxide-Free Uranium Metal Turnings. This is a modification of a literature procedure.[4] Oxide-coated depleted uranium turnings (20 g) were immersed in 100 mL of concentrated nitric acid to remove the oxide coating. The turnings were mixed and swirled in the nitric acid. The reaction of nitric acid with uranium metal was accompanied by the evolution of heat and brown NO$_2$ gas as the metal turnings lost the black oxide coating. The nitric acid was carefully decanted from the turnings. The nitric acid washing was repeated two more times until the turnings displayed a shiny, metallic surface. Residual acid was removed by rinsing the turnings three times with copious amounts of deionized water. The resulting shiny turnings were then rinsed three times (3 × 100 mL) with acetone to remove water. The turnings were then transferred into the drybox antechamber, where the residual acetone was removed under reduced pressure.

Synthesis of K(C$_5$Me$_5$). This is a modification of a literature procedure[46] and is similar to that reported for K(C$_5$Me$_4$H)[14] and K(C$_5$Me$_4$Et):[43] A 250 mL side arm flask equipped with a magnetic stir bar was charged with K[N(SiMe$_3$)$_2$] (18.3 g, 91.8 mmol) and Et$_2$O (125 mL). The resulting slurry was stirred at room temperature. To this stirring suspension was added C$_5$Me$_5$H (15.0 g, 110 mmol) dropwise by pipet over 10 min. The solution became increasingly cloudy, and the white suspension was stirred for 15 h at room temperature. The reaction mixture was filtered through a medium-porosity fritted filter to collect an off-white powder, which was washed with Et$_2$O (20 mL) and dried under reduced pressure to give K(C$_5$Me$_5$) as an off-white powder (16.0 g, 91.8 mmol, 100%). ^{1}H NMR (THF-*d*$_8$, 298 K): *δ* 1.93 (s, 15H, C$_5$*Me*$_5$).

Synthesis of K(OAr) (Ar = 2,6-^{t}Bu$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$). This is a modification of a literature procedure.[32,47] The syntheses of K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) and K(O-2,6-^{i}Pr$_2$C$_6$H$_3$) are analogous, and the preparation of K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) is given as a representative example: A 125 mL side arm flask equipped with a magnetic stir bar was charged with 2,6-di-*tert*-butylphenol (2.00 g, 9.69 mmol) and THF (30 mL). To this clear, colorless stirring solution was added K[N(SiMe$_3$)$_2$] (1.61 g, 8.08 mmol) as a solid, generating a pale yellow solution. The resulting solution was stirred at room temperature for 15 h, after which time the volatiles were removed under reduced pressure. The resulting pale pink solid was washed with pentane (25 mL), collected by filtration through a medium-porosity fritted filter, and dried under reduced pressure to afford K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) as a white solid (1.96 g, 8.04 mmol, 99%). ^{1}H NMR (THF-*d*$_8$, 298 K): *δ* 6.72 (d, 2H, *m*-Ar-C*H*), 5.77 (t, 1H, *p*-Ar-C*H*), 1.38 (s, 18H, C-C*H*$_3$). K(O-2,6-^{i}Pr$_2$C$_6$H$_3$): ^{1}H NMR (THF-*d*$_8$, 298 K): *δ* 6.69 (d, *J* = 7 Hz, 2H, *m*-Ar-C*H*), 6.07 (t, *J* = 7 Hz, 1H, *p*-Ar-C*H*), 3.51 (sept, *J* = 7 Hz, 2H, C*H*Me$_2$), 1.12 (d, *J* = 6 Hz, 12H, CH(C*H*$_3$)$_2$).

Synthesis of UI$_4$(1,4-dioxane)$_2$ (1). *Method A: Room Temperature.* A 20 mL scintillation vial was charged with a stir bar, uranium turnings (1.02 g, 4.28 mmol), iodine (2.23 g, 8.78 mmol), and 1,4-dioxane (10 mL). The reaction mixture was vigorously stirred for 7 days at room temperature to give a thick brick-red suspension. The reaction mixture was filtered over a medium-porosity fritted filter to collect a red-orange solid. The solid was washed with a 1:1 mixture of hexane and the noncoordinating ether TMS_2O (3 × 15 mL) and dried under reduced pressure to give $UI_4(1,4\text{-dioxane})_2$ (**1**) as a red-orange solid (3.75 g, 4.06 mmol, 95%). Anal. Calcd for $C_8H_{16}I_4O_4U$ (mol wt 921.86): C, 10.42; H, 1.75; I, 55.06. Found: C, 11.08; H, 1.70; I, 50.0. ^1H NMR (C_6D_6, 298 K): δ 3.31 (br s, $\nu_{1/2}$ = 69 Hz, 16H, CH_2).

