

Supporting Information

New Chemistry from an Old Reagent: Mono- and Dinuclear Macrocyclic Uranium(III) Complexes from $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$

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General Experimental Details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a glove box unless otherwise stated. Solvents (toluene, hexanes, diethyl ether (Et₂O) and tetrahydrofuran (THF)) were dried by passage through activated 4 Å molecular sieves or activated alumina towers and stored over activated 4 Å molecular sieves. Deuterated solvents were refluxed over potassium, free-pump-thaw degassed three times and vacuum transferred prior to use. ¹H NMR spectra were recorded at 298 K on either Bruker AVA400 AVA500 or PRO500 spectrometers at operating frequencies of 399.90 MHz and 500.23 MHz respectively, were referenced internally to residual protio solvent (¹H) and are reported relative to tetramethylsilane (δ = 0 ppm). ¹¹B NMR spectra were recorded at 298 K on a Bruker PRO500 at 160.49 MHz and were referenced to external BF₃·OEt₂. Infrared spectra were recorded on a Jasco 410 spectrophotometer, w = weak, m = medium, s = strong intensity. Elemental analyses were carried out by Mr Steven Boyer at London Metropolitan University, Analytische Laboratorien Germany and Medac Ltd UK. UI₃,¹ K₂L,² H₄L^{Me},³ H₄L^Λ,⁴ and NaN(SiMe₃)₂⁵ and were synthesized according to literature procedures. [NEt₃H][BPh₄] was synthesized by reaction of NEt₃·HCl with NaBPh₄ in water, recrystallized from methanol and dried under reduced pressure prior to use. MBH₄ (M = Na, K 99.9%) were purchased from Sigma Aldrich and dried under reduced pressure prior to use. LiBH₄ (99.9%) was purchased from Sigma Aldrich, recrystallized from Et₂O and dried under reduced pressure prior to use. LiN(SiMe₃)₂ (97%) was purchased from Sigma Aldrich, recrystallized from hexanes and dried under reduced pressure prior to use. All other reagents were used as purchased.

Synthesis of [U(BH₄)₃(THF)₂] **1**

THF (30 mL) was added to a dry mix of UI₃ (2.86 g, 4.62 mmol) and NaBH₄ (52 mg, 13.9 mmol, 3 equiv.) and stirred at ambient temperature for 1 hr. Volatiles were removed under vacuum and the solid residue dried thoroughly *in vacuo*. The crude reaction mixture was placed in a soxhlet apparatus containing a fine porosity glass frit and extracted into Et₂O (150 mL) at 65 °C for 6 hr. Volatiles were removed under vacuum and the red solids dried to yield [U(BH₄)₃(THF)₂] **1** (1.75 g, 4.10 mmol) as a microcrystalline red solid in 90% yield. ¹H NMR (*d*₈-THF): δ 85 (vbr s, *W*_{1/2} = 2152 Hz, 4H, BH₄). ¹H NMR (toluene-*d*₈): δ 125 (vbr s, *W*_{1/2} = 499 Hz, 4H (measured, 6 calc.; BH₄), 5.17 (br s, 4H, THF), 3.34 (br s, 4H, THF). ¹¹B NMR (*d*₈-THF): δ 233 (vbr s, *W*_{1/2} = 2252 Hz, BH₄). IR (nujol mull, BaF₂): ν 2446 (s) (ν_{B-Ht}), 2205 and 2147 (s) (ν_{B-Hb}), 1162 (s) (bridge deformation) cm⁻¹. Analysis: Found: C, 22.33; H, 6.51%, C₈H₂₈B₃O₂U requires: C, 22.52; H, 6.61%.

