

Supporting Information for

Homoleptic Thorium(IV) and Uranium(III) Alkyl Complexes

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General considerations. The syntheses and manipulations described below were conducted using standard Schlenk and glovebox techniques. All reactions were conducted in a Vacuum Atmospheres inert atmosphere (N₂) glovebox or a double-manifold Schlenk line. Anhydrous toluene, 1,2-dimethoxyethane, tetrahydrofuran, diethyl ether and hexanes were purchased, stored over activated 4 Å molecular sieves, and sparged with nitrogen prior to use. All available reactants were purchased from suppliers and used without further purification. [ThCl₄(DME)₂],¹ [UI₃(THF)₄],^{2,3} [α -K(DMBA)] (DMBA = *N,N*-dimethylbenzylamine),⁴ and (Et₂O)₂Li[CS₂(2,6-(Mes)₂C₆H₃)] (Mes = 1,3,5-trimethylbenzene),⁵ were synthesized following the previously published procedures. Benzene-*d*₆ and toluene-*d*₈ (Cambridge Isotope Laboratories) were dried over molecular sieves and degassed with three freeze-evacuate-thaw cycles. All ¹H and ¹³C NMR spectra were obtained on a 300, 500 or 600 MHz DRX Bruker spectrometer. ¹H NMR shifts given were referenced internally to the residual solvent peaks at δ 7.16 ppm (C₆D₅H) and 2.08 ppm (C₇D₇H). ¹³C NMR shifts given were referenced internally to the residual peak at δ 128.0 ppm (C₆D₆) and 138.0 ppm (C₇D₈). Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer.

Crystallographic Data Collection and Structure Determination. The selected single crystal was mounted on nylon cryoloops using viscous hydrocarbon oil. X-ray data collection was performed at 100(2) K. The X-ray data were collected on a Bruker CCD diffractometer with monochromated Mo-K α radiation (λ = 0.71073 Å). The data collection and processing utilized Bruker Apex2 suite of programs.⁶ The structures were solved using direct methods and refined by full-matrix least-squares methods on F₂ using Bruker SHELX-2014/7 program.⁷ All non-

hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and included in the refinement using a riding model. Thermal ellipsoid plots were prepared by using Olex2⁸ with 50% of probability displacements for non-hydrogen atoms. Crystal data and details for data collection for complexes **1**, **2**, **3**, and **4** are also provided in Table S1.

Magnetism Measurements. In an inert atmosphere glovebox, uranium complex **1** (9.1 mg) was powdered using an agate mortar and pestle, sandwiched between two plugs of quartz wool (Hereaus, 12.0 mg) within a 4 mm OD quartz tube, which was flame sealed on both ends. Variable temperature magnetization data were recorded at 0.1 T, 0.5 T, and 1 T using a Quantum Designs MPMS SQUID magnetometer. Variable temperature magnetization was corrected for the diamagnetism of the quartz wool using Pascal's constants (no correction for the diamagnetism of the quartz tube is needed as the quartz tube never leaves the SQUID coils). Molar susceptibility was corrected for the presence of a small amount of ferromagnetic impurity (M_{ferro}), the diamagnetism of the quartz wool (χ_{QW}), ligands and uranium (χ_{dia}) using Pascal's constants, and calculated using the following equation:

$$\chi_{\text{mol}} = \frac{(\text{molecular weight})}{(\text{sample mass})} \left[\frac{(M_{\text{meas}} - M_{\text{ferro}})}{H} - \chi_{\text{QW}} \right] - \chi_{\text{dia}}$$

where χ_{mol} is the molar susceptibility, M_{meas} is the measured magnetization, M_{ferro} is the magnetization of the ferromagnetic impurity, which is temperature independent and assumed to be identical at all fields, χ_{QW} is the contribution to the susceptibility due to the quartz wool, χ_{dia} is the diamagnetic correction, and H is the applied field. For **3** and **5**, this equation was applied to the 0.5 T and 1 T data to determine, M_{ferro} , which was 1.6×10^{-5} emu and 2.92×10^{-5} emu, respectively. The 0.1 T data was fit to the other data using $M_{\text{ferro},0.1\text{T}} = 0.63 M_{\text{ferro}}$ because the 0.1

