Supplementary Information for

Divergent Reactivity of U(III) and U(II) Complexes with Organoazides via Isolable Diazenylimido Intermediates

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1. Experimental Procedures

1.1. General Considerations

All experiments were performed under a dry argon atmosphere using standard Schlenk techniques or in a nitrogen filled Vigor glove box unless otherwise specified. Celite (purchased from Sigma-Aldrich), neutral alumina and 4 Å molecular sieves (Sinopharm) were dried under dynamic vacuum at 250 °C for at least 48 hours prior to use. All solvents were purchased from Acros, Alfa Aesar, Honeywell, and Fisher. Solvents including *n*-pentane, hexanes, diethyl ether (Et₂O), and toluene were collected from a Vigor YJC-5 Solvent Purification System under argon, transferred to the glove box without exposure to air, and stored over activated molecular sieves. Tetrahydrofuran (THF) was refluxed over sodium hydride for 72 hours and distilled from sodium-benzophenone ketyl before use. Deuterated solvents including benzene- d_6 (C₆D₆), tetrahydrofuran- d_8 (C₄D₈O), and pyridine- d_5 (C₅D₅N) were obtained from Cambridge Isotope Laboratories or J&K Chemicals, degassed three times using freeze-pump-thaw method and stored over activated molecular sieves for one week prior to use.

UI₃(1,4-dioxane)_{1.5},¹ K₃(^{Ad}TPBN₃),² (^{Ad}TPBN₃)UI,² and potassium graphite $(KC_8)^3$ were prepared following published procedures. The large-scale synthesis of (^{Ad}TPBN₃)U (1) is modified from a recently reported protocol by our group.² The early lanthanide counterparts of 1, namely (AdTPBN3)Ce and (AdTPBN3)Pr, were prepared procedures.⁴ reported 4,7,13,16,21,24-Hexaoxa-1,10following diazabicyclo[8.8.8]hexacosane (2.2.2-cryptand, 1,4,7,10,13,16crypt) and hexaoxacyclooctadecane (18-crown-6) were purchased from Amethyst and Aladdin, respectively, and dissolved in THF, passed through neutral alumina, and dried under reduced pressure before use. 1-Adamantylazide (1-azidoadamantane, AdN₃) was purchased from Sigma-Aldrich and used as received. All other reagents were purchased from commercial vendors and used as received.

Fourier transform infrared (FTIR) spectra in the range of 4000–400 cm⁻¹ were recorded on a Bruker Tensor 27 spectrometer using KBr disks (for solution samples) at 3 / 110

the Analytical Center of Peking University. ¹H NMR spectra were recorded on Bruker Avance 400 MHz or 500 MHz spectrometers at room temperature. Chemical shifts are referenced internally to the residual proteo-solvent signal. CHN analyses were performed on a Vario EL elemental analyzer at the Analytical Center of Peking University. Single crystal X-ray diffraction data were collected at 180 K using a Rigaku Oxford diffractometer equipped with a CCD collector using Mo Kα radiation, namely XtaLAB PRO 007HF(Mo). All structures were solved by the intrinsic phasing method with SHELXT⁵ and refined by full-matrix least-squares procedures utilizing SHELXL⁶, ⁷ within Olex2 crystallographic software package.⁸ The PLATON⁹ routine SQUEEZE¹⁰ was used for reasonable solvent masks. The UV-Vis-NIR absorption spectra were recorded in a 1 mm or 1 cm quartz cuvette with a Shimadzu UV3600Plus instrument at the Analytical Instrumentation Center of Peking University. The solution-state magnetic susceptibilities were measured by the Evans method.¹¹

Caution! Depleted uranium (primary isotope ${}^{238}U$) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α - and β -counting equipment.

