Supporting Information for:

Synthesis of a Heterobimetallic Actinide Nitride and an Analysis of its Bonding

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, Et₂O, pentane, and toluene were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. THF was dried by distillation from sodium/ benzophenone, and stored over 3Å sieves for 24 h prior to use. Benzene-*d*₆ and THF-*d*₈ were dried over 3Å molecular sieves for 24 h prior to use. [U{*N*(R)(SiMe₂)*C*H₂}(NR₂)₂],¹ [K(DME)][Th{*N*(R)(SiMe₂*C*H₂)}₂(NR₂)],² [Na(THF)][U{*N*(R)(SiMe₂*C*H₂)}₂(NR₂)],³ and [Th(NR₂)₃(NH₂)] (R = SiMe₃)⁴ were synthesized according to the previously reported procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on an Agilent Technologies 400-MR DD2 400 MHz Spectrometer, a Varian UNITY INOVA 500 spectrometer, or a Varian Unity Inova 600 MHz spectrometer. ¹H NMR spectra were referenced to external tetramethylsilane (TMS) using the residual protio solvent peaks as internal standards. ¹³C{¹H} NMR spectra were referenced indirectly with the ¹H resonance of TMS at 0.0 ppm, according to IUPAC standard,^{5,6} using the residual solvent peaks as internal standards. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV3600 UV-NIR Spectrometer. NIR-Visible data were fit using PseudoVoigt peaks in Excel. Elemental analyses were performed by the Micro-Analytical Facility at the University of California, Berkeley.

EPR Spectroscopy. A ca. 20 mg of crystalline powered sample of **4** was finely ground using a mortar and pestle in the glovebox. The ground sample was transferred into a quartz

tube (5 mm) and a small amount of glass wool was placed inside. The tube was placed under vacuum and then flame sealed with a propane/oxygen torch. Data were recorded at 4 K on a Bruker X-band EPR EMX Plus spectrometer equipped with a Bruker dual-mode cavity (ER 4116DM) for both parallel and perpendicular modes and an Oxford Instruments SPE62NT900 liquid helium quartz cryostat using an Oxford Instruments ITC503 temperature and gas flow controller. Microwave frequency = 9.646641 GHz; microwave power = 100.2 mW; number of scans = 10.

SQUID Magnetometry. A sample of **4** (18.2 mg) was sandwiched between two pieces of quartz wool (8.7 mg total) inside a 3 mm OD quartz tube and compressed with quartz rods to form a pellet. The ends of the tube were sealed with septa. The middle of the tube was wrapped with a Kimwipe and cooled with liquid nitrogen. One end of the tube was flame sealed with a propane/oxygen torch. The sealed end of the tube was recorded at 6 T, 5 T, 4 T, 3 T 2 T, and 1 T using a Quantum Designs MPMS magnetometer. Data were corrected for inherent diamagnetism of the compound using Pascal's constants. The data showed the presence of a ferromagnetic impurity, and the appropriate correction was applied.⁷ The correction, 2×10^{-3} emu, is large relative to the magnetization of the sample at fields below 4 T. As a result, the high temperature data is not usable at low field. For this reason, only the data at 6, 5, and 4 T are used.

An additional complication of the SQUID measurement is the presence (or absence) of two pentane molecules of solvation, which are present in the crystal structure. Since we do not know whether these pentane molecules were lost while drying and preparing the magnetic susceptibility sample, the magnetic susceptibility of **4** was calculated both with and without these pentane molecules. The fitting residual for the fit using the data that did not include the pentane molecules had an error that was half of that determined with the pentane molecules included. For this reason, we assume that the pentane molecules of solvation are not present in the susceptibility sample, and the results given here are based on this assumption.

Magnetic susceptibility of **4** and the energies of its excited states were fit using Condon 3.0, a crystal field theory analysis package.⁸ One issue with analyzing magnetic susceptibility data is the number of independent data present in the experiment, which may be estimated using van Vleck's theory.^{9,10} The energy of a state, ψ_i , in a magnetic field is given by eqn 1, where the superscripts are the orders of the energy using perturbation theory, H is the magnetic field, μ_m is the magnetic moment operator, and the other symbols have their usual meanings. The magnetic susceptibility of a complex is given by eqn 2. To second order, each thermally occupied excited state in the susceptibility measurement contributes three data: $E_i^{(0)}$, $E_i^{(1)}$, and $E_i^{(2)}$, and the ground state contributes two data since $E_1^{(0)}$ is zero. As discussed in the main manuscript, one excited state becomes thermally occupied above 160 K, so the variable temperature magnetic susceptibility experiment contains five data. For this reason, the magnetic susceptibility is fit at only 5 temperatures, 10, 50, 100, 200, and 300 K.

