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Featured Article

Convenient Syntheses of Trivalent Uranium Halide Starting Materials without Uranium Metal

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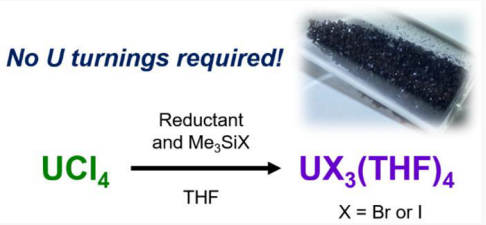
ABSTRACT: Low-valent uranium coordination chemistry continues to rely heavily on access to trivalent starting materials, but these reagents are typically prepared from uranium turnings, which are becoming increasingly difficult to acquire. Here we report convenient syntheses of $UI_3(THF)_4$ (THF = tetrahydrofuran) and $UBr_3(THF)_4$ from UCl_4, a more accessible uranium starting material that can be prepared from commercially available uranium oxides. $UCl_3(THF)_2$ (**1**), $UBr_3(THF)_4$ (**2**), and $UI_3(THF)_4$ (**3**) were prepared by single-pot reductions from UCl_4 using KH and KC_8 and converted to **2** or **3** by halide exchange with the corresponding Me_3SiX (where X = Br or I). Reduction of $UI_4(Et_2O)_2$ (**4**; Et_2O = diethyl ether) and $UI_4(1,4\text{-dioxane})_2$ (**5**) was also shown to cleanly yield **3**. Complex **1** was also synthesized separately by the addition of anhydrous HCl to $U(BH_4)_3(THF)_2$, which was prepared by thermal reduction of $U(BH_4)_4$. All three trivalent uranium halide complexes were isolated in high crystalline yields (typically 85−99%) and their formulations were confirmed by single-crystal X-ray diffraction, elemental analysis, and ^1H NMR and IR spectroscopy. Elemental analysis conducted on triplicate samples of **1**−**3** exposed to vacuum for different time intervals revealed significant THF loss for all three complexes in as little as 15 min. Overall, these results offer expedient entry into low-valent uranium chemistry for researchers lacking access to uranium turnings.



INTRODUCTION

Convenient access to starting materials plays a critical role in the advancement of all synthetic areas of chemistry. In the absence of commercial availability, ideal starting materials are those that can be prepared from readily available sources using operationally simple procedures. In the context of these requirements, access to low-valent starting materials has been a recurring challenge important to the development of non-aqueous uranium chemistry.[1−3] Sattelberger and co-workers offered one of the most important advances in this area by reporting the synthesis of $UI_3(THF)_4$ (THF = tetrahydrofuran), which was prepared by careful oxidation of uranium turnings with I_2 (Scheme 1).[4−6] Similar methods have been used to prepare $UI_3(1,4\text{-dioxane})_{1.5}$ and base-free UI_3 by oxidation of uranium metal,[7−9] as well as other solvent adducts such as $UI_3(DME)_2$ (DME = dimethyl ether) and $UI_3(py)_4$ (py = pyridine).[4,5,8] The bromide analogues $UBr_3(THF)_4$ and $UBr_3(DME)_2$ have also been prepared directly or indirectly (via UH_3) from uranium turnings.[5,10] All of these reactions are operationally simple as desired, but the problem is that uranium metal is becoming increasingly difficult to come by, especially for researchers outside of government laboratories.

Commercially available and/or commonly accessible sources of uranium tend to be high-valent oxides such as UO_3 and $UO_2(NO_3)_2$. However, there are a few methods for converting these commercially available U^{6+} oxides to low-valent UI_3 and UBr_3 starting materials commonly used for salt metathesis reactions. The closest methods rely on the renowned synthesis of UCl_4 using hexachloropropene to reduce U^{6+} oxides.[11−13] UCl_4 can then be further reduced to UCl_3 solvent adducts using a variety of reductants and common donor solvents. For example, Moody and co-workers described how NaH could be used to reduce UCl_4 in THF to $UCl_3(THF)_x$ via H_2 loss.[14,15] Other reductants such as Na_2C_2 and magnesium have also

Scheme 1. Previously Published Synthetic Pathways for $UX_3(THF)_4$ (X = Br or I), $UBr_3(DME)_2$, and $UI_3(1,4\text{-dioxane})_{1.5}$[5,9,10]

$$U + 1.5\,X_2 \xrightarrow[0\,^\circ C]{THF} UX_3(THF)_4 \quad (X = Br \text{ or } I) \qquad (1)$$

$$U + 1.5\,I_2 \xrightarrow[rt]{1.4\text{-dioxane}} UI_3(1,4\text{-dioxane})_{1.5} \qquad (2)$$

$$UH_3 + 3\,AgBr \xrightarrow[rt]{DME} UBr_3(DME)_2 \qquad (3)$$

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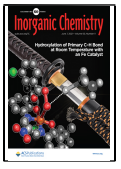

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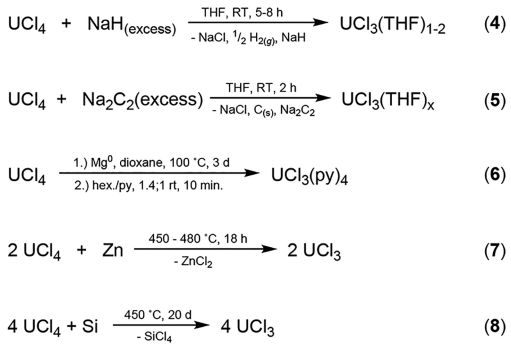
been used to make THF and other ether adducts of UCl_3 and the pyridine adduct $UCl_3(py)_4$.[16,17] Several high-temperature ampule syntheses of base-free UCl_3 are also known (Scheme 2).[18−20]

Scheme 2. Previously Published Synthetic Pathways for the Reduction of UCl_4 to UCl_3



Unlike UCl_4, no comparable solution methods have been reported for the synthesis of UBr_4 and UI_4. Instead, these base-free U^{4+} halides must be prepared by oxidation of uranium metal using the corresponding halogen or using high-temperature, solid-state reductions in sealed ampules.[21] However, donor adducts of UBr_4 and UI_4 can be prepared by a variety of methods using halosilanes. Berthet, Ephritikhine, and co-workers showed that $UX_4(MeCN)_4$ (MeCN = acetonitrile), where X = Br or I, can be prepared by reductive silylation of $UI_2O_2(THF)_3$ or $UO_2(OTf)_2$ with excess Me_3SiX in MeCN.[22] This method was extended more recently by Bart and co-workers to prepare other UX_4 donor adducts from different uranyl starting materials.[23−25] Me_3SiI has also been used to perform direct halide exchange with UCl_4. Berthet et al. showed that treating UCl_4 with 4 equiv of Me_3SiI in MeCN yielded $UI_4(MeCN)_4$, which could then be converted into the solvent adducts $UI_4(py)_3$ and $UI_4(DMF)_6$ (DMF = *N*,*N*-dimethylformamide).[26] Hayton and co-workers extended this halide exchange method in diethyl ether (Et_2O) to prepare $UI_4(Et_2O)_2$ (**4**).[10,27] Moreover, Kiplinger and co-workers demonstrated how this method could be used with thorium for the synthesis of $ThI_4(DME)_2$ from $ThCl_4(DME)_2$.[28]