1.2. Synthetic Details

1.2.1. Modified synthesis of (^{Ad}TPBN₃)U (1)²

A 100 mL round-bottom flask was charged with $K_3(^{Ad}TPBN_3)$ (1.000 g, 1.152 mmol, 1.0 equiv) and THF (40 mL). Another 100 mL round-bottom flask was charged with UI₃(1,4-dioxane)_{1.5} (0.865 g, 1.152 mmol, 1.0 equiv) and cooled at -78 °C before cold THF (15 mL) was added. Both flasks were cooled at -78 °C for at least 15 min. The cold suspension of $K_3(^{Ad}TPBN_3)$ in THF was dropwise added to the cold THF solution of uranium triiodide with stirring in a cold well. After kept at -78 °C for another 15 minutes, the reaction mixture was warmed to room temperature and stirred for an hour. The volatiles were removed under reduced pressure. The remaining solid was extracted into toluene (30 mL), filtered through a Celite-padded coarse-porosity fritted filter, and washed with toluene (10 mL). The filtrate was collected and the volatiles 4 / 110

were removed under reduced pressure. The extraction (with toluene) and filtration (through Celite) procedures were repeated one time. Then the filtrate was collected in a 40 mL vial, concentrated to ca. 8 mL, and layered with hexanes (2 mL) and *n*-pentane (25 mL). The vial was kept undisturbed at -35 °C for three days. After shaking the vial vigorously for a minute, it was kept at -35 °C for another three days. The product precipitated out from the solution, collected on a medium-porosity frit, washed with cold *n*-pentane (30 mL), and dried under reduced pressure to yield 1 as a brown solid (0.968 g, 85%). The ¹H NMR spectroscopic data is consistent with the previous report.² μ_{eff} (Evans method, C₆D₆, 298 K): 1.83 μ_{B} .

1.2.2. Synthesis of $(^{Ad}TPBN_3)U(\gamma-N_3Ad)$ (2)

To a stirring cold solution of 1 (100.0 mg, 0.10 mmol) in toluene (5 mL), a cold solution of AdN₃ (20.0 mg, 0.10 mmol, 1.0 equiv) in toluene (1 mL) was added dropwise. The resulting ink black solution was stirred at room temperature for 10 min, followed by filtration through a Celite pad. The filtrate was concentrated to ca. 3 mL, layered with *n*-pentane (6 mL), and stored at -35 °C overnight. Black crystalline solid precipitated out from the solution, which was washed with cold n-pentane and dried under reduced pressure to yield 2 as a black solid (89.0 mg, 75%). Single crystals of 2 suitable for X-ray crystallography were grown from a toluene solution at -35 °C. ¹H NMR (400 MHz, C₆D₆, 298 K) δ, ppm: 21.35 (s, 3H, CH of the anchor ring), 13.59 (s, 9H, N₃Ad (6H) & CH of side rings (3H)), 7.92 (s, 3H, N₃Ad), 6.80 (s, 3H, N₃Ad), 5.92 (s, 3H, N₃Ad), 3.92 (s, 3H, CH of side rings), 2.34 (s, 3H, CH of side rings), -0.55 (s, 18H, UNAd), -1.12 (s, 9H, UNAd), -7.11 (s, 3H, CH of side rings), -12.30 (s, 9H, UNAd), -14.34 (br s, 9H, UNAd). Anal. (%): Calcd. For C_{67.5}H₇₉N₆U, M_w = 1212.45, as in the formula of (1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)UN₃(1-Ad)·0.5 C₇H₈ (toluene): C, 66.87; H, 6.57; N, 6.93. Found: C, 66.70; H, 6.71; N, 6.95. µeff (Evans method, C₆D₆, 298 K): 2.23 $\mu_{\rm B}$. FTIR (KBr) \tilde{v} , cm⁻¹: 612 (w), 639 (w), 729 (w), 743 (m), 844 (w), 889 (w), 937 (w), 1074 (m), 1099 (w), 1142 (w), 1181 (w), 1222 (m), 1277 (w), 1303 (w), 1355 (w), 1384 (w), 1448 (m), 1466 (w), 1511 (w), 1590 (w), 2087 (w), 2848 (m), 2903 (s).