$$E_{i} = E_{i}^{(0)} + HE_{i}^{(1)} + H^{2}E_{i}^{(2)} + \cdots, \text{ where } E_{i}^{(1)} = \langle \psi_{i} | \boldsymbol{\mu}_{\boldsymbol{M}} | \psi_{i} \rangle \text{ and } E_{i}^{(2)} = \sum_{j} \frac{\left| \langle \psi_{i} | \boldsymbol{\mu}_{\boldsymbol{M}} | \psi_{j} \rangle \right|^{2}}{E_{i}^{(0)} - E_{i}^{(0)}}$$
(1)

$$\chi = \frac{N}{p_i} \sum_i p_i \left(\frac{\left(E_i^{(1)} \right)^2}{kT} - 2E_i^{(2)} \right), \text{ where } p_i = e^{-E_i^{(0)}/kT}$$
(2)

X-ray Crystallography. Data for 1, 2, 3, and 4.2C₅H₁₂ were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo K α X-ray source ($\alpha = 0.71073$ Å). The crystals were mounted on a cryoloop under Paratone-N oil. Complex 1 and 3 were collected at 100(2) K and complexes 2 and $4 \cdot 2C_5H_{12}$ were collected at 110(2) K, using an Oxford nitrogen gas cryostream. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 10, 20, 10, and 10 s were used for 1, 2, 3, and $4 \cdot 2C_5H_{12}$, respectively. Data collection and cell parameter determinations were conducted using the SMART program.¹¹ Integration of the data frames and final cell parameter refinements were performed using SAINT software.¹² Absorption corrections of the data were carried out using the multi-scan method SADABS.¹³ Subsequent calculations were carried out using SHELXTL.¹⁴ Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL or Olex2.14-16

As a consequence of the crystal symmetry, the strucutre of **1** is disordered over two positions in a 50:50 ratio, such that there are two $-NH_2$ groups and six $-N{SiMe_3}_2$ groups. Additionally, the $N{SiMe_3}_2$ groups exhibited some unresolved positional disorder. As a result, their carbon and silicon atoms were constrained with the SADI and EADP commands.

For **2**, one $N(SiMe_3)_2$ group was found to be disordered over two positions in a 50:50 ratio. As a result, this $N(SiMe_3)_2$ group was constrained using SADI and EADP to all have the same temperature factors and geometries. In additon, the THF fragment ligated to the

 K^+ cation was also disordered over two positions in a 50:50 ratio. Its carbon and oxygen atoms were also constrained using SADI and EADP. Hydrogen atoms were not added to these disordered carbon atoms. Finally, the actinide postion was modelled as a 50:50 mixture of Th and U using the EXYZ command.

For **3**, the Et_2O fragment ligated to the K⁺ cation exhibited unresolved positional disorder. Its carbon atoms were constrained with the SADI, EADP, and DFIX commands.

For $4 \cdot 2C_5H_{12}$, the two actinide postions were modelled as a 50:50 mixture of Th and U using the EXYZ command. Additionally, the two pentane solvates exhibited mild unresolved positional disorder. As a result, their carbon atoms were constrained with the SADI and EADP commands.

Further crystallographic details can be found in Table S1. Complexes $1-4 \cdot 2C_5H_{12}$ have been deposited in the Cambridge Structural Database (1: CCDC 2108832; 2: CCDC 2108833; 3: CCDC 2108834; $4 \cdot 2C_5H_{12}$: CCDC 2108835).