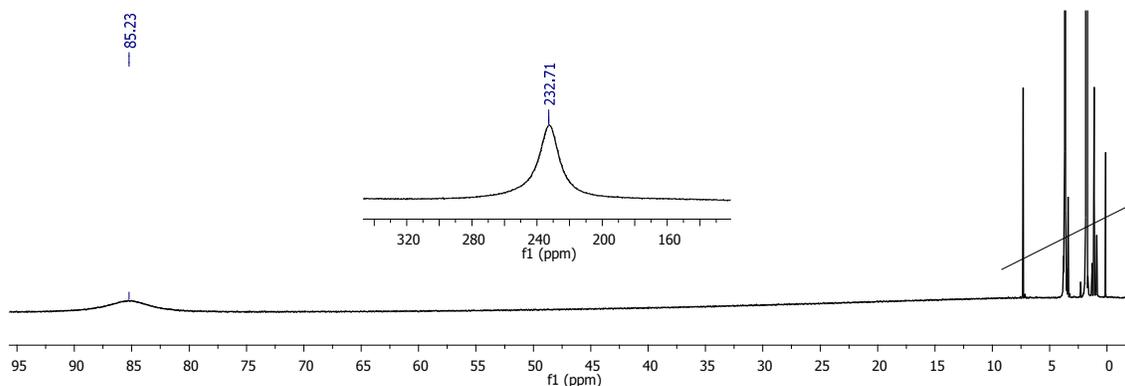


Figure S1. ^1H NMR spectrum of **1** with ^{11}B NMR spectrum inset (d_8 -THF). Resonances corresponding to *protio*-THF (containing C_6H_6 contaminant), residual Et_2O and silicone grease are scored through.

Determination of coordinated THF in **1**

The number of coordinated THF molecules in $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ was determined by elemental analysis and also by addition of excess dimethoxyethane (DME) to **1** in C_6D_6 to liberate the coordinated THF, which was then integrated against an internal standard, $\text{Si}(\text{SiMe}_3)_4$. Integration of the broad BH_4 resonance was found to be unreliable. The competitive displacement experiment was carried out in duplicate with the results tabulated below.

run	Mass $[\text{U}(\text{BH}_4)_3(\text{THF})_x]$ (mg)	Mass $\text{Si}(\text{SiMe}_3)_4$ (mg)	Theoretical relative integration THF : $\text{Si}(\text{SiMe}_3)_4$			Experimental relative integration THF : $\text{Si}(\text{SiMe}_3)_4$
			$x = 1$	$x = 2$	$x = 3$	
1.	5.2	3.0	1 : 5.74	1 : 3.45	1 : 2.69	1 : 3.49
2.	6.2	3.9	1 : 6.26	1 : 3.77	1 : 2.94	1 : 3.69

The use of toluene as solvent in the soxhlet extraction was also effective; THF solvate **1** is extracted, (the retention of coordinated THF observed by NMR spectroscopy) and not the arene adduct $(\text{PhMe})\text{U}(\text{BH}_4)_3$. However the yield was lowered (42 % assuming the empirical formula of **1**) due to the formation of a dark brown solid which precipitates from the toluene solution during extraction and is presumably the result of thermal decomposition at the higher extraction temperature. Characterising data for the thermally decomposed material (which is no longer soluble in toluene). ^1H NMR (d_8 -THF): δ 65 (vbr s, BH_4). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -THF): δ 265 (vbr s, BH_4), 250 (vbr s, BH_4) linewidths too broad in both to enable accurate $W_{1/2}$ measurement.

The ^1H NMR spectrum of $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ **1** in d_8 -THF agrees with one of the literature values quoted. Samples of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ formed when $(\text{arene})\text{U}(\text{BH}_4)_3$ is dissolved in d_8 -THF have a quoted chemical shift of -83 ppm.⁶ The ^1H NMR spectrum in d_8 -THF of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ has also previously been reported as three resonances at +246, +160, and +86 ppm, although the assignment of this to an equilibrium containing the neutral and ion-pair compounds corresponding to $3 \text{U}(\text{BH}_4)_3 \rightleftharpoons [\text{U}(\text{BH}_4)_2]_2[\text{U}(\text{BH}_4)_5]$,⁷ was questioned.⁶ ^1H NMR spectral resonances assigned to $(\text{BH}_4)^-$ bound to paramagnetic U(III) have been

recorded over a wide range of chemical shifts. We do not see any resolution of the borohydride coupling by ^1H or $^1\text{H}\{^{11}\text{B}\}$ NMR spectroscopy for any of the complexes **1 - 4**.

The ^{11}B NMR spectrum of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ made from $\text{U}(\text{BH}_4)_3$ dissolved in THF, and suggested to also contain the borohydride ion-pair complex was reported at -692, -436 and -411 ppm (relative to $\text{BF}_3\cdot\text{OEt}_2$),⁷ but no ^{11}B NMR spectroscopic data were provided for the synthesis of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ from $[\text{U}(\text{BH}_4)_3(\eta\text{-C}_6\text{H}_3\text{Me}_3)]$,⁶ or from the reaction of UCl_3 with NaBH_4 .⁸

Synthesis of known $[\text{U}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$ from $\text{U}(\text{BH}_4)_3(\text{THF})_2$