Despite their frequent use in the synthesis of tetravalent halide starting materials, we are unaware of any reports of using halosilanes such as Me_3SiI and Me_3SiBr for the synthesis of highly coveted trivalent uranium starting materials such as $UI_3(THF)_4$. Here we report their use in convenient synthetic procedures for accessing $UCl_3(THF)_2$ (**1**), $UBr_3(THF)_4$ (**2**), and $UI_3(THF)_4$ (**3**) using UCl_4 prepared from the U^{6+} starting material $UO_2(NO_3)_2$. This work builds on important contributions from others showing how Me_3SiBr and Me_3SiI are useful reagents for exchanging chloride ligands for bromide and iodide in f-metal complexes, as described above. It also builds on very recent results showing how these methods can be used to access low-valent halide starting materials with americium.[29] These results highlight how halide exchange can be combined with commonly available reduction methods to prepare **3** as well as **2** without uranium metal.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of N_2 or Ar using glovebox or standard Schlenk techniques. All glassware was heated at 150 °C for at least 2 h and allowed to cool under vacuum before use. Solvents were dried and deoxygenated using a Pure Process Technologies Solvent Purification System and stored over 3 Å molecular sieves. 1,4-Dioxane was dried over sodium/benzophenone and distilled before use. Deuterated solvents were deoxygenated with five freeze−pump−thaw cycles and stored over 3 Å molecular sieves for at least 3 days before use. KH (Sigma-Aldrich) was received as a dispersion in mineral oil, washed with pentane, and evaporated to dryness under vacuum before use. KC_8 was prepared as previously described.[30] Me_3SiI and Me_3SiBr (Sigma-Aldrich) were purified by vacuum distillation and stored over small pieces (ca. 2−5 mm) of dry abraded copper wire. UCl_4 was prepared by reduction of $UO_2(NO_3)_2{\cdot}6H_2O$ with hexachloropropene (Sigma-Aldrich), as described previously.[13] $UO_2(NO_3)_2{\cdot}6H_2O$ was obtained by digesting an impure mixture of depleted uranium turnings and oxide in fuming nitric acid. The mixture was filtered to remove any insoluble material, and the yellow solution was allowed to evaporate to dryness in the back of a well-ventilated hood for several days. The solid was collected, placed under vacuum briefly to remove any residual HNO_3, and then dissolved in a minimum amount of Et_2O. Crystals of $UO_2(NO_3)_2{\cdot}6H_2O$ were grown by evaporation of the Et_2O solution and dried under vacuum overnight prior to use. All other reagents were purchased from commercial sources and used as received.

^1H NMR data were collected on a Bruker AVANCE-400 spectrometer operating at 400 MHz or on a Bruker AVANCE-500 spectrometer operating at 500 MHz. ^{11}B NMR data were collected on a Bruker AVANCE-400 spectrometer operating at 128 MHz or a Bruker AVANCE-500 spectrometer operating at 160 MHz. Chemical shifts are reported in δ units relative to residual NMR solvent peaks (^1H) and $BF_3{\cdot}Et_2O$ (^{11}B; δ 0.0). Microanalytical data (CHN) were collected using an EAI CE-440 elemental analyzer at the University of Iowa's Shared Instrumentation Facility. Halide analysis was conducted at the University of Illinois Microanalysis Laboratory. IR spectra were acquired with a Thermo Scientific Nicolet iS5 spectrometer in a nitrogen-filled glovebox using an attenuated-total-reflectance (ATR) accessory. Mechanochemical reactions were carried out using a FlackTek SpeedMixer, Form-Tech Scientific (FTS) 5 mL stainless steel "SmartSnap" grinding jars, and stainless-steel balls (304 grade) as grinding media. A specialty Teflon insert fabricated by FlackTek allowed the FTS grinding jars to be used in the FlackTek SpeedMixer.

Caution! *$U(BH_4)_4$ and $U(BH_4)_3(THF)_2$ are highly pyrophoric complexes that can ignite in the presence of air and water. $LiBH_4$, KH, and KC_8 are also pyrophoric and should be handled with the same care. ^{238}U, the major isotope in depleted uranium, is a long-lived α emitter with a half-life of 4.5 × 10^9 years. It should be handled with appropriate radiological monitoring and controls.*

$U(BH_4)_4$. UCl_4 (0.300 g, 0.790 mmol), $LiBH_4$ (0.0688 g, 3.16 mmol), and four 5 mm stainless steel balls were added to an FTS jar inside a solvent-free glovebox. The jar was hermetically sealed and removed from the glovebox. The mixture was milled for five cycles of 5 min at 1800 rpm in a FlackTek SpeedMixer. The jar was allowed to rest for 5 min between each cycle to prevent overheating and thermal degradation of the generated $U(BH_4)_4$. Upon completion, the jar was transferred back into an argon glovebox and the contents were scraped into a cryogenic sublimator. The sublimation apparatus was removed from the glovebox, and the mixture was sublimed on a Schlenk line at 50−60 °C at 2.5 × 10^{-2} Torr for 2 h (or until only white solid remained at the bottom of the sublimator) using liquid N_2 to cool the coldfinger. Upon completion, the sublimation apparatus was transferred to the glovebox and the dark-green crystalline sublimate was isolated. Yield: 0.150 g (64%). X-ray diffraction (XRD) data matched those previously reported for $U(BH_4)_4$.[31,32] ^1H NMR (C_6D_6, 400 MHz): δ 134.8 [br s, full width at half-maximum (fwhm) = 478 Hz]. ^{11}B NMR (toluene, 161 MHz): δ 140.0 (br s, fwhm = 320 Hz). ^{11}B NMR (C_6D_6, 128 MHz): δ 131.6 (p, J = 86 Hz).