Synthesis of $[U(NR_2)3(NH_2)]$ (R = SiMe3) (1). To a stirring, cold (-25 °C), orange solution of $[U\{N(R)(SiMe_2)CH_2\}(NR_2)_2]$ (111.6 mg, 0.162 mmol) in THF (2 mL) was added a THF solution of NH₃ (1.2 mL, 0.47 mmol, 0.4 M). The orange reaction mixture was allowed to warm to room temperature with stirring. After 1 h, the volatiles were removed *in vacuo* to provide a dark brown-orange solid. The solid was then extracted into pentane (3 mL) and the resulting dark-brown, cloudy suspension was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The filtrate was transferred to a 4 mL vial, which was placed inside a 20 mL scintillation vial and iso-octane (2 mL) was added to the outer vial. Storage of this two-vial system at -25 °C for 5 d resulted in the deposition of dark brown-orange blocks. The solid was isolated by decanting the supernatant and then dried *in vacuo* to yield **1** (17.0 mg). The supernatant was transferred to a new 4 mL vial, which was placed inside a 20 mL scintillation vial and iso-octane (2 mL) was added to the outer vial. Storage of this two-vial system at -25 °C for 2 d resulted in the deposition of more dark brown-orange crystalline solid (62.3 mg). Total yield: 0.0793 g, 69% yield. Anal. Calcd for $C_{18}H_{56}N_4Si_6U$: C, 29.41; H, 7.68; N, 7.62. Found: C, 29.38; H, 7.38; N, 7.24. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ -2.95 (s, SiCH₃). IR (KBr pellet, cm⁻¹): 432 (s), 525 (s), 609 (s), 613 (s), 864 (w), 1180 (s), 1246 (s), 1402 (m), 1504 (s), 1618 (m), 1919 (m), 2949 (w), 3336 (s, v_{NH}).

Synthesis of [K(18-crown-6)(THF)2][(NR2)3U(μ-N)Th(NR2)3] (2) and [(K(18-crown-6)][K(18-crown-6)(Et₂O)₂][(NR₂)₂U(μ -N)(μ - κ^2 -C,N-CH₂SiMe₂NR)Th(NR₂)₂]₂ (3). To a stirring, cold (-25 °C), dark brown solution of 1 (90.7 mg, 0.123 mmol) in THF (2 mL) added a cold (-25 °C). pale-yellow solution of was $[K(DME)][Th{N(R)(SiMe_2CH_2)}_2(NR_2)]$ (103 mg, 0.123 mmol) and 18-crown-6 (33.2) mg, 0.126 mmol) in THF (4 mL). After 24 h, the solution was filtered through a Celite column supported on glass wool $(0.5 \times 2 \text{ cm})$, concentrated *in vacuo* to 2 mL, and layered with pentane (4 mL). Storage at -25 °C for 24 h resulted in the deposition of pale orange crystalline material, which was isolated by decanting the supernatant and then dried *in vacuo* to yield 2, which co-crystallized with small amounts of $[(R_2N)_3Th(\mu-N)Th(NR_2)_3]^{-1}$ and $[(R_2N)_3U^{IV}(\mu-N)U^{IV}(NR_2)_3]^{-4.17}$ Total yield: 0.111 g, 48% yield. According to the -75 °C ¹H NMR spectrum, complexes 2, $[(R_2N)_3U(\mu-N)U(NR_2)_3]^-$, and $[(R_2N)_3Th(\mu-N)U(NR_2)_3]^-$ N)Th(NR₂)₃]⁻ are present in this sample in a ca. 20:3.3:1 ratio. Anal. Calcd for C₅₆H₁₄₈KN₇O₈Si₁₂ThU: C, 35.51; H, 7.88; N, 5.18. Found: C, 35.64; H, 7.74; N, 5.00. ¹H NMR (400 MHz, 25 °C, THF- d_8): δ 0.39 (s, SiCH₃, [(R₂N)₃Th(µ-N)Th(NR₂)₃]⁻), 3.39 (s, 18-crown-6), 9.93 (br s, 54H, SiCH₃, **2**). ¹H NMR (500 MHz, -10 °C, THF-*d*₈): δ -44.66 (br s, SiCH₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), 0.37 (s, SiCH₃, [(R₂N)₃Th(µ-N)Th(NR₂)₃]⁻), 3.56 (s, 24H, 18-crown-6), 8.71 (br s, 27H, SiCH₃, **2**), 13.81 (br s, 27H, SiCH₃, **2**). ¹H NMR (500 MHz, -75 °C, THF-*d*₈): δ -98.95 (br s, SiCH₃, **2**), -62.34 (br s, SiCH₃, **2**), -61.27 (br s, SiCH₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), -48.34 (br s, SiCH₃, **2**), -37.78 (br s, SiCH₃, **1**, (R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), -34.80 (br s, SiCH₃, **2**), -14.82 (br s, SiCH₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), -2.49 (br s, SiCH₃, **2**), 3.57 (s, 24H, 18-crown-6), 9.77 (br s, SiCH₃, **2**), 13.43 (br s, SiCH₃, **2**), 14.59 (br s, SiCH₃, **2**), 18.51 (br s, SiCH₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), 23.39 (br s, SiCH₃, **2**). Three methyl resonances for **2** were not observed in the -75 °C spectrum, presumably because of paramagnetic broadening. UV-vis/NIR (THF, 0.5 mM, 25 °C, L mol⁻¹cm⁻¹): 326 (ε = 260), 370 nm (ε = 200). IR (KBr pellet, cm⁻¹): 594 (s), 656 (s), 744 (s), 843 (w), 930 (w), 1111 (m), 1250 (m), 1352 (s), 2895 (w), 2949 (w), 3448 (w).