The chemical identity of $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ was also confirmed by the synthesis of the known complex $[\text{U}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$: a solution of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ (4.2 mg, 0.010 mmol) in $\text{THF-}d_8$ was added to $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ (5 mg, 0.010 mmol) in a Teflon-valved NMR tube. Effervescence was observed. The ^1H and ^{11}B NMR spectra were consistent with those previously reported for $[\text{U}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$.⁹ Single crystals suitable for X-ray diffraction formed in the NMR tube and were confirmed to be $[\text{U}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$ by unit cell check.^{9b}

NMR scale control reactions to form $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ using MBH_4 ($\text{M} = \text{Na, Li, K}$)

In a Teflon-valved NMR tube, UI_3 (8.5 mg, 0.014 mmol), $\text{Si}(\text{SiMe}_3)_4$ (3.8 mg, 0.012 mmol) and NaBH_4 (1.5 mg, 0.040 mmol, 3.3 equiv.) were combined in $\text{THF-}d_8$. There was an immediate colour change from blue to red and the only contact-shifted ^1H and ^{11}B NMR spectral resonances observed were at 95 ppm and 230 ppm respectively which we assign to the $(\text{BH}_4)^-$ ligands of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$. Heating for 48 h at 70 °C did not result in any change to the spectrum. We note that the ^1H NMR resonance observed for $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ formed *in situ* in d_8 -THF differs by ~ 10 ppm to that of isolated **1**, though the ^{11}B NMR resonances are identical. We suggest this may be due to the formation of higher oligomers upon exposure of $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ to high vacuum during experimental work up, *i.e.* through loss of THF. Reactivity studies have shown that $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ and **1** are chemically identical.

The analogous reaction between UI_3 (8.5 mg, 0.014 mmol) and LiBH_4 (1.5 mg, 0.040 mmol, 3.3 equiv.) in d_8 -THF in the presence of $\text{Si}(\text{SiMe}_3)_4$ (3.8 mg, 0.012 mmol) resulted in a colour change to red but no resonances for a paramagnetic species were observed.

The analogous reaction between UI_3 (15.2 mg, 0.025 mmol) and KBH_4 (4.0 mg, 0.074 mmol, 3.3 equiv.) in d_8 -THF in the presence of $\text{Si}(\text{SiMe}_3)_4$ (1.9 mg, 0.006 mmol) did not result in a colour change from blue and although resonances consistent with paramagnetic species were observed, those due to $[\text{U}(\text{BH}_4)_3(\text{THF})_n]$ were not seen.

After 7 days: ^1H NMR (d_8 -THF): δ 20 (vbr s, BH_4). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -THF): δ 270 (vbr s, BH_4), 250 (vbr s, BH_4).

After 14 days: ^1H NMR (d_8 -THF): δ 70 (vbr s, BH_4), 20 (vbr s, BH_4). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -THF): δ 270 (vbr s, BH_4), 250 (vbr s, BH_4).

Synthesis of [U(BH₄)(L)] **2**

THF (35 mL) was added to a dry mix of [U(BH₄)₃(THF)₂] (443 mg, 1.03 mmol) and K₂L (438 mg, 0.83 mmol) and the reaction mixture stirred at ambient temperature for 48 h. The resulting dark brown solution was filtered and volatiles were removed under vacuum. The brown residues were washed with hexanes (2 x 20 mL) and heated at 170 °C at 10⁻⁶ Torr to remove an H₂L impurity, yielding [U(BH₄)(L)] (453 mg, 0.65 mmol, 77%) as a dark brown solid. Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexanes into a THF solution of [U(BH₄)(L)] at ambient temperature over 2 d. **¹H NMR (toluene-*d*₈):** δ 113.14 (vbr s, 4H, BH₄, $W^{1/2} = 994$ Hz), 15.38 (s, 4H, pyrrolide CH), 3.10 (s, 12H, CH₃), -0.74 (s, 12H, CH₃), -15.08 (br, s, 4H, meta-C₆H₄), -15.61 (br, s, 2H, C₆H₄), -23.33 (v br, s, 2H, C₆H₄). **¹¹B{¹H} NMR (toluene-*d*₈):** δ 170 (br s, BH₄). **IR (nujol mull, BaF₂):** ν 3075 (w), 2725 (w), 2414 and 2384 (s) (ν_{B-Ht}), 2327 (w), 2226 (w), 2120 (s) (ν_{B-Hb}), 2029 (w), 1571 (m), 1409 (s), 1290 (s), 1260 (s), 1219 (s), 1181 (w), 1160 (m), 1119 (w), 1081 (w), 1045 (s) cm⁻¹. **Analysis:** Found: C, 54.62; H, 5.86; N, 3.87%, C₃₂H₄₀BN₂U requires: C, 54.79; H, 5.75; N, 3.99%.