Method B: 50 °C. A 50 mL round-bottom flask was charged with a large stir bar, uranium turnings (2.13 g, 8.94 mmol), iodine (4.65 g, 18.3 mmol), and 1,4-dioxane (12 mL). The reaction mixture was vigorously stirred for 18 h at 50 °C, using a thermocouple-equipped IKA stirring hot plate, yielding a brick-red suspension. The reaction mixture was cooled to room temperature and filtered over a medium-porosity fritted filter to collect a red-orange solid. The solid was washed with a 1:1 mixture of hexane and the noncoordinating ether TMS_2O (3 × 15 mL) and dried under reduced pressure to give $UI_4(1,4\text{-dioxane})_2$ (**1**) as a red-orange solid (7.94 g, 8.61 mmol, 96%).

Synthesis of $UI_4(Et_2O)_2$ (2). A 20 mL scintillation vial was charged with a stir bar, $UI_4(1,4\text{-dioxane})_2$ (**1**) (0.101 g, 0.110 mmol), and diethyl ether (15 mL). The reaction mixture was stirred for 1 h at room temperature and then concentrated to ~3 mL. Pentane (10 mL) was added, resulting in precipitation of a red solid. The solid was collected by filtration on a medium-porosity fritted filter and dried under reduced pressure to give $UI_4(Et_2O)_2$ (**2**) as a red solid (0.069 g, 0.078 mmol, 71%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **2**.[21] ^1H NMR (C_6D_6, 298 K): δ −10.53 (s, 6H, $O(CH_2CH_3)_2$), −22.54 (s, 4H, $O(CH_2CH_3)_2$).

Synthesis of $[UCl_4(1,4\text{-dioxane})]_2$ (3). A 125 mL side arm flask was charged with a stir bar, $UI_4(1,4\text{-dioxane})_2$ (**1**) (1.50 g, 1.63 mmol), and 1,4-dioxane (35 mL). To this suspension was added HCl (4 M/1,4-dioxane, 2 mL, 8 mmol) over 1 min. Initially, the red-orange suspension clears up and turns dark red. Additional HCl causes the rapid formation of a yellow precipitate. The reaction mixture was vigorously stirred for 10 min at room temperature to give a yellow precipitate. The yellow solid was collected by filtration over a medium-porosity fritted filter, washed sequentially with 1,4-dioxane (5 mL) and hexane (2 × 15 mL), and dried thoroughly under reduced pressure. The product changed color from yellow to orange while drying, to give $[UCl_4(1,4\text{-dioxane})]_2$ (**3**) as an orange solid (0.655 g, 0.700 mmol, 86%). Anal. Calcd for $C_8H_{16}Cl_8O_4U_2$ (mol wt 935.89): C, 10.27; H, 1.72. Found: C, 9.90; H, 1.39. ^1H NMR (C_6D_6, 298 K): δ 1.25 (br s, 16H, CH_2). Note: This compound has poor solubility in C_6D_6, and the chemical shift of the product can vary between δ 1.25 and 1.75 depending on the concentration and temperature.

Synthesis of $UCl_4(TMEDA)_2$ (4). A 20 mL scintillation vial was charged with a stir bar, $UI_4(1,4\text{-dioxane})_2$ (**1**) (0.194 g, 0.211 mmol), and toluene (10 mL). TMEDA (0.0538 g, 0.463 mmol) was added to the resulting solution, and the reaction was stirred for 18 h at room temperature to give an orange precipitate ($UI_4(TMEDA)_2$). Excess HCl (4 M/1,4-dioxane, 0.26 mL, 1.0 mmol) was added to the suspension, and the reaction mixture was stirred at room temperature for 4 h. Next, TMEDA (0.1226 g, 1.055 mmol) was added to the reaction mixture, which was stirred for 1 h to give a light green precipitate. The volatiles were then removed under reduced pressure to give $UCl_4(TMEDA)_2$ (**4**) as a light green solid (0.118 g, 0.192 mmol, 91%). The ^1H NMR spectrum collected in toluene-d_8 was consistent with the data previously reported for complex **4**.[27] ^1H NMR (toluene-d_8, 298 K): δ 6.56 (br s, 12H, $N(CH_3)_2$), −6.79 (br s, 12H, $N(CH_3)_2$), −34.8 (s, 4H, CH_2), −60.6 (s, 4H, CH_2).