The supernatant was dried in vacuo to yield a dark solid which was extracted with Et₂O (4 mL). The resulting dark brown solution was filtered through a Celite column supported on glass wool $(0.5 \times 2 \text{ cm})$, concentrated *in vacuo* to 2 mL, and layered with pentane (4 mL). Storage at -25 °C for 2 weeks resulted in the deposition of golden brown crystalline material, which was isolated by decanting the supernatant and then dried *in vacuo* to yield $CH_2SiMe_2NR)U(NR_2)_2$ and the known uranium bis(metallacycle), $[K(DME)][U\{N(R)(SiMe_2CH_2)\}_2(NR_2)].$ According to the ¹H NMR spectrum, 3, $[K(solvent)][(NR_2)_2U(\mu-N)(\mu-CH_2SiMe_2NR)U(NR_2)_2],$ and $[K(solvent)][U{N(R)(SiMe_2CH_2)}_2(NR_2)]$ are present in an 21:3.5:1 ratio. Total yield:

0.070 g, 34% yield. Anal. Calcd for C₄₆H₁₂₃KN₆O₇Si₁₀ThU: C, 33.23; H, 7.46; N, 5.06. Found: C, 32.87; H, 7.32; N, 5.04. ¹H NMR (400 MHz, 25 °C, THF-*d*₈): δ -52.97 (br s, 6H, $SiMe_2CH_2$, $[(NR_2)_2U(\mu-N)(\mu-CH_2SiMe_2NR)U(NR_2)_2]^-$, -42.43 (br s, 6H, $SiMe_2CH_2$, 3), -36.44 (br s, 18H, N(SiMe_3)₂, [U{N(R)(SiMe_2CH_2)}_2(NR_2)]⁻), -8.90 (br s, 36H, NSiMe_3, 3), -5.49 (br s, 36H, NSiMe₃, $[(NR_2)_2U(\mu-N)(\mu-CH_2SiMe_2NR)U(NR_2)_2]^{-}$), 3.31 (s, 18-crown-6), 5.45 (s, 9H, Me_3 SiNSiMe₂CH₂, [(NR₂)₂U(μ -N)(μ -CH₂SiMe₂NR)U(NR₂)₂]⁻), 5.95 (s, 9H. *Me*₃SiNSiMe₂CH₂, 3), -9.56 (br s, $N(SiMe_3)_2$, $[(NR_2)_2U(\mu - N)(\mu CH_2SiMe_2NR$)U(NR₂)₂]⁻), 10.51 (br s, 36H, NSi CH_3 , 3), 31.40 (br s, 6H, Si(CH₃)₂, $[U{N(R)(SiMe_2CH_2)}_2(NR_2)]^{-}),$ 38.82 (br s, 18H, $N(SiMe_3)_2$, $[U{N(R)(SiMe_2CH_2)}_2(NR_2)]^{-}$. The methylene resonance of **3** was not observed. IR (KBr pellet, cm⁻¹): 596 (s), 663 (s), 746 (sh w), 773 (w), 837 (w), 849 (w), 1109 (m), 1250 (m), 1352 (s), 1454 (m), 2895 (w), 2900 (w).