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$U(BH_4)_3(THF)_2$. $U(BH_4)_4$ (0.200 g, 0.673 mmol) was added to a 200 mL Schlenk tube inside a glovebox and then transferred to a Schlenk line. Toluene (100 mL) was added to the reaction flask by cannula transfer, and the mixture was stirred until $U(BH_4)_4$ was fully dissolved. The reaction flask was then heated to 100−105 °C overnight (18 h) under a slow argon bubble. The reaction mixture slowly changed color from light brown to dark red and generated a precipitate. The mixture was allowed to cool to room temperature (RT), and the solvent was removed under vacuum to yield a dark-red microcrystalline solid. The reaction flask was transferred back into the glovebox. The solid was washed twice with pentane (2 × 50 mL) with 1 h of stirring between washes to completely remove any unthermalized $U(BH_4)_4$. THF (50 mL) was added to dissolve the solid, and the solution was left to stir for 1 h to ensure complete conversion to the Lewis base adduct. The solution was concentrated under vacuum to 10 mL and transferred to a 20 mL scintillation vial. Vapor diffusion with pentane at −30 °C yielded red crystals after 4 days. Yield: 0.210 g (73%).^{1}H NMR (C_6D_6, 400 MHz): δ 2.30 (br s, 8H, THF), 5.20 (br s, 8H, THF), 119 (br s, 12H, BH_4, fwhm = 345 Hz). ^{11}B NMR (C_6D_6, 128 MHz): δ 153 (br s, fwhm = 230 Hz).

$UCl_3(THF)_2$ (1). *Method A.* $U(BH_4)_3(THF)_2$ (0.620 g, 1.45 mmol) was loaded into a Schlenk tube in a glovebox. The red solid was dissolved in THF (ca. 50 mL) and stirred for 1 h before the mixture was transferred to a Schlenk line. To the solution was added 1 M HCl in Et_2O (6.5 mL, 6.5 mmol) dropwise via a gastight syringe. The reaction bubbled aggressively with the initial addition of HCl and then slowed after 1 min. The solution was stirred overnight but is typically complete after 2 h, as determined by the absence of $U(BH_4)_3(THF)_2$ resonances in the ^{11}B NMR spectrum collected on the reaction mixture. The mixture was evaporated to dryness under vacuum and transferred into a glovebox. The solid was washed with 50 mL of pentane (stirred for 30 min before filtering). The solid was dissolved in a minimal amount of THF and was subsequently precipitated by the addition of excess pentane to yield a microcrystalline purple-burgundy solid. Yield: 0.600 g (85%). Anal. Calcd for $C_8H_{16}Cl_3O_2U$; C, 19.67; H, 3.30; Cl, 21.8. Found: C, 20.23; H, 3.20; Cl, 22.1. Samples prepared using this method were also used in the time-dependent elemental analysis (EA) studies discussed below. IR (cm^{-1}): 2968 (m), 2889 (m), 1456 (m), 1062 (m), 1017 (s), 915 (m), 859 (s), 669 (m).

Method B. UCl_4 (0.100 g, 0.263 mmol) and KC_8 (0.0534 g, 0.395 mmol) were added to a 20 mL scintillation vial with THF (15 mL). The solution quickly changed color from green to purple and generated a white solid (presumed to be KCl). The mixture was stirred for 30 min and then filtered over a pad of Celite. The filtrate was concentrated to 15 mL. Vapor diffusion with Et_2O at −30 °C yielded blue crystals after 4 days. Yield: 63.9 mg (50%). EA data collected on crystals exposed to vacuum were consistent with $UCl_3(THF)_{1.1}$. Anal. Calcd for $C_{4.4}H_{8.8}Cl_3O_{1.1}U$; C, 12.47; H, 2.09. Found: C, 12.73; H, 2.15. Samples prepared using this method were also used in the time-dependent EA studies discussed below.

Method C. UCl_4 (0.100 g, 0.263 mmol) and KH (0.0106 g, 0.263 mmol) were added to a 20 mL scintillation vial with THF (15 mL). The solution slowly changed color from green to purple and generated a gas (presumed to be H_2) and a white solid (presumed to be KCl). The reaction was stirred for at least 2 h, but should not go longer than 8 h, as a red intractable solid begins to form and plate the glass. This insoluble solid cannot be separated from the KCl byproduct and decreases the overall yield of the reaction. The mixture was filtered over a pad of Celite, and the filtrate was concentrated to 10 mL under vacuum. Vapor diffusion with Et_2O yielded a blue crystalline solid after 3 days. Yield: 0.084 g (65%). Samples prepared using this method were also used in the time-dependent EA studies discussed below.

$UBr_3(THF)_4$ (2). *Method A.* UCl_4 (0.102 g, 0.269 mmol) and KH (0.011 g, 0.274 mmol) were added to a 20 mL scintillation vial. The vial was filled with THF (20 mL) and stirred for 2 h (the reaction should not be allowed to go more than 8 h, as described for the synthesis of **1** above). Me_3SiBr (0.110 mL, 0.834 mmol) was added, and the mixture was stirred for 1 h. The solution was filtered and evaporated to dryness under vacuum to reveal a dark crystalline solid. The solid was dissolved in 10 mL of THF and filtered, and the filtrate was layered with toluene. The layered mixture was stored in a −30 °C freezer for 3 days to yield a crop of dark needles (0.175 g). The mother liquor was decanted, concentrated to 5 mL, and layered with additional toluene to yield a second crop of crystals. Yield: 0.268 g (91%). Anal. Calcd for $C_{16}H_{32}Br_3O_4U$; C, 25.08; H, 4.21. Found: C, 25.12; H, 4.20. ^{1}H NMR (C_6D_6): δ 1.26 (br s, 16 H, THF), 3.21 (br s, 16 H, THF). Samples prepared using this method were also used in the time-dependent EA studies discussed below. IR (cm^{-1}): 2976 (m), 2890 (m), 1445 (m), 1345 (w), 1178 (w), 1015 (s), 915 (m), 856 (s), 669 (m).

Method B. UCl_4 (0.100 g, 0.263 mmol) and KC_8 (0.0473 g, 0.350 mmol) were added to a 20 mL scintillation vial. The vial was filled with THF (ca. 15 mL) and stirred for 1 h. Me_3SiBr (0.130 mL, 0.9812 mmol) was then added using a micropipette. The reaction was left to stir for 1 h and then filtered over a pad a Celite. The purple solution was concentrated to dryness to reveal a dark crystalline solid. The solid was further purified by adding 10 mL of THF, layering with toluene, and storing at −30 °C for 3 days to yield large dark (almost black) crystals at the bottom of the vial. Yield: 0.177 g (88%). ^{1}H NMR data collected on the crystals matched those obtained for **2** prepared using Method A. EA data collected on crystals exposed to vacuum were consistent with $UBr_3(THF)_{2.5}$. Anal. Calcd for $C_{10}H_{20}Br_3O_{2.5}U$; C, 18.25; H, 3.06. Found: C, 18.27; H, 2.91. Samples prepared using this method were also used in the time-dependent EA studies discussed below.