Synthesis of $fc[NSi(^tBu)Me_2]_2UI_2(THF)$ (5). A 20 mL scintillation vial was charged with $[K_2(OEt_2)_2]fc[NSi(^tBu)Me_2]_2$ (1.33 g, 1.99 mmol) and THF (20 mL). A second 20 mL scintillation vial was charged with $UI_4(1,4\text{-dioxane})_2$ (**1**) (1.84 g, 1.99 mmol) and THF (20 mL). Both solutions were cooled at −35 °C for at least 30 min. The cooled THF solution of $UI_4(1,4\text{-dioxane})_2$ (**1**) was transferred to a 100 mL round-bottom flask containing a stir bar, and the cooled THF solution of $[K_2(OEt_2)_2]fc[NSi(^tBu)Me_2]_2$ was added to it dropwise with stirring. The reaction mixture was allowed to warm to room temperature while stirring for 1 h. The volatiles were removed under reduced pressure. The resulting brown solid was extracted into toluene (~40 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The Celite plug was rinsed until the washings were colorless. The filtrate was collected, and the volatiles were removed under reduced pressure. The extraction, filtration, and drying were repeated. The dried solid was scraped from the flask walls, transferred to a medium-porosity fritted filter, washed with hexane (~40 mL) until the filtrate was nearly clear, and dried under reduced pressure, giving $fc[NSi(^tBu)Me_2]_2UI_2(THF)$ (**5**) as a brown solid (1.21 g, 1.21 mmol, 61%). The ^1H NMR spectrum was consistent with the data previously reported for complex **5**.[28] ^1H NMR (C_6D_6, 298 K): δ 56.6 (s, 12H, $SiCH_3$), 40.5 (s, 18H, $SiC\text{-}CH_3$), −20.3 (m, 4H, C_5H_4), −26.1 (s, 4H, THF-CH_2), −41.0 (m, 4H, C_5H_4), −74.0 (s, 4H, THF-CH_2).

Synthesis of $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ (6). *Method A: From $UI_4(1,4\text{-dioxane})_2$.* A 250 mL Schlenk flask was charged with a stir bar, $UI_4(1,4\text{-dioxane})_2$ (**1**) (2.03 g, 2.20 mmol), $K[N(SiMe_3)_2]$ (1.76 g, 8.81 mmol), and toluene (100 mL). The resulting yellow-orange suspension was transferred to a ventilation hood and heated in a 110 °C oil bath with stirring. After 15 h, the flask was cooled to room temperature, the stoppers were secured with electrical tape, and the flask was brought into an inert atmosphere drybox. The volatiles were then removed under reduced pressure to give a yellow residue, which was extracted into hexane (50 mL) and filtered through a Celite-padded medium-porosity fritted filter to remove salt byproducts. The Celite plug was washed with hexane (~10 mL) until the washings went colorless. The filtrate was collected, and the volatiles were removed under reduced pressure to give $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ (**6**) as a waxy yellow solid (1.10 g, 1.53 mmol, 70%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **6**.[30] ^1H NMR (C_6D_6, 298 K): δ 11.3 (s, 6H, $Si(CH_3)_2$), 9.7 (s, 9H, $Si(CH_3)_3$), −13.1 (s, 36H, $N[Si(CH_3)_3]_2$), −117.7 (s, 2H, U-CH_2).