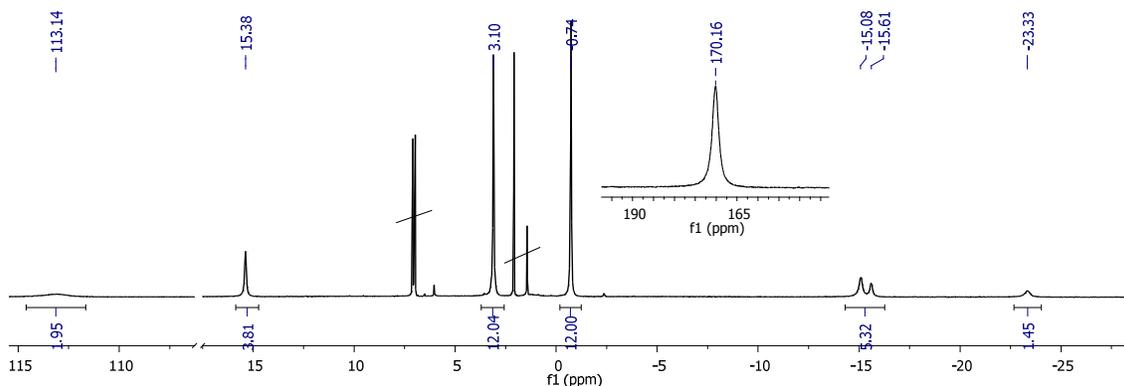


Figure S2. ¹H NMR spectrum of **2** with ¹¹B NMR spectrum inset (*d*₈-toluene). Resonances corresponding to *protio*-toluene and free H₂L by-product are scored through.

Reaction of $\text{U}(\text{BH}_4)_3(\text{THF})_2$ **1** with H_2L

In a Teflon-valved NMR tube, **1** (12.0 mg, 0.028 mmol) and H_2L (10.0 mg, 0.022 mmol, 0.8 equiv.) were combined in benzene- d_6 . No colour change was observed and only the resonances assigned to starting material were observed. Heating for 48 h at 70 °C did not result in any change to the spectrum.

Authors' Notes: We have previously reported that H_4L complexation by protonolysis using $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ does not result in U(III) products¹⁰ and therefore the analogous reactions of $\text{H}_4\text{L}^{\text{Me}}$ and $\text{H}_4\text{L}^{\text{A}}$ with **1** were not attempted.

Synthesis of $[\text{Li}(\text{THF})_4][\{\text{U}(\text{BH}_4)\}_2(\mu\text{-BH}_4)(\text{L}^{\text{Me}})]$ **3**

To a Schlenk charged with $\text{H}_4\text{L}^{\text{Me}}$ (410 mg, 0.62 mmol) and $\text{LiN}(\text{SiMe}_3)_2$ (415 mg, 2.48 mmol) was added THF (20 mL) and the resulting brown solution was stirred for 10 min before being transferred to a stirred suspension of $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ (530 mg, 1.24 mmol) in THF (20 mL). The dark red-brown mixture was stirred overnight during which time a small quantity of orange precipitate formed. The mixture was filtered, and the filtrate concentrated to 15 mL and stored at -30 °C to afford $[\text{Li}(\text{THF})_4][\{\text{U}(\text{BH}_4)\}_2(\mu\text{-BH}_4)(\text{L}^{\text{Me}})]$ as dark brown crystals (220 mg, 24%). **^1H NMR (d_8 -THF):** δ 63.07 (br, $W_{1/2} = 702$ Hz, terminal BH_4), 50.66 (s, 4H), 33.88 (s, 4H), 30.50 (s, 4H), 8.25 (s, 6H, *meso* Me), -2.45 (s, 6H *meso* Me) - 2.53 (s, 12H, aryl Me), -66.86 (s, 4H). **^{11}B NMR (d_8 -THF):** δ 324.84 (s, 1B, bridging BH_4), 212.30 (s, 2B, terminal BH_4). **^7Li NMR (d_8 -THF):** δ -1.10 (s, $[\text{Li}(\text{THF})_4]$). **IR (nujol mull, BaF_2):** ν 2414(w), 2333(w), 2193(w), 2124(w) (B-H deformations) cm^{-1} . **Analysis:** Found: C, 47.11; H, 5.55; N, 7.78%, $\text{C}_{58}\text{H}_{84}\text{B}_3\text{Li}_1\text{N}_8\text{O}_4\text{U}_2$ requires: C, 47.30; H, 5.75; N, 7.61%.