T data is below the anisotropy field of the ferromagnetic impurity (see below); the value of 0.63 was determined by fitting the 0.1 T data to the 0.5 T and 1 T data. For 7, the amount of ferromagnetic impurity was determined using the 0.1 T, 0.5 T and 1 T data and $M_{\text{ferro},0.1\text{T}} = 0.63 M_{\text{ferro}}$; $M_{\text{ferro}} = 2.7 \times 10^{-5}$ emu.

Two ferromagnetic impurities are commonly encountered in laboratory samples, steel or iron metal and magnetite or other ferrites from oxide coating on stainless steel lab equipment. Of these, magnetite is far more likely to be encountered. In general, the magnetization of ferromagnets is temperature independent below the Curie temperature, which is 860 K for magnetite, so magnetization of the impurity is temperature independent for this experiment. The magnetization of ferromagnets is also largely field-independent above the anisotropy field, which is approximately 0.2 T for magnetite, above which the magnetization is ~ 90 emu/g.⁹ Below the anisotropy field, the magnetization of a magnet is roughly linear with applied field. Based on the assumption that the impurity is magnetite or some other ferrite resulting from the abrasion of stainless steel lab equipment, the data were corrected for a temperature and field independent ferromagnetic impurity. M_{ferro} was allowed to vary to minimize least squares difference between χ_{mol} at different fields, which produced a saturation magnetization of M_{ferro} of 2.7×10^{-5} emu, which corresponds to ~ 0.25 ug of magnetite.

Variable field magnetization data were collected at 2 K, 3 K, 5 K, and 298 K from -4 T to 4 T then back to -4 T to determine whether the sample displayed hysteresis. The data at 2 K, 3 K, and 5 K and low field were used to determine the magnetic susceptibility at 0 K.

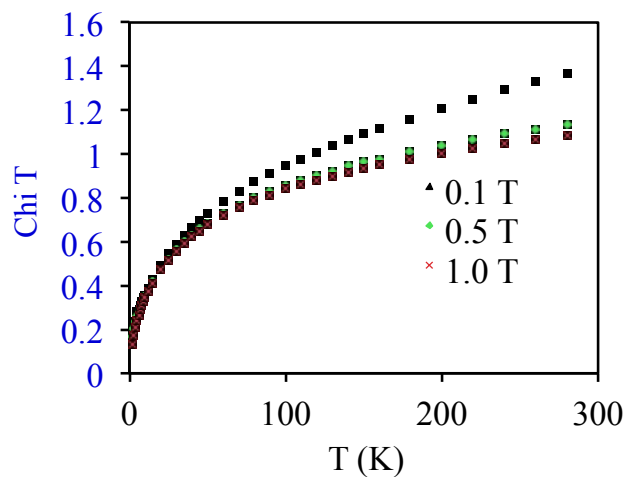


Figure S1. Variable temperature magnetic susceptibility of **1** without ferromagnetic correction.

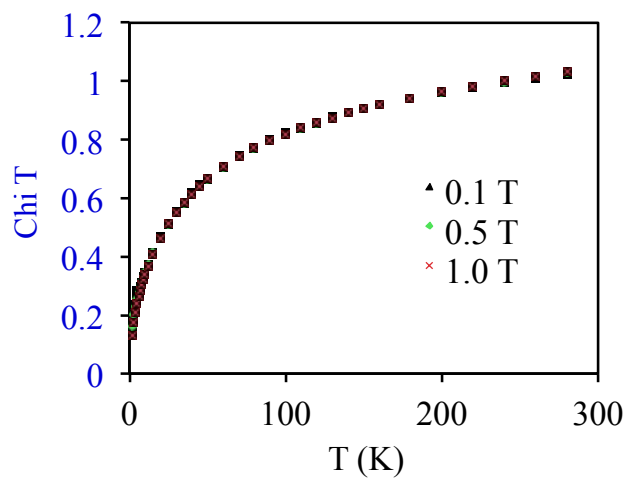


Figure S2. Variable temperature magnetic susceptibility of **1** corrected for the presence of a ferromagnetic impurity equivalent to ~ 0.25 μg of magnetite.