Method B: From $[UCl_4(1,4\text{-dioxane})]_2$. A 100 mL round-bottom flask was charged with a stir bar, $[UCl_4(1,4\text{-dioxane})]_2$ (**3**) (0.250 g, 0.267 mmol), $Na[N(SiMe_3)_2]$ (0.462 g, 2.52 mmol), and toluene (45 mL). The flask was sealed, and the resulting yellow suspension was stirred for 15 h at 110 °C, using a thermocouple-equipped IKA stirring hot plate. The flask was then cooled to room temperature, and the volatiles were removed under reduced pressure to give a yellow residue, which was extracted into hexane (25 mL) and filtered through a Celite-padded medium-porosity fritted filter to remove salt byproducts. The Celite plug was washed with hexane (~10 mL) until the washings went colorless. The filtrate was collected, and the volatiles were removed under reduced pressure to give $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ (**6**) as a waxy yellow solid (0.309 g, 0.431 mmol, 80%).

Synthesis of $U(O\text{-}2,6\text{-}^tBu_2C_6H_3)_4$ (7). *Method A: From $UI_4(1,4\text{-dioxane})_2$.* A 20 mL scintillation vial was charged with a stir bar, $UI_4(1,4\text{-dioxane})_2$ (**1**) (0.112 g, 0.121 mmol), $K(O\text{-}2,6\text{-}^tBu_2C_6H_3)$ (0.121 g, 0.495 mmol), and THF (5 mL). The resulting yellow suspension was stirred for 12 h at rt. The volatiles were removed under reduced pressure. The residue was dissolved in toluene (5 mL) and filtered through a Celite-padded coarse-porosity fritted filter. The orange filtrate was collected, and the volatiles were removed under reduced pressure to give an orange solid residue. The residue was then extracted with hexane (5 mL) and filtered through a Celite-padded medium-porosity fritted filter. The filtrate was collected, and the volatiles were removed under reduced pressure to give $U(O\text{-}2,6\text{-}^tBu_2C_6H_3)_4$ (**7**) as a dark yellow solid (0.082 g, 0.0774 mmol, 64%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **7**.[31,32] ^1H NMR (C_6D_6, 298 K): δ 10.6 (d, 8H, *m*-Ar-CH), 8.4 (t, 4H, *p*-Ar-CH), −0.96 (br s, 72H, C-CH_3).

Method B: From $[UCl_4(1,4\text{-dioxane})]_2$. A 20 mL scintillation vial was charged with a stir bar, $[UCl_4(1,4\text{-dioxane})]_2$ (**3**) (0.0520 g, 0.0556 mmol), $K[O\text{-}2,6\text{-}{}^tBu_2C_6H_3]$ (0.118 g, 0.484 mmol), and toluene (10 mL). The reaction mixture was stirred for 15 h at 70 °C, using a thermocouple-equipped IKA stirring hot plate. The resulting yellow suspension was filtered through a Celite-padded coarse-porosity fritted filter. The volatiles were removed under reduced pressure to give a yellow-orange crystalline solid, which was extracted with hexane (20 mL) and filtered through a Celite-padded medium-porosity frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_4$ (**7**) as a dark yellow solid (0.0764 g, 0.0722 mmol, 65% yield).

Synthesis of $(C_5Me_5)_2UI_2$ (8). A 125 mL side arm flask equipped with a magnetic stir bar was charged with $K(C_5Me_5)$ (0.427 g, 2.45 mmol), $UI_4(1,4\text{-dioxane})_2$ (**1**) (1.13 g, 1.23 mmol), and toluene (35 mL). The reaction mixture was stirred for 18 h at 110 °C using a thermocouple-equipped IKA stirring hot plate. The resulting red-brown suspension was filtered through a Celite-padded coarse-porosity fritted filter, and the Celite plug was washed with toluene (20 mL) until the washings went colorless. Excess solvent was removed under reduced pressure. The red-brown residue was extracted into hexane (50 mL) and filtered through a Celite-padded coarse-porosity fritted filter, and the Celite plug was washed with hexane (50 mL) until the washings went colorless. The volatiles were removed under reduced pressure to give $(C_5Me_5)_2UI_2$ (**8**) as a waxy red-brown solid (0.605 g, 0.797 mmol, 65%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **8**.[34−36] ^1H NMR (C_6D_6, 298 K): δ 17.9 (s, 30H, C_5Me_5).