Authors' Notes: Isolated crystalline **3** cannot be re-dissolved in THF so the resonances reported above and in the spectrum below are taken from a small scale reaction in an NMR tube to form **3** *in situ*. Dissolution of **3** in pyridine results in decomposition. Although the macrocycle $\text{H}_4\text{L}^{\text{Me}}$ may also be readily deprotonated by both $\text{NaN}(\text{SiMe}_3)_2$ and $\text{KN}(\text{SiMe}_3)_2$, subsequent reaction with 2 equivalents of **1** does not yield a product analogous to **3** containing a sodium or potassium counter-ion but instead unidentifiable paramagnetic products.

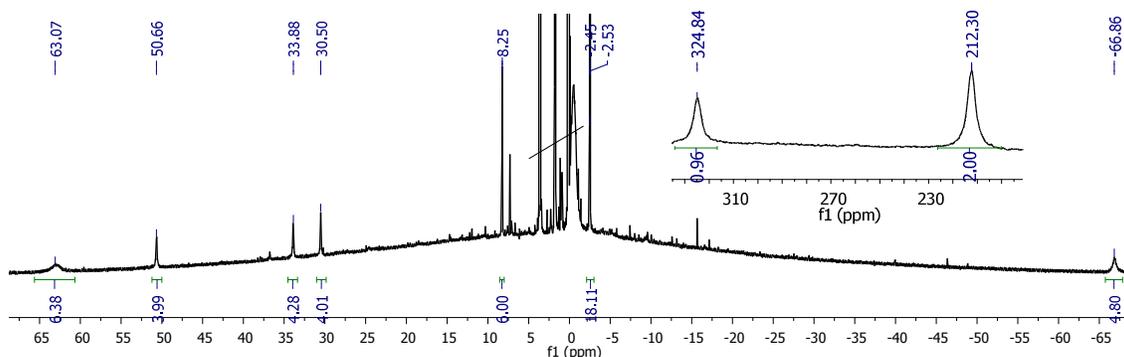


Figure S3. ^1H NMR spectrum of **3** with ^{11}B NMR spectrum inset (crude, d_8 -THF). Resonances corresponding to *protio*-THF and $\text{HN}(\text{SiMe}_3)_2$ and LiBH_4 by-products are scored through.

Synthesis of $[\text{Na}(\text{THF})_4][\{\text{U}(\text{BH}_4)\}_2(\mu\text{-BH}_4)(\text{L}^\wedge)(\text{THF})_2]$ **4**

To a Schlenk charged with $\text{H}_4\text{L}^\wedge$ (763 mg, 0.89 mmol) and $\text{NaN}(\text{SiMe}_3)_2$ (650 mg, 3.54 mmol) was added THF (30 mL) and the resulting orange suspension was stirred for 20 min before being transferred onto a stirred suspension of $[\text{U}(\text{BH}_4)_3(\text{THF})_2]$ (760 mg, 1.78 mmol) in THF (15 mL). The brown-green mixture was stirred overnight and then the solvent was removed under reduced pressure leaving khaki solids which were extracted into THF (10 mL). The extract was stored at -30°C for 1 week to afford $[\text{Na}(\text{THF})_4][\{\text{U}(\text{BH}_4)\}_2(\mu\text{-BH}_4)(\text{L}^\wedge)(\text{THF})_2]$ as dark green needles (480 mg, 30%). **^1H NMR ($d_8\text{-THF}$):** δ 35.14 (s, 4H), 18.52 (s, 4H), 15.83 (s, 4H), 11.08 (s, 2H, Ar-H), 10.27 (d, $^3J = 8.25$ Hz, 4H, pyrrole H), 10.05 (d, $^3J = 8.25$ Hz, 4H, pyrrole H), 8.79 and 8.71 (overlapping, 8H), 5.15 (s, 6H, *meso* CH_2CH_3), 4.64 (s, 4H), -0.14 (s, 6H, *meso* CH_2CH_3), -13.60 (s, 2H, Ar-H), -70.06 (br, $W_{1/2} = 498$ Hz, terminal BH_4). **$^1\text{H}\{^{11}\text{B}\}$ NMR ($d_8\text{-THF}$):** resonance at $\delta_{\text{H}} = -70.06$ sharpens to $W_{1/2} = 364$ Hz. **^{11}B NMR ($d_8\text{-THF}$):** δ 211.71 (s, 1B, bridging BH_4), 206.74 (s, 2B, terminal BH_4). **IR (nujol mull, BaF_2):** ν 2435 (w), 2313 (w), 2200 (w), 2144 (w) (B-H deformations) cm^{-1} . **Analysis:** Found: C, 53.59; H, 6.07; N, 6.17 %, $\text{C}_{82}\text{H}_{108}\text{B}_3\text{N}_8\text{Na}_1\text{O}_6\text{U}_2$ requires: C, 53.72; H, 5.94; N, 6.11 %.