$UI_3(THF)_4$ (3). *Method A.* UCl_4 (0.102 g, 0.269 mmol) and KH (0.0112 g, 0.279 mmol) were added to a 20 mL scintillation vial. THF was added (20 mL), and the mixture was stirred for 2 h. A white precipitate was generated over the course of the reaction (presumed to be KCl). Me_3SiI (0.115 mL, 0.808 mmol) was then added. The reaction was stirred for 1 h and then evaporated to dryness under vacuum to reveal a purple gummy solid. The solid was washed with pentane (2 × 20 mL) and redissolved in THF (10 mL). The solution was vapor-diffused with pentane in a −30 °C freezer to yield purple crystals after 4 days. Yield: 0.208 g (85%). Anal. Calcd for $C_{16}H_{32}I_3O_4U$; C, 21.18; H, 3.56. Found: C, 21.03; H, 3.62. ^{1}H NMR (C_6D_6): δ 5.86 (br s, 16 H, THF, fwhm = 210 Hz), 10.6 (br s, 16 H, THF, fwhm = 500 Hz). IR (cm^{-1}): 2975 (m), 2886 (m), 1445 (m), 1345 (m), 1177 (m), 1013 (s), 914 (m), 854 (s), 668 (m). Samples prepared using this method were also used in the time-dependent EA studies discussed below.

Method B. UCl_4 (0.108 g, 0.284 mmol) and KC_8 (0.080 g, 0.592 mmol) were added to a 20 mL scintillation vial. THF (20 mL) was added, and the mixture instantly changed color from light green to purple and generated a gray solid (presumed to be a mixture of KCl and graphite). After stirring for 20−30 min, Me_3SiI (0.180 mL, 1.27 mmol) was added using a micropipette, and the solution color changed to purple-blue. The mixture was stirred for 1 h and then filtered over Celite. The filtrate was evaporated to dryness under vacuum to yield a purple solid. The solid was washed with pentane (10 mL), dissolved in the minimal amount of THF, and stored at −30 °C to yield crystals after 3 days (0.180 g). The mother liquor was decanted, concentrated under vacuum to ca. 5 mL, and stored at −30 °C for 1 week to yield a second crop of crystals. Yield: 0.228 g (88%). ^{1}H NMR data collected on the crystals matched those obtained for **3** prepared using Method A. EA data collected on crystals exposed to vacuum were consistent with $UI_3(THF)_{2.4}$. Anal. Calcd for $C_{9.6}H_{19.2}I_3O_{2.4}U$; C, 14.56; H, 2.44. Found: C, 14.33; H, 2.31. Samples prepared using this method were also used in the time-dependent EA studies discussed below.

Method C. $UI_4(1,4\text{-dioxane})_2$ (**5**; 0.100 g, 0.108 mmol) and KH (0.0048 g, 0.120 mmol) were added to a 20 mL scintillation vial, followed by THF (20 mL). The reaction instantly began to effervesce and generated a white precipitate (presumed to be KI), and the solution changed color from orange to brown to purple over the course of 10 min. The reaction mixture was left to stir for 2 h. The purple solution was filtered over Celite and concentrated to 5 mL under vacuum. The solution was vapor-diffused with pentane at RT to

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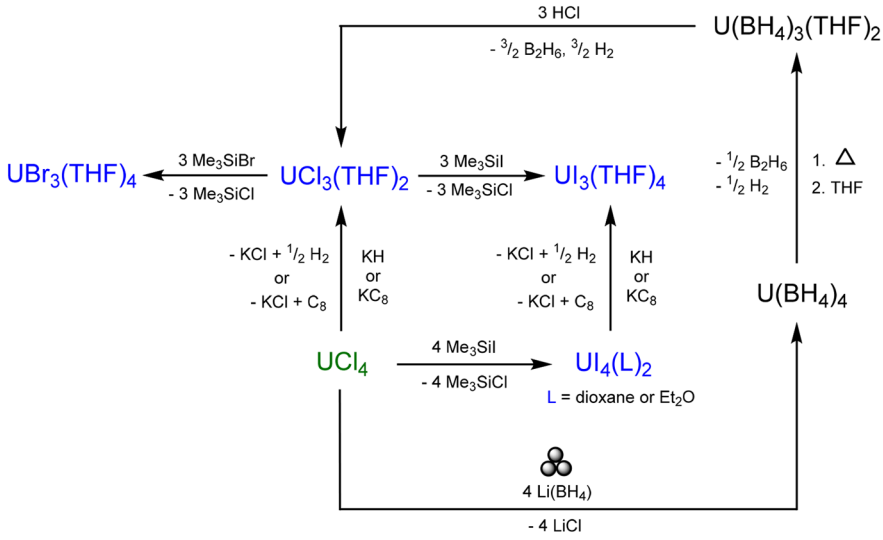
Scheme 3. Syntheses Discussed for $UCl_3(THF)_2$ (1), $UBr_3(THF)_4$ (2), and $UI_3(THF)_4$ (3) Starting from UCl_4



yield large purple needles after 2 days. Yield: 0.0971 g (99%). ^{1}H NMR data collected on the crystals matched those obtained for **3** prepared using Method A. EA data collected on crystals exposed to vacuum were consistent with $UI_3(THF)_3$. Anal. Calcd for $C_{12}H_{24}I_3O_3U$; C, 17.26; H, 2.90. Found: C, 17.45; H, 2.76.

Method D. **5** (0.100 g, 0.109 mmol), KC_8 (0.0153 g, 0.113 mmol), and THF (15 mL) were added to a 20 mL scintillation vial. The reaction instantly turned from orange-red to purple and generated a gray precipitate (presumed to be a mixture or KCl and graphite). After stirring for 30 min, the reaction was filtered over a pad of Celite to reveal a deep-blue-purple solution. The solution was reduced to 5 mL under vacuum, and ca. 15 mL of pentane was added to precipitate a purple microcrystalline solid. The purple solid was isolated by filtration and evaporated to dryness under vacuum. Yield: 0.0969 g (98%). ^{1}H NMR data collected on the solid matched those obtained for **3** prepared using Method A. EA data collected on samples exposed to vacuum were consistent with $UI_3(THF)_{2.5}$. Anal. Calcd for $C_{7.5}H_{15}I_3O_{2.5}U$; C, 15.03; H, 2.52. Found: C, 14.96; H, 2.52.

Method E. **4** (0.202 g, 0.226 mmol) and KH (0.0183 g, 0.456 mmol) were added to a 20 mL scintillation vial. The vial was filled with 20 mL of THF, and the reaction instantly began to bubble and change color from orange to brown to purple after a couple of minutes and generated a white solid (presumed to be KI). The reaction was left to stir for 2 h and then filtered over Celite. The solution was concentrated to 10 mL under vacuum and vapor-diffused with pentane. After 2 days, the pentane layer had fully diffused to yield large purple needles inside the purple-tinted mother liquor. Yield: 0.125 g (61%). ^{1}H NMR data collected on the crystals matched those obtained for **3** prepared using Method A.