Synthesis of $(C_5Me_5)_2UCl_2$ (9). A 125 mL side arm flask equipped with a magnetic stir bar was charged with $(C_5Me_5)MgCl(THF)$ (0.740 g, 2.77 mmol), $[UCl_4(1,4\text{-dioxane})]_2$ (**3**) (0.648 g, 0.692 mmol), and toluene (55 mL). To this solution was added 1,4-dioxane (2 mL), and the reaction mixture was capped and stirred for 15 h at 110 °C using a thermocouple-equipped IKA stirring hot plate. The resulting red suspension was filtered through a Celite-padded coarse-porosity fritted filter, and the Celite plug was washed with toluene (35 mL) until the washings went colorless. 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, and the Celite plug was washed with hexane (50 mL) until the washings went colorless. The filtrate was collected, and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2UCl_2$ (**9**) as a red crystalline solid (0.560 g, 0.964 mmol, 70%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **9**.[37] ^1H NMR (C_6D_6, 298 K): δ 13.5 (s, 30H, C_5Me_5).

Synthesis of $UI_3(1,4\text{-dioxane})_{1.5}$ (10). *Method A: Room Temperature.* A 20 mL scintillation vial was charged with a stir bar, uranium turnings (2.50 g, 10.5 mmol), iodine (3.60 g, 14.2 mmol), and dioxane (10 mL). The reaction was vigorously stirred for 18 h at room temperature, during which time the reaction mixture changed color from red to a blue-violet suspension. The reaction mixture was filtered through a medium-porosity fritted filter to collect the blue-violet solid. During the solid collection, care was taken to leave behind any unreacted uranium turnings. The solid was washed with diethyl ether (~20 mL) and dried under reduced pressure to give $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) as a blue-violet solid (7.05 g, 9.38 mmol, 99%). Anal. Calcd for $C_6H_{12}I_3O_3U$ (mol wt 750.90): C, 9.60; H, 1.61; I, 50.70; U, 31.70. Found: C, 11.06; H, 1.70; I, 50.4; U, 28.7.

Method B: 80 °C. A 50 mL thick-walled Schlenk tube sealed with a Teflon valve and equipped with a magnetic stir was charged with uranium turnings (2.58 g, 10.8 mmol), iodine (3.71 g, 14.6 mmol), and 1,4-dioxane (12 mL). The reaction mixture was vigorously stirred in an 80 °C oil bath for 18 h. The flask was cooled to room temperature and brought into a drybox. The blue-violet suspension was concentrated to a thick sludge under reduced pressure, and Et_2O (10 mL) was added to precipitate a blue-violet solid. The solid was isolated by filtration through a coarse-porosity fritted filter, being careful to leave unreacted uranium turnings behind. The solid was dried under reduced pressure to give $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) as a blue-violet solid (5.77 g, 7.68 mmol, 79%).

Synthesis of $UI_3(THF)_4$ (11). A 20 mL scintillation vial was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (0.346 g, 0.461 mmol), and THF (10 mL) to give a clear blue solution. The solution was stirred for 1 h at room temperature. The volatiles were then removed under reduced pressure to give $UI_3(THF)_4$ (**11**) as a dark blue solid (0.410 g, 0.452 mmol, 98%). The ^1H NMR spectrum collected in toluene-d_8 was consistent with the data previously reported for complex **11**.[4] ^1H NMR (toluene-d_8, 298 K): δ 10.78 (br s, 4H, THF-CH_2), 6.16 (br s, 4H, THF-CH_2).

Synthesis of $UI_3(py)_4$ (12). A 20 mL scintillation vial was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (0.338 g, 0.450 mmol), and pyridine (10 mL) to give a blue-black solution. The solution was stirred for 4 h at room temperature. The volatiles were then removed under reduced pressure to give $UI_3(py)_4$ (**12**) as a black microcrystalline solid (0.376 g, 0.402 mmol, 89%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **12**.[4] ^1H NMR (C_6D_6, 298 K): δ 18.17 (br s, py-CH), 14.88 (br s, py-CH), 11.46 (br s, py-CH).