Authors' Notes: In contrast to **3**, isolated crystalline **4** is highly soluble in THF. Furthermore, NMR scale reactions indicate that the lithium and potassium analogues of **4** may be successfully prepared by changing the identity of the silylamide base used in the initial macrocycle deprotonation step. Here we present the Na route as the most convenient for isolating crystalline material due to the different solubilities of **4** and NaBH_4 by-product.

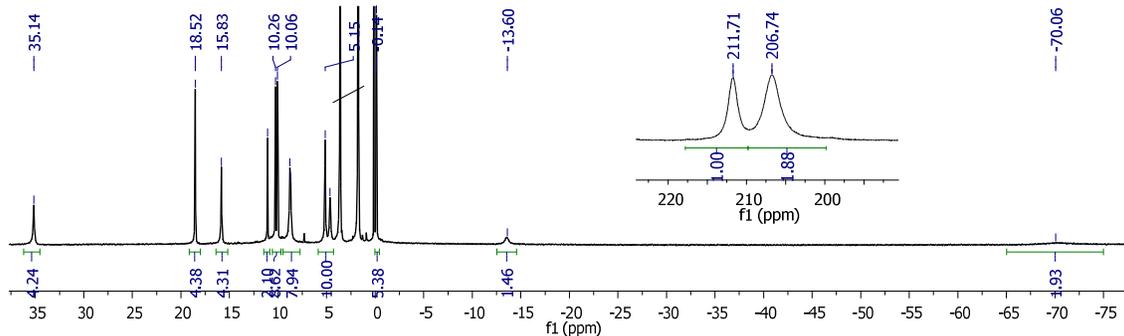


Figure S4. ^1H NMR spectrum of **4** with ^{11}B NMR spectrum inset ($d_8\text{-THF}$). Resonances corresponding to *protio*-THF are scored through.

Reaction of UI_3 with $\text{K}_4\text{L}^\wedge$: In a Teflon-valved NMR tube $\text{H}_4\text{L}^\wedge$ (9 mg, 0.010 mmol) and $\text{KN}(\text{SiMe}_3)_2$ (9 mg, 0.045 mmol) were combined in $d_5\text{-pyridine}$ (0.5 mL) and allowed to stand for 10 min forming an orange suspension. Upon addition of $[\text{UI}_3(\text{dioxane})_{1.5}]$ (16 mg, 0.021 mmol) the mixture turned dark green. **^1H NMR ($d_5\text{-pyridine}$):** δ 38.34 (s, 4H), 20.67 (s, 4H), 19.44 (s, 4H), 18.73 (s, 4H), 11.72 (s,

4H), 10.28 (s, 2H, ArH), 10.11 (s, 4H), 10.01 (s, 4H), 5.51 (s, 6H, *meso* Me), 3.63 (s, 37H, dioxane), 1.45 (s, 4H), 0.17 (s, 106H, HN(SiMe₃)₂), -2.09 (s, 6H, *meso* Me), -24.26 (s, 2H, ArH).

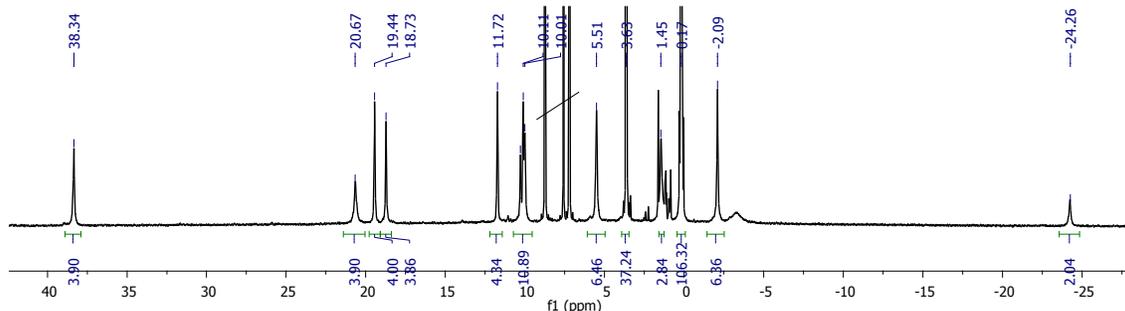


Figure S4. ¹H NMR spectrum of **5** (*d*₅-pyridine). Resonances corresponding to *protio*-pyridine are scored through.