Synthesis of $[(NR_2)_3U^v(\mu-N)Th^{Iv}(NR_2)_3]$ (4). To a stirring, cold (-25 °C), pale orange solution of 2 (65.6 mg, 0.0346 mmol) in THF (2 mL) was added a cold (-25 °C), red-orange solution of I₂ (4.80 mg, 0.0189 mmol) in THF (2 mL). After 2 min of stirring, the volatiles were removed *in vacuo* to provide a dark red-brown solid. The solid was then extracted into diethyl ether (3 mL) and the resulting dark red-brown solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The solution was concentrated *in vacuo* and stored at -25 °C for 24 h, which resulted in the deposition of red-brown solid. The sample (supernatant and solid) was again dried *in vacuo* and extracted into 3 mL pentane and the resulting dark red-brown solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). (Note: the reaction mixture can be extracted directly into pentane (skipping the Et₂O extraction step); however, direct extraction into pentane

results in slightly lower yields of **4**). The filtrate was transferred to a 4 mL vial, which was placed inside a 20 mL scintillation vial and iso-octane (2 mL) was added to the outer vial. Storage of this two-vial system at -25 °C for 24 h resulted in the deposition of dark brown blocks. The crystalline solid was isolated by decanting the supernatant and then dried *in* vacuo to yield 4, which co-crystallized with a small amount of $[(NR_2)_3 U^V(\mu -$ N)U^{IV}(NR₂)₃]¹⁷ (20.8 mg, 42% yield). According to the -75 °C ¹H NMR spectrum, complexes 4 and $[(NR_2)_3 U^V(\mu-N)U^{IV}(NR_2)_3]$ are present in a 12:1 ratio in this sample. Anal. Calcd for C₃₆H₁₀₈N₇Si₁₂ThU·2C₅H₁₂: C, 34.73; H, 8.36; N, 6.16. Anal. Calcd for C₃₆H₁₀₈N₇Si₁₂ThU: C, 29.89; H, 7.53; N, 6.78. Found: C, 30.11; H, 7.97; N, 6.44. ¹H NMR (400 MHz, 25 °C, THF-*d*₈): δ -12.47 (br s, SiCH₃), 4.79 (br s, SiCH₃). ¹H NMR (500 MHz, $-75 \,^{\circ}$ C, THF- d_8): $\delta -39.77 \,(\text{br s, SiCH}_3, 4), -21.91 \,(\text{br s, SiCH}_3, 4), -19.57 \,(\text{br s, SiCH}_3, 4),$ -12.22 (br s, SiCH₃, 4), -10.71 (br s, SiCH₃, $[(R_2N)_3U^V(\mu-N)U^{IV}(NR_2)_3]$), -9.11 (br s, SiCH₃, $[(R_2N)_3U^{V}(\mu-N)U^{IV}(NR_2)_3])$, -3.79 (br s, SiCH₃, $[(R_2N)_3U^{V}(\mu-N)U^{IV}(NR_2)_3])$, 4.67 (br s, SiCH₃, **4**), 5.40 (br s, SiCH₃, **4**), 7.16 (br s, SiCH₃, $[(R_2N)_3U^V(\mu-N)U^{IV}(NR_2)_3])$, 10.56 (br s, SiCH₃, 4), 18.13 (br s, SiCH₃, 4), 29.13 (br s, SiCH₃, [(R₂N)₃U^V(µ-N)U^{IV}(NR₂)₃]), 47.78 (br s, SiCH₃, 4). UV-vis/NIR (THF, 10.44 mM, 25 °C, L mol⁻¹cm⁻¹): 979 nm ($\varepsilon =$ 83.4), 1221 ($\varepsilon = 56.5$), 1410 ($\varepsilon = 70.0$), 1599 ($\varepsilon = 69.2$). IR (KBr pellet, cm⁻¹): 609 (s), 654 (m), 725 (s), 773 (s), 849 (w), 879 (w), 912 (s), 1182 (s), 1248 (m), 1401 (m), 2899 (m), 2954 (m).

NMR scale reaction of [Na(THF)][U{ $N(\mathbf{R})(SiMe_2CH_2)$ }2(NR)₂] with [Th(NR₂)₃(NH₂)]. An NMR tube fitted with a J-Young valve was charged with [Th(NR₂)₃(NH₂)]⁴ (14.6 mg, 0.02 mmol). A bright green THF- d_8 (0.5 mL) solution of [Na(THF)][U{ $N(\mathbf{R})(SiMe_2CH_2)$ }2(NR₂)]³ (16.7 mg, 0.02 mmol) was then added to the