Synthesis of $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3(THF)$ (13). A 20 mL scintillation vial was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (0.240 g, 0.320 mmol), and THF (5 mL). With stirring, a THF (5 mL) solution of $K(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (0.234 g, 0.960 mmol) was added to the THF solution of $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**), and the reaction mixture was stirred for 1 h at room temperature. The volatiles were then removed under reduced pressure. The resulting solid was then extracted into pentane (10 mL) and filtered through a Celite-padded pipet filter. The filtrate was collected, and the volatiles were removed under reduced pressure to give $U(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3(THF)$ (**13**) as a brown solid (0.239 g, 0.258 mmol, 81%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **13**.[38] ^1H NMR (C_6D_6, 298 K): δ 16.07 (s, 6H, *m*-Ar-CH), 13.37 (s, 3H, *p*-Ar-CH), −1.61 (br s, 54H, C-CH_3), −16.32 (br s, 4H, THF-CH_2), −39.71 (br s, 4H, THF-CH_2).

Synthesis of $U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3(THF)$ (14). A 20 mL scintillation vial was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (0.324 g, 0.431 mmol), and THF (5 mL). A solution of $K(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (0.280 g, 1.29 mmol) in THF (5 mL) was added with stirring. The resulting reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter, and the Celite plug was rinsed with THF (3 × 2 mL). The volatiles were removed under reduced pressure. The resulting solid was extracted into toluene (10 mL) and filtered through a Celite-padded pipet filter. The filtrate was collected, and the volatiles were removed under reduced pressure to give $U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3(THF)$ (**14**) as a brown solid (0.297 g, 0.352 mmol, 82%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the formation of complex **14**.[38,39] ^1H NMR (C_6D_6, 298 K): δ 11.23 (s, 6H, *m*-Ar-CH), 9.47 (s, 3H, *p*-Ar-CH), 1.06 (s, 6H, ^{i}Pr-CH), −1.39 (s, 36H, ^{i}Pr-CH_3), −3.31 (br s, 4H, THF-CH_2), −6.06 (br s, 4H, THF-CH_2).

Synthesis of $U[N(SiMe_3)_2]_3$ (15). A 125 mL side arm flask was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (1.00 g, 1.33 mmol), $Na[N(SiMe_3)_2]$ (0.733 g, 4.00 mmol), and THF (45 mL). The resulting cloudy purple suspension was stirred for 1 h at room temperature. The solution was filtered through a Celite-padded medium-porosity fritted filter, and the volatiles were removed under reduced pressure. The red-purple residue was extracted into pentane (50 mL) and filtered through a Celite-padded medium-porosity fritted filter. The filtrate was collected, and the volatiles were removed under reduced pressure to give $U[N(SiMe_3)_2]_3$ (**15**) as a red-purple powder (0.700 g, 0.970 mmol, 73%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **15**.[40,41] ^{1}H NMR (C_6D_6, 298 K): δ −11.4 (s, 54H, Si*Me*$_3$).

Synthesis of $(C_5Me_5)_2$UI(THF) (16). A 125 mL side arm flask was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (3.34 g, 4.45 mmol), and THF (80 mL). To the resulting dark blue solution was added K(C_5Me_5) (2.33 g, 13.3 mmol) as a solid. The solution immediately changed color to green. The reaction mixture was stirred for 36 h at room temperature and filtered through a Celite-padded medium-porosity fritted filter to remove salt byproducts. The Celite plug was washed with THF (15 mL) until the washings went colorless. The filtrate was collected, and the volatiles were removed under reduced pressure. The resulting green-brown residue was extracted into toluene (60 mL) and filtered through a Celite-padded medium-porosity fritted filter. The filtrate was collected, and THF (10 mL) was added to the solution. The volatiles were removed under reduced pressure to give a green-brown residue, which was extracted into hexane (75 mL) and filtered through a Celite-padded medium-porosity fritted filter. The Celite plug was then washed with THF (∼10 mL) until the washings went colorless. The dark green filtrate was collected, and the volatiles were removed under reduced pressure to give $(C_5Me_5)_2$UI(THF) (**16**) as a dark green solid (2.35 g, 3.34 mmol, 75%). The ^{1}H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **16**.[42] ^{1}H NMR (C_6D_6, 298 K): δ −1.1 (br s, 30H, C_5*Me*$_5$), −17.4 (br s, 4H, THF-C*H*$_2$), −54.7 (br s, 4H, THF-C*H*$_2$).