1.2.3. Transformation of (AdTPBN₃)U(γ-N₃Ad) (2) to (AdTPBN₃)UN₃ (3)

a) *NMR scale in benzene-d₆ at room temperature.* **2** (10.5 mg, 9.0 μ mol, 1.0 equiv) was dissolved in C₆D₆ (0.6 mL) in a vial and transferred to a J. Young tube. The reaction mixture was regularly monitored by ¹H NMR spectroscopy at room temperature (Figure S22). ¹H NMR spectra showed the full conversion of **2** and the formation of (^{Ad}TPBN₃)UN₃ (**3**) as the only paramagnetic product together with unidentified diamagnetic by-products in the aliphatic region over two months at room temperature. NMR yield of **3**: 57%.

b) *NMR scale in THF-d₈ at 80 °C.* **2** (8.0 mg, 6.9 µmol, 1.0 equiv.) was dissolved in THF- d_8 (0.5 mL) in a vial and transferred to a J. Young tube. The reaction mixture was heated at 80 °C in an oil bath, and regularly monitored by ¹H NMR spectroscopy (Figure S23). ¹H NMR spectra showed the full consumption of **2** within a day and the formation of **3** as the major product (NMR yield: 67%). After prolong heating at 80 °C for 11 days, **3** was the only paramagnetic product with negligible change in concentration.

1.2.4. Independent synthesis of (AdTPBN₃)UN₃ (3)

Route A: Metathesis reaction between (^{Ad}TPBN₃)UI and NaN₃.

(^{Ad}TPBN₃)UI (50 mg, 0.045 mmol) and NaN₃ (4.4 mg, 0.067 mmol, 1.5 equiv) were weighed in a vial, suspended in THF (4 mL), and transferred to a 25 mL Schlenk tube. The suspension was heated at 80 °C for 20 days with stirring. The volatiles were removed under reduced pressure, and the remaining solid was extracted into toluene and filtered through a Celite pad. The filtrate was concentrated to ca. 1.5 mL, layered with *n*-pentane (6 mL), and stored at -35 °C for 3 days. A red crystalline solid precipitated out from the solution, which was washed with cold *n*-pentane and dried under reduced pressure to yield **3** (29 mg, 63%). Single crystals of **3** or **3**·1.5Et₂O suitable for X-ray crystallography were grown from a *n*-pentane solution at 25 °C (Figure S2), or from an Et₂O solution at -35 °C (Figure S3), respectively. ¹H NMR (400 MHz, C₆D₆, 298 K) δ , ppm: 15.07 (s, 3H, CH of the anchor ring), 13.45 (d, *J* = 7.6 Hz, **6** / 110

3H, CH of side rings), 3.64 (t, J = 7.0 Hz, 3H, CH of side rings), 3.37 (t, J = 7.2 Hz, 3H, CH of side rings), -0.98 (s, 9H, Ad), -1.62 (m, 18H, Ad), -9.12 (d, J = 8.3 Hz, 3H, CH of side rings), -12.36 (s, 9H, Ad), -17.42 (br s, 9H, Ad). Anal. (%): Calcd. for C57.5H64N6U, M_{w} = 1077.22, as in the formula of (1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)UN₃·0.5 C₇H₈ (toluene): C, 64.11; H, 5.99; N, 7.80. Found: C, 63.80; H, 5.91; N, 7.85. μ_{eff} (Evans method, C₆D₆, 298 K): 2.65 μ_{B} . FTIR (KBr) \tilde{v} , cm⁻¹: 613 (w), 645 (w), 666 (w), 714 (w), 743 (m), 797 (w), 843 (w), 892 (w), 936 (w), 1068 (m), 1099 (w), 1118 (w), 1159 (w), 1221 (m), 1277 (w), 1305 (w), 1357 (m), 1384 (w), 1448 (m), 1466 (w), 1510 (w), 1591 (w), 2086 (s, azide stretch), 2848 (m), 2904 (s).

Route B: Metathesis reaction between (AdTPBN₃)UI and KN₃.