NMR tube, along with a colorless THF- d_8 (0.5 mL) solution of 18-crown-6 (5.4 mg, 0.02 mmol). A ¹H NMR spectrum was then recorded (Figures S6-S7). ¹H NMR (400 MHz, 25 °C, THF- d_8): δ -36.94 (s, 18H, N(Si Me_3)₂, [U{ $N(R)(SiMe_2CH_2)$ }₂(NR₂)]⁻), -6.16 (br s, 6H, Si(CH_3)₂, [U{ $N(R)(SiMe_2CH_2)$ }₂(NR₂)]⁻), 0.38 (s, 54H, [Th(NR₂)₃(NH₂)]), 2.07 (s, 24H, 18-crown-6), 4.06 (t, 2H, NH₂, [Th(NR₂)₃(NH₂)]), 31.88 (br s, 6H, Si(CH_3)₂, [U{ $N(R)(SiMe_2CH_2)$ }₂(NR₂)]⁻), 39.47 (s, 18H, N(Si Me_3)₂, [U{ $N(R)(SiMe_2CH_2)$ }₂(NR₂)]⁻). After 24 h, a ¹H NMR spectrum was re-recorded, which revealed no change. The reaction mixture was then heated at 50 °C for 24 h, whereupon the solution turned an orange color. The ¹H NMR spectrum was re-recorded, which revealed an increase in the resonances assignable to HN(SiMe₃)₂, along with decreases in the resonances assigned to uranium bis(metallacycle) anion and thorium parent amide. However, no signals attributable to complex **2** were observed.

NMR scale reaction of [Na(THF)][U{N(R)(SiMe₂CH₂)}₂(NR)₂] with [U(NR₂)₃(NH₂)] (1). An NMR tube fitted with a J-Young valve was charged with a bright green THF-*d*₈ (0.5 mL) solution of [Na(THF)][U{N(R)(SiMe₂CH₂)}₂(NR₂)]³ (13.8 mg, 0.017 mmol). [U(NR₂)₃(NH₂)] (12.6 mg, 0.017 mmol) was then added to the NMR tube, along with a colorless THF-*d*₈ (0.5 mL) solution of 18-crown-6 (4.4 mg, 0.017 mmol). A ¹H NMR spectrum was then recorded (Figure S10). ¹H NMR (400 MHz, 25 °C, THF-*d*₈): δ -36.73 (br s, 18H, N(Si*Me*₃)₂, [U{N(R)(SiMe₂CH₂)}₂(NR₂)]⁻), -6.19 (br s, 6H, Si(CH₃)₂, [U{N(R)(SiMe₂CH₂)}₂(NR₂)]⁻), -2.93 (br s, 54H, 1), 2.26 (s, 24H, 18-crown-6), 31.54 (br s, 6H, Si(CH₃)₂, [U{N(R)(SiMe₂CH₂)}₂(NR₂)]⁻), 39.11 (s, 18H, N(Si*Me*₃)₂, [U{N(R)(SiMe₂CH₂)}₂(NR₂)]⁻). After 36 h, a ¹H NMR spectrum was re-recorded revealing the presence of two new broad peaks assignable to [(R₂N)₃U^{IV}(μ-N)U^{IV}(NR₂)₃]^{-.17 1}H NMR (400 MHz, 25 °C, THF-*d*₈): δ -36.69 (br s, 18H, N(Si*Me*₃)₂, [U{*N*(R)(SiMe₂CH₂)}₂(NR₂)]⁻), -25.36 (br s, 54H, SiC*H*₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), -6.17 (br s, 6H, Si(C*H*₃)₂, [U{*N*(R)(SiMe₂CH₂)}₂(NR₂)]⁻), -2.91 (br s, 54H, **1**), 2.26 (s, 24H, 18-crown-6), 22.13 (br s, 54H, SiC*H*₃, [(R₂N)₃U^{IV}(µ-N)U^{IV}(NR₂)₃]⁻), 31.58 (br s, 6H, Si(C*H*₃)₂, [U{*N*(R)(SiMe₂CH₂)}₂(NR₂)]⁻), 39.14 (s, 18H, N(Si*Me*₃)₂, [U{*N*(R)(SiMe₂CH₂)}₂(NR₂)]⁻).



Figure S1. ¹H NMR spectrum of $[U(NR_2)_3(NH_2)]$ (1) in C₆D₆. (^) indicates HN(SiMe₃)₂,

(%) indicates pentane, and (*) indicates an unidentified impurity.



Figure S2. Room temperature ¹H NMR spectrum of $[K(18-crown-6)(THF)_2][(NR_2)_3U(\mu-N)Th(NR_2)_3]$ (**2**) in THF-*d*₈. (*) indicates HN(SiMe_3)_2 and (@) indicates resonance assignable to $[K(solvent)][(R_2N)_3Th(\mu-N)Th(NR_2)_3]$.