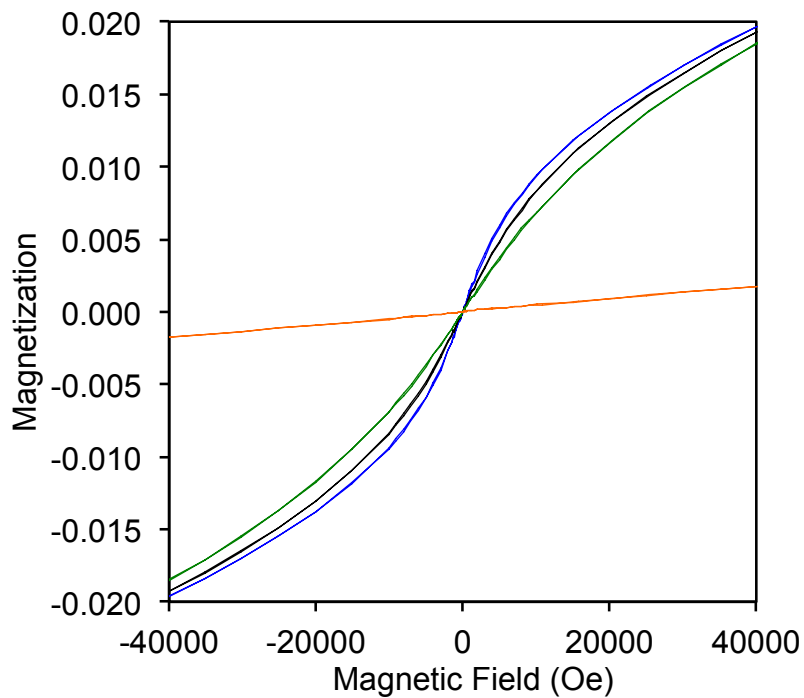


Figure S3. Variable field magnetization data at 2 K (blue), 3 K (black), 5 K (green), and 300 K (orange). Data were obtained as a full hysteresis curve from -4 T to 4 T and back to -4 T.

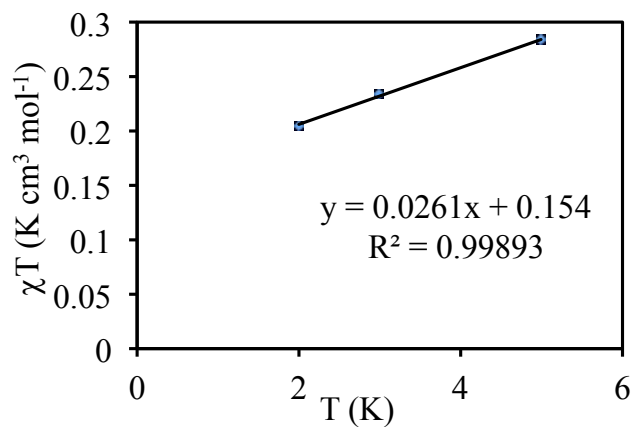


Figure S4. Low temperature magnetic susceptibility of **1** determined from the linear regions of the variable field data shown in Figure 3.