Method F. **4** (0.101 g, 0.113 mmol) and KC_8 (0.0163 g, 0.121 mmol) were added to a 20 mL scintillation vial. The vial was filled with THF (ca. 15 mL), and the solution changed color from red to purple and generated a gray solid (presumed to be a mixture or KCl and graphite). The reaction was left to stir for 1 h, then filtered, and concentrated (ca. 5 mL) under vacuum. Pentane (15 mL) was then added, and the solution was stirred for several minutes to precipitate a purple microcrystalline solid. The solvent was decanted, and the solid evaporated to dryness under vacuum. Yield: 0.0619 g (60%). ^{1}H NMR data collected on the crystals matched those obtained for **3** prepared using Method A.

$UI_4(Et_2O)_2$ (4). Prepared with slight modifications to the procedure reported by Hayton and co-workers.[10] UCl_4 (0.101 g, 0.266 mmol) was added to a 200 mL Schlenk flask with a large stir bar. The flask was sealed, removed from the glovebox, and transferred to a Schlenk line. To the reaction flask was added Et_2O (100 mL) followed by excess Me_3SiI (ca. 1 mL). The mixture was stirred for 3 h, during which time the clear solution and green suspension turned to a red solution and orange suspension. The mixture was evaporated to dryness under vacuum to reveal an orange solid, which was transferred into the glovebox for purification and crystallization. The orange microcrystalline solid was washed with pentane (2 × 50 mL) and then suspended in Et_2O (80 mL). The mixture was stirred for 1 h to dissolve as much of the complex as possible and then filtered over a fine-frit funnel. The remaining orange solid on the frit was washed with an additional 20 mL of Et_2O. The combined filtrate was reduced to ca. 20 mL and stored at −30 °C for 4 days to yield 0.115 g of red crystals. The mother liquor was concentrated, vapor-diffused with pentane, and placed in a −30 °C freezer. After 3 days, an additional 0.034 g of red crystals was isolated. Yield: 0.149 g (63%). Anal. Calcd for $C_8H_{20}I_4O_2U$; C, 10.75; H, 2.26. Found: C, 10.93; H, 2.17. ^{1}H NMR (C_6D_6): δ −10.5 (s, 12 H, CH_3) −22.6 (s, 8 H, CH_2). IR (cm^{-1}): 2975 (w), 2931 (w), 2896 (w), 1385 (m), 1251 (m), 1090 (m), 1044 (s), 1014 (m), 987 (m), 921 (m), 836 (s), 759 (s).

UI_4(1,4-dioxane)$_2$ (5). In a well-purged glovebox free of THF, UCl_4 (0.100 g, 0.263 mmol) was added to an 11 Dram vial (ca. 40 mL volume) with 1,4-dioxane (35 mL). Me_3SiI (0.170 mL, 1.20 mmol) was added by a micropipette to the solution. The reaction was left to stir for 3 h, over which time the solution changed color from green to red-orange. The mixture was filtered and slowly evaporated to dryness under vacuum with vigorous stirring (to prevent 1,4-dioxane from freezing) to yield an orange solid. Aliquots of a 10:1 toluene/dioxane solution were added to the resulting solid with aggressive stirring until the solid was completely dissolved (ca. 30 mL). The red-orange solution was stored at −30 °C for 3 days to yield red crystals. Yield: 0.155 g (64%). Anal. Calcd for $C_8H_{16}I_4O_4U$; C, 10.42; H, 1.75. Found: C, 10.96; H, 1.80. ^{1}H NMR (C_6D_6): δ 3.34 (br s, 16 H, CH_2). IR (cm^{-1}): 2960 (w), 2901 (w), 2848 (w), 1443 (m), 1290 (m), 1249 (m), 1121 (m), 1038 (m), 1010 (m), 883 (m), 857 (s), 831 (m), 786 (s), 609 (m).

Crystallographic Studies. Crystals used for single-crystal XRD were grown from THF (**1** and **3**), THF and toluene (**2**), 1,4-dioxane (**4**), Et_2O (**5**), THF and pentane (**6**), and 1,4-dioxane and toluene (**7**) or by sublimation [$U(BH_4)_4$] and mounted on a MiTeGen micromount with Paratone N oil. Crystallographic data were collected with a Bruker Nonius Kappa Apex II diffractometer equipped with a charge-coupled-device (CCD) detector or with a Bruker D8 Venture Duo diffractometer equipped with a Bruker photon III detector. Samples were cooled to 150 K using an Oxford Cryostream 700 low-temperature device. All of the data were collected with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) using ϕ and ω scans except for the smaller crystals of **1**, which were collected using Cu Kα radiation (λ = 1.5406 Å). The data were corrected for absorption from redundant reflections using the *SADABS* program. Structures were solved with intrinsic phasing (*SHELXT*), and least-

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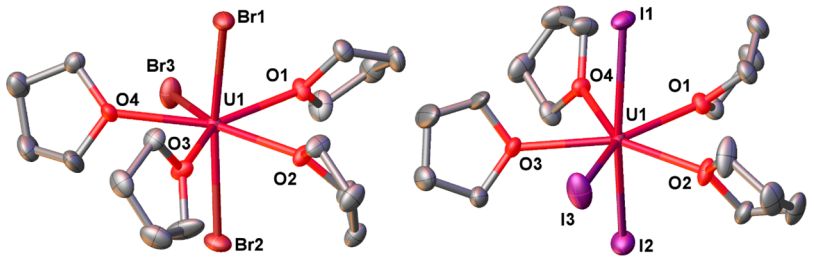

Figure 1. Molecular structure of **2** (left) and comparison to the structure of **3** (right). Thermal ellipsoids shown at 50% probability. Hydrogen atoms were omitted from the figure.

Table 1. Comparison of XRD Unit Cells for 2 and 3 to the Structures of $PuBr_3(THF)_4$ and 3 in References 35 and 36

	2	$PuBr_3(THF)_4$[35]	3	3[36]
formula	$C_{16}H_{32}Br_3O_4U$	$C_{16}H_{32}Br_3O_4Pu$	$C_{16}H_{32}I_3O_4U$	$C_{16}H_{32}I_3O_4U$
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.1735(17)	8.1698(12)	8.4782(9)	8.3635(4)
b (Å)	9.454(2)	9.3859(14)	9.5475(10)	9.5865(4)
c (Å)	15.576(3)	15.414(2)	15.8588(17)	15.7254(7)
α (deg)	78.321(5)	78.526(2)	79.074(5)	78.010(2)
β (deg)	87.127(5)	86.813(2)	86.385(5)	86.027(2)
γ (deg)	74.791(5)	74.934(2)	74.490(5)	74.462(2)
V (Å^3)	1137.4(4)	1118.5(3)	1214.4(2)	1188.1(9)
Z	2	2	2	2

squares refinement (*SHELXL*) confirmed the positions of all non-hydrogen atoms.[33] All hydrogen-atom positions were idealized and allowed to ride on the attached boron, carbon, and oxygen atoms. Structure solution and refinement were performed with *Olex2*.[34] Crystallographic details for all of the structures are compiled in Table S1.