A product could not be isolated from pyridine solution but on one occasion poorly-diffracting single crystals of a U(IV)/U(IV) hydrolysis product [$\{U(\text{py})\}\{U(\text{OH})(\text{py})\}(\mu\text{-O})(L^A)$] **5** were obtained from a pyridine/hexanes mixture. Although the crystal data are poor, the molecular structure was determined and is shown in Figure S5. The reaction may be carried out in THF to yield the same product in solution but attempts to isolate solid material either by removal of the solvent under reduced pressure or diffusion of hexanes into the THF solution resulted in decomposition to yellow insoluble material.

X-ray crystal structure of [$\{U(\text{py})\}\{U(\text{OH})(\text{py})\}(\mu\text{-O})(L^A)$] **5**

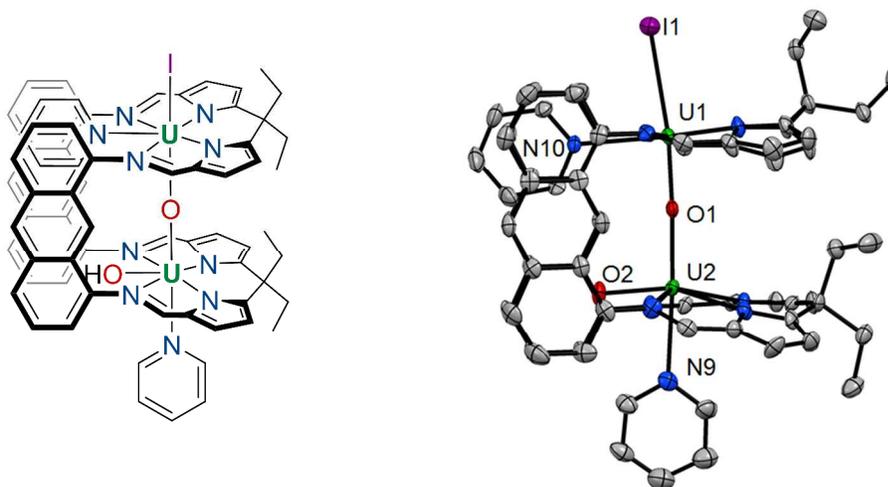


Figure S5. Molecular structure of [$\{U(\text{py})\}\{U(\text{OH})(\text{py})\}(\mu\text{-O})(L^A)$] **5**. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms and lattice solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): U1-I1 3.1032(8), U1-O1 2.047(7), U1-N10 2.655(8), U2-O1 2.201(7), U2-O2 2.065(8), U2-N9 2.629(7), U1...U2 4.2472(5), I1-U1-O1 171.5(2), N9-U2-O1 176.4(2), U1-O1-U1 177.0(4).

Experimental X-ray Crystallographic Information

	2	3	4	5
Chemical formula	C ₃₂ H ₄₀ BN ₂ U	C ₄₂ H ₅₂ B ₃ N ₈ U ₂ ·C ₁₆ H ₃₂ LiO ₄ ·3(C ₄ H ₈ O)	C ₈₈ H ₉₀ B ₃ N ₁₄ NaU ₂ ·3(C ₅ H ₅ N)	C ₆₈ H ₅₉ IN ₁₀ O ₂ U ₂ ·3(C ₅ H ₅ N)
M_r	701.52	1177.42	2112.52	1888.51
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1	Monoclinic, <i>P</i> 2 ₁	Triclinic, <i>P</i> ⁻ 1	Triclinic, <i>P</i> ⁻ 1
Temperature (K)	170	120	170	170
a, b, c (Å)	10.186 (5), 11.735 (5), 13.030 (5)	14.2234 (1), 17.8038 (2), 14.2288 (1)	11.6073 (2), 16.4500 (3), 26.2923 (6)	11.0751 (2), 15.0152 (3), 24.1321 (5)
α, β, γ (°)	79.413 (5), 72.025 (5), 75.355 (5)	90, 90.588 (1), 90	103.397 (2), 101.111 (2), 99.360 (2)	87.395 (2), 84.766 (2), 69.187 (2)
V (Å³)	1423.9 (11)	3602.98 (5)	4677.74 (16)	3735.17 (13)
Z	2	2	2	2
Radiation type	Mo <i>K</i> α	Cu <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm⁻¹)	5.72	12.99	3.52	4.80
Crystal size (mm)	0.96 × 0.53 × 0.29	0.13 × 0.12 × 0.08	0.64 × 0.20 × 0.02	0.24 × 0.11 × 0.01
Diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Analytical	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.046, 0.227	0.703, 1.000	0.526, 1.000	0.784, 1.000
No. of measured, independent and observed reflections	38645, 6529, 6173 { <i>I</i> > 2σ(<i>I</i>)}	119820, 15028, 14418 { <i>I</i> > 2σ(<i>I</i>)}	68401, 19119, 13698 { <i>I</i> > 2σ(<i>I</i>)}	9100, 9100, 7133 { <i>I</i> > 2σ(<i>I</i>)}
R_{int}	0.038	0.046	0.055	0.0000
θ_{max} (°)	27.5	76.7	26.4	22.0
(sin θ/λ)_{max} (Å⁻¹)	0.649	0.631	0.625	0.526
R[F² > 2σ(F²)], wR(F²), S	0.032, 0.098, 1.15	0.039, 0.102, 1.06	0.043, 0.092, 1.06	0.045, 0.105, 0.91
No. of reflections	6529	15028	19119	9100
No. of parameters	325	824	1172	918
No. of restraints	0	324	180	962
H-atom treatment	Riding	Riding	Mixture of independent and constrained	Mixture of independent and constrained
Δ_{max}, Δ_{min} (e Å⁻³)	4.70, -1.30	2.28, -1.19	2.34, -0.83	1.80, -0.72
CCDC Number	999591	999592	999593	999594