Synthesis of MesterphCS₂H. A 50 mL Schlenk flask was charged with (Et₂O)₂Li[CS₂(2,6-(Mes)₂C₆H₃)] (600 mg, 1.10 mmol) and 20 mL of Et₂O. 4 M HCl in dioxane (0.3 mL) was added dropwise via syringe to a stirred solution of (Et₂O)₂Li[CS₂(2,6-(Mes)₂C₆H₃)] at 0 °C. The resulting cloudy red solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum and the solid washed with hexanes and extracted with toluene. The cloudy red solution was filtered through Celite and dried under vacuum to obtain MesterphCS₂H as a pink crystalline powder (260 mg, 51%). ¹H NMR (C₆D₆): δ 7.07 (t, 1H, ³J_{H-H} = 7.8 Hz, *p*-C₆H₃), 6.89 (d, 2H, ³J_{H-H} = 7.8 Hz, *m*-C₆H₃), 6.83 (s, 4H, *m*-Mes), 5.61 (s, 1H, CS₂H), 2.21 (s, 12H, *o*-Mes), 2.16 (s, 6H, *p*-Mes). ¹³C{¹H} NMR (C₆D₆, 298K): 229.2, 145.4, 138.2, 137.2, 137.0, 136.6, 129.6, 129.3, 128.5, 21.5, 21.2. IR (KBr, cm⁻¹): 3046 (w), 2969 (w), 2941 (w), 2911 (m), 2852 (w), 2501 (vs, ν(S-H)), 1611 (m), 1569 (w), 1449 (m), 1374 (m), 1266 (w), 1243 (w), 1184 (w), 1101 (s), 1056 (s), 934 (s), 851 (s), 783 (w), 751 (vs), 688 (m), 617 (w), 585 (w). Anal. Calcd for C₂₅H₂₆S₂: C, 76.87; H, 6.71; S, 16.47. Found: C, 76.66; H, 6.63; S, 16.08.

Synthesis of α-U(DMBA)₃, (1). A 20 mL scintillation vial was charged with UI₃(THF)₄ (363 mg, 0.4 mmol), diethyl ether (10 mL) and placed in a -25 °C freezer for 30 minutes. A second 20 mL scintillation vial was charged with α-K(DMBA) (215 mg, 1.2 mmol) and added as a solid to the UI₃(THF)₄ mixture. The reaction was allowed to stir for three hours and the solvent was removed under vacuum to yield a black solid. The solid was extracted with toluene (2 x 10 mL), filtered over Celite, concentrated and placed in a -25 °C freezer for 48 h. The product was recovered as a black crystalline material (197 mg, 77%). X-ray quality crystals were grown from a concentrated toluene solution at -25 °C. ¹H NMR (C₇D₈, -78 °C): δ 46.86 (s, 9H, N(CH₃)₂), 39.65 (s, 3H, ArH), 24.50 (s, 3H, ArH), -9.39 (s, 3H, ArH), -44.24 (s, 3H, ArH), -53.39 (s, 3H, ArH), -71.63 (s, 9H, N(CH₃)₂), -94.42 (s, 3H, CH). IR (KBr, cm⁻¹): 3034 (m), 2959 (m), 2855

(s), 2773 (s), 1912 (w), 1785 (w), 1696 (w), 1654 (w), 1588 (s), 1525 (m), 1462 (s), 1326 (m), 1220 (m), 1164 (s), 1028 (s), 968 (m), 851 (m), 734 (s), 634 (m). UV-vis (0.5 mM, C₇H₈): 401 nm ($\epsilon = 5600 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Calcd for C₂₇H₃₆N₃U: C, 50.62; H, 5.66; N, 6.65. Found: C, 50.51; H, 5.42; N, 6.56.