RESULTS AND DISCUSSION

Synthesis and Characterization. Our approach for preparing the most highly sought-after trivalent uranium starting materials **3** and **2** relied on two general strategies: (1) reduction of UCl_4 to **1** followed by halide exchange with Me_3SiI and Me_3SiBr and (2) halide exchange with UCl_4 followed by reduction (Scheme 3). Both methods work for the synthesis of **3** using a variety of reductants. We first prepared **1** by reducing UCl_4 with KC_8 or KH, similar to that described in previous reports.[14] Both methods are glovebox-friendly and allowed **1** to be prepared within a couple of hours. EA collected on multiple samples of crystalline **1** immediately removed from the mother liquor indicated the presence of two THF molecules. XRD analysis of crystals grown from THF corroborated the presence of two THF molecules, but the data were only of sufficient quality to establish connectivity (see the Supporting Information). Each uranium atom in the structure is bound to two cis THF molecules as well as six bridging chloride atoms that connect adjacent uranium atoms to form a polymeric chain similar to that reported for $AmCl_3(THF)_2$.[29]

Once prepared, **1** was treated with 3 equiv of Me_3SiBr or Me_3SiI in THF to form **2** and **3**. Both complexes were isolated as single crystals in 91% and 88% yield, respectively. Single-crystal XRD studies of **2** and **3** revealed that they are isostructural to $PuBr_3(THF)_4$ and the polymorph of **3** recently reported by Heinemann et al.,[35,36] as indicated by a comparison of the space group and unit cell (Figure 1 and Table 1). Both complexes are monomeric and adopt a pentagonal-bipyramidal geometry, with the three halides oriented in a *mer*-like conformation around the metal center. Two halides reside in the axial positions, and the third halide lies in the equatorial plane with the four THF molecules. The Br1−U1−Br2 angle in **2** and the I1−U1−I2 angle in **3** are 163.81(2)° and 165.46(2)°, respectively, due to repulsion from the third equatorial halide. The U−Br distances of the two axial bromides in **2** are 2.8962(7) and 2.9161(7) Å, and the third bromide in the equatorial plane is slightly longer at 2.9221(8) Å. The average U−O bond distance of the four THF ligands are 2.540(2) Å.

We also demonstrated that **3** can be prepared by reduction of **4** or **5**. Treating UCl_4 with Me_3SiI in Et_2O yielded **4** as described previously, and here we report that doing the same reaction in 1,4-dioxane yields **5**. The yields of **4** and **5** are good when isolated as single crystals (63 and 64%), but they can be further improved by precipitating them as microcrystalline solids. Isolation of both complexes was confirmed by single-crystal XRD, ^{1}H NMR and IR spectroscopy, and EA. Our structure of **4** revealed a different polymorph of the structures reported previously by Arnold and Hayton (space group *Pbcn* vs $I4_1/acd$)[8,10] and is reported here for completeness. The unit cell for single crystals of **5** matched the unit cell reported previously by Kiplinger and co-workers.[9] Both complexes adopt octahedral geometries, with iodides occupying the equatorial sites and solvent molecules occupying the axial sites, as described previously.[8−10]

Reducing isolated samples of **4** or **5** with KC_8 or KH in THF cleanly yielded **3**. Similar attempts to prepare **3** by the in situ synthesis of $UI_4(THF)_x$ followed by reduction were unsuccessful because of the ring opening of THF. Treating UCl_4 with Me_3SiI in THF yielded a rapid color change from green to red-orange as expected, but the reaction reverts to green after ca. 5 min. XRD analysis conducted on single crystals isolated from the reaction mixture revealed the complex $UCl_3[O(CH_2)_4I](THF)$ (**6**). The structure, which is similar to ring-opened complexes described in separate

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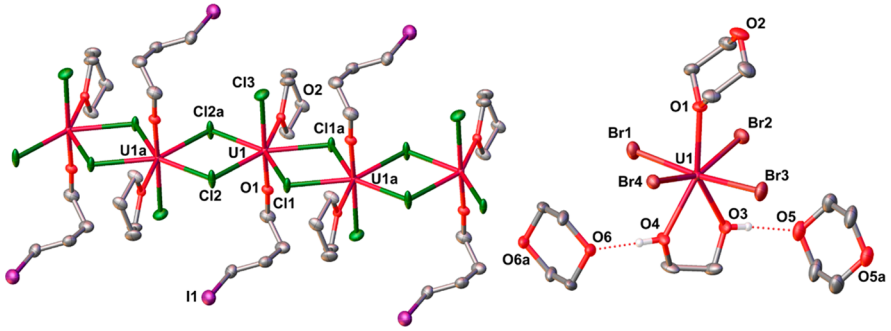

Figure 2. Molecular structures of **6** (left) and **7** (right). Thermal ellipsoids shown at 50% probability. Hydrogens atoms attached to carbon were omitted from the figure.

reports by KcKee and Santos,[37,38] shows uranium bound to one terminal and four bridging chlorides as well as a ring-opened THF with an iodide bound to the last carbon to form an iodobutoxide chain (Figure 2). The lack of an O−H stretch in the IR spectrum confirmed that no hydroxyl group was present, and the relatively short U1−O1 bond distance of 2.003(3) Å was consistent with an anionic $[O(CH_2)_4I]^-$ ligand to give a formal oxidation state of U^{4+}. In a related observation, we discovered that conducting the synthesis of both **4** and **5** inside a glovebox in the presence of THF vapor yields similar color changes and precipitation of a yellow-green insoluble byproduct believed to be similar to **6**. The generation of this byproduct lowers the overall reaction yields and purity of the target complexes, so we recommend conducting the synthesis of **4** and **5** on a Schlenk line or in a well-purged glovebox free of THF. These observations of ring-opened THF products are similar to those described by Kiplinger and co-workers in their attempted syntheses of $ThI_4(THF)_4$.[28]