Figure S3. Partial ¹H NMR spectrum of [(K(18-crown-6)][K(18-crown-

6)(Et₂O)₂][(NR₂)₂U(μ -N)(μ - κ ²-*C*,*N*-CH₂SiMe₂NR)Th(NR₂)₂]₂ (**3**) in THF-*d*₈. (*)

indicates HN(SiMe₃)₂, (&) indicates residual diethyl ether and pentane, and (@) indicates resonances assignable to $[K(solvent)][(NR_2)_2U(\mu-N)(\mu-CH_2SiMe_2NR)U(NR_2)_2].$



Figure S4. ¹H NMR spectrum of $[(K(18-crown-6)][K(18-crown-6)(Et_2O)_2][(NR_2)_2U(\mu-N)(\mu-\kappa^2-C,N-CH_2SiMe_2NR)Th(NR_2)_2]_2$ (**3**) in THF-*d*₈. (*) indicates HN(SiMe_3)_2, (\$) indicates $[K(DME)][U\{N(R)(SiMe_2CH_2)\}_2(NR_2)],$ (&) indicates residual diethyl ether and pentane, and (@) indicates resonances assignable to $[K(solvent)][(NR_2)_2U(\mu-N)(\mu-CH_2SiMe_2NR)U(NR_2)_2].$



Figure S5. ¹H NMR spectrum of $[(NR_2)_3U^V(\mu-N)Th^{IV}(NR_2)_3]$ (4) in THF-*d*₈. The inset highlights the second SiMe₃ resonance. (*) indicates the presence of HN(SiMe₃) and (#) indicates the presence of pentane.





Figure S7. Partial ¹H NMR spectrum of the reaction of $[Th(NR_2)_3(NH_2)]$ with $[Na(THF)][U\{N(R)(SiMe_2CH_2)\}_2(NR_2)]$ (R = SiMe_3) and 18-crown-6 in THF-*d*₈ over the course of 24 h. (*) indicates $[Th(NR_2)_3(NH_2)]$, (^) indicates 18-crown-6, and (&) indicates HN(SiMe_3)_2.



Figure S8. Variable temperature ¹H NMR spectra of [K(18-crown-

6)(THF)₂][(NR₂)₃U^{IV}(μ -N)Th^{IV}(NR₂)₃] (**2**) in THF-*d*₈. (*) indicates resonances assignable to [(R₂N)₃U^{IV}(μ -N)U^{IV}(NR₂)₃]⁻.



Figure S9. ¹H NMR spectrum of $[(NR_2)_3U^V(\mu-N)Th^{IV}(NR_2)_3]$ (4) in THF-*d*₈ at -75 °C. (*) indicates resonances assignable to $[(R_2N)_3U^V(\mu-N)U^{IV}(NR_2)_3]$.



Figure S10. ¹H NMR spectrum of the reaction of $[U(NR_2)_3(NH_2)]$ (1) with $[Na(THF)][U\{N(R)(SiMe_2CH_2)\}_2(NR_2)]$ (R = SiMe_3) and 18-crown-6 in THF-*d*₈ over the course of 36 h. (*) indicates 1, (@) indicates $[Na(THF)][U\{N(R)(SiMe_2CH_2)\}_2(NR_2)]$, (%) indicates $[(R_2N)_3U^{IV}(\mu-N)U^{IV}(NR_2)_3]^-$, (^) indicates unidentified products, and (&) indicates HN(SiMe_3)_2.