 $(^{Ad}TPBN_3)UI (50 \text{ mg}, 0.045 \text{ mmol}) \text{ and } KN_3 (5.5 \text{ mg}, 0.067 \text{ mmol}, 1.5 \text{ equiv}) were weighed in a vial, suspended in THF (4 mL), and transferred to a 25 mL Schlenk tube. The suspension was heated at 80 °C for 7 days with stirring. The volatiles were removed under reduced pressure, the residues were extracted into toluene and filtered through a Celite pad. The filtrate was slowly concentrated to ca. 0.5 mL, layered with$ *n*-pentane (2.5 mL), and stored at <math>-35 °C for 2 days. The product precipitated out from solution, and was washed with cold *n*-pentane and dried under reduced pressure to yield **3** as a red solid (36 mg, 78%).

Route C: One-electron oxidation of [K(crypt)][(^{Ad}TPBN₃)UN₃] (9-crypt).

To a solution of **9-crypt** (13.5 mg, 9.3 µmol, 1.0 equiv) and benzene (2 µL, internal standard) in THF- d_8 (0.5 mL), [Cp₂Co][PF₆] (3.2 mg, 9.6 µmol, 1.0 equiv) was added at room temperature. The solution color turned from near dark red to brownish red within a minute. ¹H NMR (400 MHz, C₄D₈O) spectroscopy revealed the quantitative formation of **3** and Cp₂Co in a 1:1 molar ratio with the concomitant generation of free 2.2.2-cryptand (Figure S25). ¹H NMR assignment for *in situ* formed **3** (δ , ppm): 15.17 (s, 3H, CH of the anchor ring), 13.66 (d, J = 7.8 Hz, 3H, CH of side rings), 3.43 (t, J = 7.4 Hz, 3H, CH of side rings), -1.06 (s, 9H,

Ad), -1.64 (m, 18H, Ad), -9.10 (d, *J* = 8.3 Hz, 3H, C*H* of side rings), -12.23 (s, 9H, Ad), -17.56 (br s, 9H, Ad).

1.2.5. Synthesis of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ-N₃Ad)] (4)

Route A: One-electron reduction of 2.

2 (75.0 mg, 0.064 mmol, 1.0 equiv) and 18-crown-6 (17.0 mg, 0.064 mmol, 1.0 equiv) were weighed in a vial, dissolved in THF (6 mL), and cooled at -35 °C for 15 min. KC₈ (13.0 mg, 0.096 mmol, 1.5 equiv) was added in small portions. The reaction mixture was warmed to room temperature and rigorously stirred for 10 min. The dark brownish red suspension was then filtered through Celite and washed with THF (1.5 mL). The filtrate was concentrated to ca. 3.5 mL, layered with hexanes (10 mL), and stored at -35 °C for three days. The product precipitated out from the solution, and was washed with cold hexanes (2 mL) and dried under reduced pressure to yield 4 as a brownish yellow solid (98 mg, 94%). Single crystals of 4 suitable for X-ray crystallography were grown from a THF solution layered with hexanes at 25 °C. ¹H NMR (400 MHz, pyridine- d_5 , 298 K) δ , ppm: 53.80 (s, 3H, CH of the anchor ring), 37.98 (s, 6H, N₃Ad), 25.80 (s, 3H, CH of side rings), 17.99 (s, 3H, N₃Ad), 17.71 (d, J = 15.1 Hz, 3H, N_3Ad), 13.94 (d, J = 15.6 Hz, 3H, N_3Ad), 3.66 (m, 8H, OCH₂CH₂ of THF), 3.55 (s, 24H, 18-crown-6), 2.97 (s, 3H, CH of side rings), 1.62 (m, 8H, OCH₂CH₂ of THF), -2.76 (br s, 9H, UNAd), -5.53 (s, 9H, UNAd), -6.37 (s, 3H, CH of side rings), -8.95 (s, 9H, UNAd), -31.04 (s, 3H, CH of side rings), -39.38 (br s, 9H, UNAd). A peak (9H) belonging to the Ad groups of the (^{Ad}TPBN₃)³⁻ ligand was not found in the range of -500 to +500 ppm, probably due to signal broadening. Anal. (%): Calcd. for C_{91.75}H_{130.75}KN₆O_{9.75}U, M_w 1750.96, in the formula of = as $[K(C_{12}H_{24}O_6)(C_4H_8O)_2][(1,3,5-[2-(1-AdN)C_6H_4]_3C_6H_3)UN_3Ad]$ 1.75 C_4H_8O (THF)·0.125 C₆H₁₄ (*n*-hexane): C, 62.94; H, 7.53; N, 4.80. Found: C, 63.16; H, 7.13; N, 4.41. μ_{eff} (Evans method, C₄D₈O, 298 K): 2.62 μ_B . FTIR (KBr) \tilde{v} , cm⁻¹: 743 (m), 839 (w), 962 (w), 1109 (s), 1181 (w), 1250 (w), 1285 (w), 1308 (w), 1355 (m), 1408 (w), 1451 (m), 1510 (m), 1580 (m), 1602 (w), 2074 (w), 2849 (s), 2903 (s).