Synthesis of $(C_5Me_4Et)_2$UI(THF) (17). A 125 mL side arm flask was charged with a stir bar, $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (1.18 g, 1.57 mmol), and THF (75 mL). To the resulting dark blue solution was added K(C_5Me_4Et) (0.888 g, 4.71 mmol) as a solid. The solution immediately changed color to green. The reaction mixture was stirred for 15 h at room temperature and filtered through a Celite-padded medium-porosity fritted filter to remove salt byproducts. The Celite plug was washed with THF (15 mL) until the washings went colorless. The filtrate was collected, and the volatiles were removed under reduced pressure. The resulting green-brown residue was extracted into toluene (30 mL) and filtered through a Celite-padded medium-porosity fritted filter. The Celite plug was washed with toluene (5 mL) until the washings went colorless. The filtrate was collected, and THF (10 mL) was added to the solution. The volatiles were removed under reduced pressure to give a green-brown residue, which was extracted into hexane (35 mL) and filtered through a Celite-padded medium-porosity fritted filter. The Celite plug was then washed with THF (∼5 mL) until the washings went colorless. The dark green filtrate was collected, and the volatiles were removed under reduced pressure to give $(C_5Me_4Et)_2$UI(THF) (**17**) as a dark green solid (0.775 g, 1.05 mmol, 67%). The ^{1}H NMR spectrum collected in C_6D_6 was consistent with the data previously reported for complex **17**.[43] ^{1}H NMR (C_6D_6, 298 K): δ 16.85 (br s, 6H, $-CH_2$C*H*$_3$), 0.09 (br s, 4H, THF-C*H*$_2$), −0.963 (br s, 4H, THF-C*H*$_2$), −3.51 (br s, 12H, −C*H*$_3$), −4.01 (br s, 12H, −C*H*$_3$), −18.21 (br s, 4H, −C*H*$_2$CH$_3$).

Synthesis of $U(=N^tBu)_2(I)_2(O=PPh_3)_2$ (18). A 20 mL scintillation vial was charged with $UI_3(1,4\text{-dioxane})_{1.5}$ (**10**) (0.208 g, 0.277 mmol) and THF (5 mL). A stir bar, ^{t}BuNH$_2$ (0.138 g, 1.89 mmol), and I_2 (0.106 g, 0.416 mmol) were added to the vial, which was then stirred vigorously with frequent shaking for 10 min (giving $U(=N^tBu)_2(I)_2(THF)_{2-3}$). The volatiles were removed under reduced pressure. The resulting solid was extracted into toluene (10 mL) and filtered through a Celite-filter-plugged pipet. The filtrate was collected, and a solution of $Ph_3P=O$ (0.163 g, 0.585 mmol) in toluene (5 mL) was added with stirring. The solution was stored at room temperature for 15 h, and $U(=N^tBu)_2(I)_2(O=PPh_3)_2$ (**18**) deposited as bright red crystals (0.143 g, 0.120 mmol, 46%). The ^{1}H NMR spectrum collected in CD_2Cl_2 was consistent with the data previously reported for complex **18**.[44] ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.38 (m, 12H, *o*-Ar-C*H*), 7.61 (m, 18H, *m*- and *p*-Ar-C*H*), 0.00 (s, 18H, C-C*H*$_3$).

X-ray Crystallography. A crystal (0.10 × 0.08 × 0.08 mm) of complex **1** was 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 Kα X-ray source (λ = 0.71073 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans. Data collection and initial indexing and cell refinement were handled using APEX II software.[48] Frame integration, including Lorentz−polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[49] The data were corrected for absorption using the SADABS program.[50] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[51] Additional details regarding data collection are provided in the CIF file.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information for complex **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

For financial support of this work, we acknowledge the LANL G. T. Seaborg Institute for Transactinium Science (Graduate Student Fellowship to M.J.M.; PD Fellowships to R.K.T. and N. E.T.), LANL (Director's PD Fellowship to T.C.), the Division of Chemical Sciences, Office of Basic Energy Science, Heavy Element Chemistry Program, and the LANL LDRD program. The authors thank Prof. Paula L. Diaconescu (UCLA) for a donation of $[K_2(OEt_2)_2]fc[NSi(^tBu)Me_2]_2$. Drs. Rebecca M. Chamberlin, David L. Clark, Stosh A. Kozimor, and David E. Morris (all LANL) are acknowledged for helpful discussions and for sharing unpublished results.

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