	1	2	3	$4 \cdot 2C_5H_{12}$
empirical formula	$C_{18}H_{56}N_4Si_6U$	C56H148KN7O8Si12ThU	$C_{46}H_{123}KN_6O_7Si_{10}ThU$	$C_{46}H_{132}N_7Si_{12}ThU$
crystal habit, color	Block, Brown	Block, Pale Orange	Needle, Brown	Block, Dark Brown
crystal size (mm)	$0.2 \times 0.2 \times 0.15$	0.2 imes 0.2 imes 0.15	0.25 imes 0.15 imes 0.1	0.2 imes 0.15 imes 0.1
space group	$R\overline{3}c$	<i>C</i> 2/m	<i>P-1</i>	$P2_{1}/n$
volume (Å ³)	4972.8(5)	4477(2)	3915.2(12)	7396.9(6)
<i>a</i> (Å)	18.4115(8)	23.339(7)	12.170(2)	16.2396(6)
$b(\mathbf{A})$	18.4115(8)	17.672(5)	14.705(3)	16.3992(8)
<i>c</i> (Å)	16.9393(10)	11.858(3)	23.648(4)	28.8104(12)
α (deg)	90	90	83.016(3)	90
β (deg)	90	113.746(7)	84.664(3)	105.408(2)
γ (deg)	120	90	68.977(2)	90
Ζ	6	2	2	4
formula weight (g/mol)	735.23	1894.06	1662.57	1590.73
density (calculated) (Mg/m ³)	1.473	1.405	1.410	1.423
absorption coefficient (mm ⁻¹)	5.125	3.717	4.209	4.422
F ₀₀₀	2208	1932	1676	3204
total no. reflections	11002	27158	33783	32067
unique reflections	1193	4742	16197	15054
Final R Indices	$R_1 = 0.0720$	$R_1 = 0.0719$	$R_1 = 0.0402$	$R_1 = 0.0671$
$(I > 2\sigma(I)]$	$wR_2 = 0.2179$	$wR_2 = 0.1757$	$wR_2 = 0.0798$	$wR_2 = 0.1593$
largest diff. peak and hole $(e^{-} A^{-3})$	1.191 and -2.295	1.976 and -1.983	2.411 and -2.238	5.491 and -2.466
GOF	1.455	1.190	0.986	1.104

Table S1. X-ray Crystallographic Data for 1, 2, 3, and $4 \cdot 2C_5H_{12}$.



Figure S11. Solid-state molecular structure of **1** shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): U1-N1 = 2.16(4), U1-N2 = 2.26(2), N1-U1-N2 = 100.4(6), N2-U1-N2^{*} = 116.8(3).



Figure S12. IR spectrum of [U(NR₂)₃(NH₂)] (1) (KBr pellet).



Figure S13. IR spectrum of $[K(18\text{-}crown-6)(THF)_2][(NR_2)_3U^{IV}(\mu-N)Th^{IV}(NR_2)_3]$ (2) (KBr pellet).



Figure S14. IR spectrum of $[(K(18 - crown - 6))[K(18 - crown - 6)(Et_2O)_2][(NR_2)_2U(\mu - N)(\mu - \kappa^2 - C, N - CH_2SiMe_2NR)Th(NR_2)_2]_2$ (**3**) (KBr pellet).



Figure S15. IR spectrum of $[(NR_2)_3U^V(\mu-N)Th^{IV}(NR_2)_3]$ (4) (KBr pellet).



Figure S16: UV-vis spectrum of $[K(18\text{-}crown-6)(THF)_2][(NR_2)_3U^{IV}(\mu-N)Th^{IV}(NR_2)_3]$ (2) in THF.



Figure S17: UV-vis/NIR spectrum of $[(NR_2)_3U^V(\mu-N)Th^{IV}(NR_2)_3]$ (4) in THF.



Figure S18. Magnetic moment of **4** versus temperature with ferromagnetic impurity correction.



Figure S19. Magnetic susceptibility of **4** versus temperature without correction for a ferromagnetic impurity.



Figure S20. Magnetic moment of **4** versus temperature without correction for a ferromagnetic impurity.

As shown in Figure S18, the data at different fields are in good agreement once corrected for the presence of a ferromagnetic impurity. The ferromagnetic impurity is assumed to be iron, chromium, and nickel oxides from the surface of stainless steel equipment. The corrected data are shown as χT vs T in Figure 4 of the main manuscript. From 50 to 150 K, χT is linear in T, which indicates that a single state (the ground state) is occupied over this temperature range. The deviation from linearity above 150 K is due to excited states becoming thermally populated. The deviation from linearity below 50 K is due to magnetization of **4** no longer being linear in H. This is a property of the magnetization vs field curve (the magnetization is no longer in the linear region of the Brillioun function). The χT vs T curve can be fit with a linear function between 50 and 150 K to determine the value of χT extrapolated to 0 K (χT_0).



Figure S21. X-band EPR spectrum of a powdered sample of 4, recorded at 4 K.



Figure S22. Qualitative relationship between the f-orbitals in T_d symmetry and in C_{3v} symmetry. The T_d molecule has 4 ligands (red dots) equidistant from the metal (black circle). In the C_{3v} molecule, one of the ligands (the one above the metal) has been shorted to simulate a uranium nitride bond.

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