Synthesis of Th[η^4 -Me₂NC(H)C₆H₅]₂[η^5 -(CH₂)MeNC(H)C₆H₅], (2). An oven dried 100 mL Schlenk flask was charged with ThCl₄(DME)₂ (639 mg, 1.2 mmol), 20 mL tetrahydrofuran and cooled to -78 °C. An oven dried 250 mL Schlenk flask was charged with α -K(DMBA) (799 mg, 4.6 mmol) and cooled to -78 °C. The solution of ThCl₄(DME)₂ was added to α -K(DMBA) by cannula and stirred for 2.5 h at 0 °C. The volatiles were removed *in vacuo*, extracted with 30 mL toluene and filtered through Celite. X-ray quality crystals were grown at -25 °C from a concentrated toluene solution. Yield: 620 mg, 73%. ¹H (C₇D₈, -78 °C): δ 7.36 (d, J = 6.3 Hz, 1H, ArH), 7.10 (br s, 1H, ArH), 6.98 (br s, 1H, ArH), 6.90-6.84 (m, 2H, ArH), 6.80-6.73 (m, 2H, ArH), 6.54-6.49 (m, 2H, ArH), 6.46-6.38 (m, 2H, ArH), 6.27 (d, J = 7.8 Hz, 1H, ArH), 3.83 (s, 1H, CH), 3.59 (d, J = 6.3 Hz, 1H, *o*-H), 3.17 (d, J = 5.7 Hz, 1H, *o*-H), 3.21 (s, 1H, CH), 3.18 (s, 1H, CH), 2.98 (d, J = 6.3 Hz, 1H, *o*-H), 2.43 (s, 3H, CH₃), 2.19 (s, 6H, N(CH₃)₂), 1.94 (s, 2H, CH₂), 1.92 (s, 3H, CH₃), 1.70 (s, 3H, CH₃). ¹³C{¹H} (C₇D₈, -78 °C): δ 138.95, 138.61, 136.89, 135.31, 131.09, 130.40, 129.85, 128.92, 127.38, 124.44, 121.08, 120.77, 120.52, 114.24, 113.51, 108.76, 98.72, 98.27, 91.78, 90.84, 90.43, 72.08, 44.02, 43.41, 41.65, 40.29, 40.01. IR (KBr, cm⁻¹): 3035 (m), 2959 (m), 2910 (m), 2863 (m), 2785 (m), 1599 (m), 1531 (m), 1479 (s), 1449 (m), 1332 (m), 1306 (m), 1259 (m), 1205 (m), 1171 (m), 1075 (m), 1028 (m), 1012 (m), 977 (m), 859 (m), 811 (m), 743 (s), 708 (m), 666 (m). Anal. Calcd for C₂₇H₃₅N₃Th: C, 51.18; H, 5.57; N, 6.63. Found: C, 51.10; H, 5.53; N, 6.61.

Synthesis of Th[S₂C(2,6-Mes₂C₆H₃)₄](THF), (3). A 20 mL scintillation vial was charged with **2** (104 mg, 0.17 mmol) and 7 mL THF. A second 20 mL scintillation vial was charged with MestrophCS₂H (260 mg, 0.67 mmol) and 10 mL THF. The solutions were combined and stirred for 18 hours. The resulting orange suspension was centrifuged and the precipitate washed with pentane (2 x 2 mL). The precipitate was dried under vacuum resulting in an orange powder (159 mg, 52%). X-ray quality crystals were grown from a concentrated toluene solution at -25 °C. ¹H NMR (C₆D₆): δ 7.03 (t, 4H, ³J_{H-H} = 7.2 Hz, *p*-C₆H₃), 6.93 (s, 8H, *m*-C₆H₃), 6.87 (s, 8H, *m*-Mes), 6.86 (s, 8H, *m*-Mes), 3.44 (s, 4H, THF), 2.45 (s, 24H, CH₃), 2.33 (s, 24H, CH₃), 2.00 (s, 24H, CH₃), 1.39 (s, 4H, THF). ¹³C{¹H} (C₆D₆): δ 252.11, 150.60, 139.74, 138.75, 137.66, 136.05, 135.49, 130.69, 129.22, 128.34, 127.90, 68.73, 25.80, 23.31, 22.32, 21.47. IR (KBr, cm⁻¹): 2964 (m), 2916 (s), 2856 (m), 1611 (m), 1572 (w), 1450 (m), 1376 (m), 1263 (m), 1207 (m), 1184 (m), 1100 (s), 1009 (vs), 916 (m), 847 (s), 807 (m), 758 (m), 742 (w), 698 (w), 583 (w), 466 (m). Anal. Calcd for C₁₀₄H₁₀₈OS₈Th: C, 67.07; H, 5.84; S, 13.77. Found: C, 67.45; H, 6.05.