Unlike **3**, attempts to prepare **2** by reduction of UBr_4 etherate adducts were unsuccessful because we were unable to cleanly isolate etherates with 1,4-dioxane or Et_2O. Treating UCl_4 with Me_3SiBr in Et_2O yielded no obvious evidence of reactivity after 18 h, but reactions conducted in 1,4-dioxane slowly produced a brownish, amber-colored solution. Upon further workup, brown crystals were isolated from the 1,4-dioxane reaction and analyzed by single-crystal XRD to reveal the unusual complex $UBr_4[HO(CH_2)_2OH](1,4\text{-dioxane})$ (**7**). The structure contains uranium bound to four equatorially bound bromide ligands. The 1,4-dioxane ligand occupies the axial position opposite to the bidentate $HO(CH_2)_2OH$. The two O−H groups in $HO(CH_2)_2OH$ form hydrogen bonds with two cocrystallized 1,4-dioxane molecules (Figure 2). As with **6**, the IR spectrum showed no evidence of O−H stretches, but the U−O bond distances in **7** are consistent with a neutral glycol ligand. The U−O3 and U−O4 distances of 2.418(3) and 2.408(4) Å are similar to the U1−O1 bond distance with the neutral dioxane at 2.449(4) Å. The U−Br distances, which a range from 2.7496(6) to 2.792(1) Å, also appear to be consistent with those expected for U^{4+}; the U−Br distances reported previously for $UBr_4(DME)_2$ are 2.783(1)−2.805(1) Å.[10]

Synthesis of 1 from $U(BH_4)_4$. In an effort to identify other potential starting materials for producing **1**−**3**, we sought other U^{4+} complexes known to undergo reduction to U^{3+}. One such complex is $U(BH_4)_4$, which is a highly volatile complex discovered during the Manhattan Project.[39,40] It is known that $U(BH_4)_4$ can be thermally reduced to $U(BH_4)_3$ via elimination of H_2 and B_2H_6.[39,41] Our goal was to evaluate whether this could provide another route to access uranium trihalide starting materials. It should be noted that $U(BH_4)_3(THF)_2$ has also been used as a starting material to prepare U^{3+} complexes, as championed by Arnold and co-workers.[42−44] $U(BH_4)_3(THF)_2$ used as a starting material in prior work was prepared by metathesis reactions using **3** obtained from uranium metal rather than thermal reduction of $U(BH_4)_4$ as described here.[42]

We prepared $U(BH_4)_4$ by ball milling UCl_4 with 4 equiv of $LiBH_4$ (Scheme 3). $U(BH_4)_4$ was isolated from the reaction mixture by sublimation using a liquid-N_2-cooled sublimator, and its purity was confirmed by ^1H and ^{11}B NMR spectroscopy and single-crystal XRD data collected on sublimed crystals. XRD studies revealed the polymeric 14-coordinate structure of $U(BH_4)_4$ and provided a space group and unit cell match to the data reported previously by Lippard and co-workers.[31,32] The ^1H NMR data collected in C_6D_6 revealed broad resonance at δ 134.8 (fwhm = 478 Hz), and the ^{11}B NMR spectrum revealed a paramagnetically shifted but resolved pentet at δ 131.6 with a $^1J_{BH}$ coupling of 86 Hz.

Once isolated, $U(BH_4)_4$ was thermally reduced in toluene at ca. 100 °C to $U(BH_4)_3$ as described previously and converted to $U(BH_4)_3(THF)_2$ by stirring in THF.[41] $U(BH_4)_3(THF)_2$ was isolated as red crystals in 73% yield by vapor diffusion of the THF solution with pentane, and the purity was confirmed by NMR spectroscopy in C_6D_6. The ^1H NMR data revealed the β-CH_2 and α-CH_2 resonances at δ 2.30 and 5.20, respectively, and the broad BH_4 resonance was observed at δ 119 (fwhm = 345 Hz), consistent with those previously reported in toluene.[42] Likewise, a broad ^{11}B NMR resonance was observed at δ 153 (fwhm = 230 Hz).

The addition of 3 equiv of HCl (1 M solution in Et_2O) to $U(BH_4)_3(THF)_2$ afforded **1** in yields as high as 85%. The reaction generated a gas presumed to be mostly H_2, and ^{11}B NMR data collected on the reaction mixture revealed resonances indicative of BH_3·THF and B_2H_6. EA and ^1H NMR data collected were identical with those for **1** prepared using the other methods reported above. Presumably, this method could be used to prepare **2** and **3**, but it was not pursued given the lack of commercially available solutions of anhydrous HBr and HI and the expense of purchasing these reagents as gases.

Analysis of THF Lability. During our studies, we observed that samples of **1**−**3** changed color and lost crystallinity when they were placed under dynamic vacuum for extended periods of time. For example, the color of **1** changed from blue to red-purple, whereas **2** and **3** changed from dark purple to dark green. Similar color changes were observed when the

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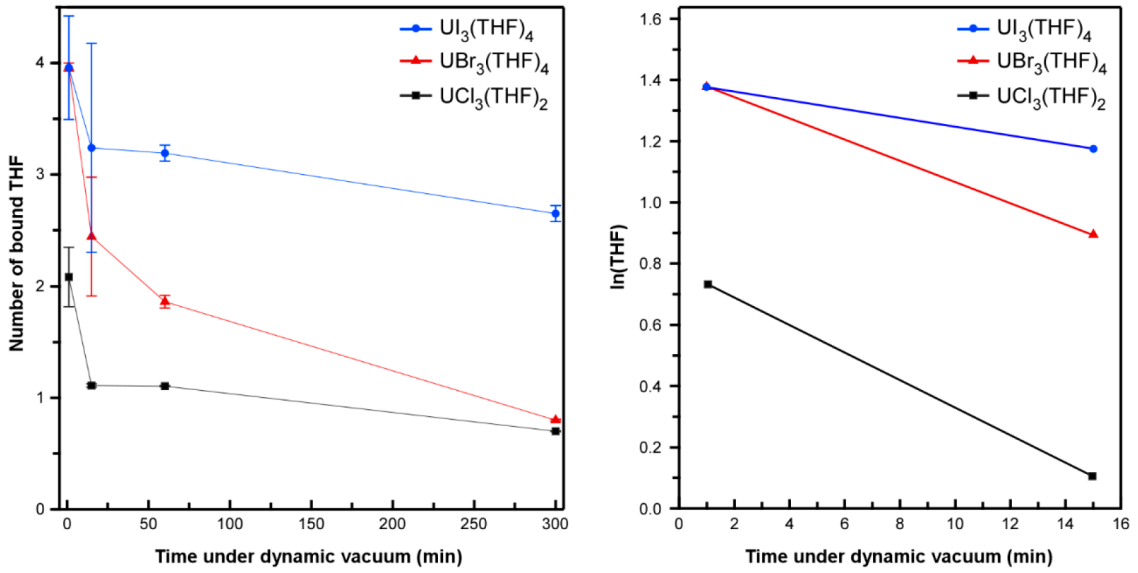

Figure 3. (Left) Analysis of THF equivalents present in samples of **1**−**3** exposed to dynamic vacuum (2.5×10^{-2} Torr) at different time intervals, as determined by % C from EA data. Data were collected on triplicate samples, and error bars represent standard deviations. (Right) First-order rate analysis of THF loss at early time points.

complexes were stirred for extended periods (8−12 h) in nonpolar solvents such as pentane. Once the complexes changed color, their solubility was greatly diminished in solvents such as toluene and benzene. These observations were initially mistaken for oxidation/hydrolysis until it was discovered that the original colors of each complex could be restored in less than 10 min when placed in a THF-saturated atmosphere or dissolved in THF. This suggested that the change in color was instead due to loss of coordinated THF.