X-ray diffraction data were recorded for **2**, **4** and **5** on an Excalibur Eos diffractometer at 170(2) K using Mo *K*α radiation whilst data for **3** was collected at 120(2) K on a Supernova dual source Atlas diffractometer, utilising the Cu *K*α source. The structures of **2**, **3** and **5** were solved using Sir-92 whilst **4**

was solved using Superflip. All structures were least-square refined using SHELXL97 in WinGX.¹¹ All non-H atoms were refined anisotropically and all H atoms (except for the 12 BH₄ hydrogens in **4**, and OH proton in **5**, see below) were placed in calculated positions and refined using a riding model.

No restraints were applied during the refinement of **2**.

The [Li(THF)₄]⁺ cation of **3** was found to be considerably disordered. Unfortunately this disorder could not be satisfactorily modelled, instead appropriate restraints were applied to the 1,2 and 1,3 distances of the THF rings and all Li-O distances were fixed to 1.94(2) Å. Due to this unresolved disorder of the ligating THFs, H atoms on neighbouring THFs approached too close to one another. The BUMP command was used to increase the separation of carbon atoms whose H atoms were approaching too close to each other. ADDSYM suggests additional symmetry but the space group is confirmed as *P2*₁.

Two molecules of pyridine lattice solvent located at the corners of the unit cell of **4** were necessarily refined for reasons of crystal symmetry with two ring positions half N and half C occupied. The N and C components were constrained to occupy the same position and possess the same atom displacement parameters. The SIMU (su 0.04 Å²) and DELU (su 0.01 Å²) commands were applied to the atoms of two pyridine rings (one ligating Na⁺, the other bound to U(III) in the fifth equatorial site) to normalise the magnitude and direction of the atomic displacement parameters of neighbouring atoms.

The OH proton of **5** was located in the residual electron density map and its position refined with a distance restraint of 0.82(2) Å applied to the O-H bond length. The SIMU (su 0.04 Å²) and DELU (su 0.01 Å²) commands were applied to all atoms in the structure of **5** to normalise the magnitude and direction of the atomic displacement parameters of neighbouring atoms. Data were cut at high angle. The structure of **5** also contained a solvent accessible void. The PLATON SQUEEZE function was employed to remove residual electron density of 31e⁻ from the void, corresponding to approximately half a molecule of hexane anti-solvent per unit cell.

Treatment of BH₄ hydrogens The H atoms of the three BH₄ groups in **4** were located in the Fourier difference map and their positions refined. The following constraints were imposed on the BH₄ groups: (a) all B-H distances were constrained to be equal within a standard uncertainty of 0.02 Å (b) H···H distances within the same BH₄ group were constrained to be equal within a standard uncertainty of 0.04 Å (c) the atomic displacement parameters of all H atoms were constrained to be equal (d) for the bridging BH₄ group only, all H-U distances were constrained to be equal within a standard uncertainty of 0.02 Å. The BH₄ H atoms could not be located in the residual electron density maps of **2** or **3** so they have been omitted from the structural models.

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