Synthesis of U[S₂C(2,6-Mes₂C₆H₃)₄](THF), (4). A 20 mL scintillation vial was charged with **1** (126 mg, 0.20 mmol) and 5 mL THF. A second 20 mL scintillation vial was charged with MestrophCS₂H (237 mg, 0.61 mmol) and 5 mL THF. The solutions were combined and stirred for 48 h. The brown suspension was centrifuged and the pellet washed with pentane (2 x 2 mL). The pellet was extracted with toluene, filtered through Celite and volatiles removed *in vacuo* resulting in a dark red solid (64 mg, 17%). X-ray quality crystals were grown from a concentrated toluene solution layered with pentane at -25 °C. ¹H NMR (C₆D₆): δ 6.83 (br s, 16H, *m*-C₆H₃), 6.76 (t, 4H, ³J_{H-H} = 7.2 Hz, *p*-C₆H₃), 6.33 (d, 8H, ³J_{H-H} = 7.2 Hz, *m*-C₆H₃), 6.87 (s, 8H, *m*-Mes), 2.55 (s, 24H, *p*-CH₃). Due to the paramagnetism of uranium, we were unable to unambiguously identify the *o*-CH₃ and THF chemical shifts. IR (KBr, cm⁻¹): 2950 (s), 2917 (s),

2856 (m), 1612 (m), 1568 (w), 1484 (w), 1450 (s), 1376 (m), 1208 (m), 1185 (w), 1101 (m), 1011 (s), 998 (s), 936 (w), 918 (m), 848 (s), 808 (m), 779 (w), 760 (m), 742 (m), 698 (w), 585 (w). Anal. Calcd for C₁₀₄H₁₀₈OS₈U: C, 66.86; H, 5.61. Found: C, 66.53; H, 5.35.

Table S1. X-ray crystallography data is shown for complexes **1**, **2**, **3**, and **4**.

	1	2	3	4
CCDC deposit number	1507960	1507961	1507962	1507963
Empirical formula	C ₂₇ H ₃₆ N ₃ U	C ₂₇ H ₃₅ N ₃ Th	C ₁₀₄ H ₁₀₈ OS ₈ Th	C ₁₀₄ H ₁₀₈ OS ₈ U
Formula weight (g/mol)	640.63	633.62	1862.52	1868.51
Crystal habit, color	Prism, black	Prism, yellow	Prism, orange	Prism, red
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Volume (Å ³)	2469.6(6)	1211.2(4)	10384.7(16)	10248.6(14)
<i>a</i> (Å)	14.318(2)	9.590(2)	15.0263(13)	15.0040(12)
<i>b</i> (Å)	11.5400(17)	11.143(2)	25.217(2)	25.0884(19)
<i>c</i> (Å)	14.975(2)	11.619(2)	27.433(2)	27.253(2)
<i>α</i> (°)	90.00	88.275(2)	90.00	90.00
<i>β</i> (°)	93.520(2)	77.613(2)	92.5570(10)	92.527(10)
<i>γ</i> (°)	90.00	87.316(2)	90.00	90.00
<i>Z</i>	4	2	4	4
Calculated density (Mg/m ³)	1.723	1.737	1.343	1.330
Absorption coefficient (mm ⁻¹)	6.591	6.174	1.644	1.796
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R = 0.0233 R _w = 0.0496	R = 0.0262 R _w = 0.0648	R = 0.0517 R _w = 0.1264	R = 0.0611 R _w = 0.1276

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