To better understand the lability of the bound THF molecules in **1**−**3**, EA data were collected on samples exposed to dynamic vacuum (2.5×10^{-2} Torr) at different time intervals (1 min, 15 min, 1 h, and 5 h). The % C values were used to assess the number of THF molecules present, and the data plotted in Figure 3 were corroborated by plots obtained using the % H data (see the Supporting Information). Data were collected on triplicate samples prepared by multiple methods at each time point to provide standard deviations. Samples of **1** included in the study were prepared by Methods A−C, whereas samples of **2** and **3** were prepared by Methods A and B (see the Experimental Section). Not surprisingly, the greatest uncertainties were observed at the earliest time points (1 and 15 min), but the uncertainties decreased significantly at longer time intervals despite the samples being prepared by different methods.

It is useful to frame the EA results in the context of thermogravimetric analysis (TGA) studies conducted previously on **3** at atmospheric pressure.[5] These TGA experiments showed that the first 1 equiv of THF was not lost from samples of **3** until temperatures exceeded 75 °C. In contrast, our EA studies revealed that all three complexes lose a significant amount of THF after just 15 min under dynamic vacuum regardless of halide identity. The chloride complex **1** starts with 2.1 ± 0.3 mol of THF, but the average value decreases to 1.11 ± 0.01 after only 15 min, consistent with the prior discrepancies in the reported number of THF molecules in the formula of this complex.[14] After loss of one THF molecule, the desolvation rate slowed to give $UCl_3(THF)_{0.7}$ at the end of 5 h.

We next compared THF loss in isostructural **2** and **3**. The EA data revealed an average of 4.0 THF molecules for both complexes after 1 min under vacuum, consistent with their XRD structures. However, the number THF molecules decreased much more rapidly for **2** to give a formula of $UBr_3(THF)_{1.9}$ after 1 h and $UBr_3(THF)_{0.8}$ after 5 h. For comparison, **3** showed the least amount of THF loss over the 5 h period, yielding a formula of $UI_3(THF)_{2.7}$.

To better quantify the rate of THF loss with respect to the different starting numbers of THF in **1**−**3**, we attempted to fit the data to several kinetic models. The simplest mechanism to model is the initial loss of a single THF molecule, as shown below in eq 9, which is defined by a rate constant of k_1 ($M^{-1}min^{-1}$).

$$UX_3(THF)_a \rightarrow UX_3(THF)_{a-1} + THF \quad (9)$$

This represents the first step in a multistep mechanism, which likely includes structural rearrangements to achieve polymeric and halide-bridged structures like those observed for **1** when complexes **2** and **3** become more deficient in THF. At sufficiently early times (i.e., when loss of the first THF accounts for the majority of total THF loss), the first-order rate law k_1 is well characterized by the slope of ln(THF) versus time (min) because the intercept crosses close to the expected value of $\ln(a)$, where a is the initial number of THF molecules. At later times (>15 min), the desolvation rate is described by a serial mechanism of sequential THF loss that requires more data points to fit the more complicated mathematical expression. For this reason, we have only modeled and compared the initial rates defined by k_1.

The initial rate data are plotted in Figure 3 and summarized in Table 2. The initial rate uses the first two data points at 1 and 15 min, where loss of the first THF molecule predominates for all three complexes. The model shows that k_1 values for **1** and **2** with X = Cl and Br have comparable slopes with a rate constant of ca. 0.04 M^{-1} min^{-1}, whereas k_1 for the iodide complex **3** is significantly lower at 0.014 M^{-1} min^{-1}. We postulate that the origin of this difference can be attributed to a linear free energy relationship with the THF

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Table 2. Initial Rate Analysis for $UX_3(THF)_a$ from Data at 1 and 15 min

	1	2	3
k_1 (slope; M^{-1} min^{-1})	0.045	0.035	0.014
y intercept	0.8	1.4	1.4
expected y intercept based on the starting THF	0.7	1.4	1.4
number of THF molecules lost at 15 min	1	1.5	0.7

dissociation energy, as would be expected for a dissociative reaction mechanism. Under these circumstances, it would appear reasonable that the THF dissociation energy is highest for **3** because of the softer, less electronically saturating iodide ligands that enhance the U^{III}-THF binding affinity, especially with respect to **1** with chloride. However, it is still somewhat unusual that the initial rates are comparable for **1** and **2** with softer bromide. This may point to other factors contributing to THF loss in **2**. As discussed above, it is likely that monomeric **2** will adopt oligomeric structures like that of **1** as THF is removed, and this process may be more favorable for **2** relative to **3**. Additional studies are ultimately needed to investigate how changes in structure may contribute to these empirically observed differences in THF loss under vacuum.

CONCLUSION

In summary, we have reported a variety of high-yielding methods to access the desirable low-valent uranium starting materials **3** and **2** without using uranium metal. The syntheses are glovebox-friendly, use commercially available reagents, and can be conducted in one-pot reactions to yield crystalline starting materials in good to excellent yields after workup. We have described several circumstances that should be avoided to prevent formation of ring-opened complexes and impurities, as revealed by the structures of **6** and **7**. We have also reported an alternative synthesis of **1** from $U(BH_4)_4$. Time-dependent EA studies revealed how a significant amount of THF can be removed under dynamic vacuum for all three halide complexes in as little as 15 min, and this should be accounted for before using **1**−**3** as starting materials in subsequent reactions (especially in situations where the exact stoichiometry is critical). Overall, these results provide convenient entries into low-valent uranium chemistry that will facilitate new opportunities and expedite progress for researchers lacking access to uranium turnings.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00598.

Tabulated crystallographic data, NMR and IR spectra, plot of THF loss for **1**−**3** under vacuum based on % H from EA, and molecular structures of **1**, **4**, and $U(BH_4)_4$ (PDF)

Accession Codes

CCDC 2065220−2065223 and 2065374 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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