Route B: Two-electron oxidation of [K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (5).

To a stirring cold solution of **5** (30.0 mg, 0.022 mmol, 1.0 equiv) in THF (2.5 mL), a cold solution of AdN₃ (4.3 mg, 0.024 mmol, 1.1 equiv) in THF (0.5 mL) was added dropwise. The resulting brownish yellow solution was stirred at room temperature for 15 min. The volatiles were removed under reduced pressure. The remaining solid was extracted into THF (1.5 mL) and filtrated through a Celite pad. The filtrate was layered with hexanes (3 mL) and kept undisturbed at -35 °C for two days. The product precipitated out from the solution, and was washed with cold hexanes (1 mL) and dried under reduced pressure to yield 4 as a brownish yellow solid (24 mg, 68%).

Alternatively, **4** can be synthesized directly from **1** via *in situ* formed **5** with a higher overall yield from **1**. **1** (71.6 mg, 0.072 mmol, 1.0 equiv) and 18-crown-6 (19.5 mg, 0.074 mmol, 1.0 equiv) were weighed in a vial, dissolved in THF (4.5 mL), and cooled at -35 °C for 10 min. Then KC₈ (14.7 mg, 0.11 mmol, 1.5 equiv) was added. The reaction mixture was warmed to room temperature and rigorously stirred for 5 min. The dark-brown suspension was then filtered through Celite and washed with THF (0.5 mL × 3). The filtrate containing uranium(II) species was slowly concentrated to ca. 2 mL, and then cooled at -35 °C for 5 min. A cold THF (1 mL) solution of AdN₃ (14.1 mg, 0.080 mmol, 1.1 equiv) was added dropwise to the uranium(II) solution with shaking. The resulting mixture was layered with cold hexanes (6 mL) and stored at -35 °C overnight. Brownish yellow solid precipitated out from the solution, which was washed with cold hexanes and dried under reduced pressure to yield **4** (83 mg, 71%).

1.2.6. Synthesis of [K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (5)

1 (100 mg, 0.10 mmol, 1.0 equiv) and 18-crown-6 (27 mg, 0.10 mmol, 1.0 equiv) were weighed in a vial, dissolved in THF (5 mL), and cooled at -78 °C for 15 min. KC₈ (16 mg, 0.12 mmol, 1.2 equiv) was added in small portions. The reaction mixture was warmed to room temperature and rigorously stirred for 10 min. The dark-brown suspension was then filtered through Celite and washed with THF (1 mL × 3). The filtrate was concentrated to ca. 5 mL, layered with hexanes (3 mL) and *n*-pentane (10 mL), and stored at -35 °C for 48 hours. The precipitate was collected on a medium-9 / 110

porosity fritted filter, washed with cold *n*-pentane, and dried under reduced pressure to yield **5** as a brownish red solid (126 mg, 92%). Single crystals of **5** suitable for X-ray crystallography were grown from a THF solution at room temperature. ¹H NMR (400 MHz, C4D₈O, 298 K) δ , ppm: 16.34 (d, *J* = 8.5 Hz, 3H, *CH* of side rings), 7.75 (t, *J* = 7.0 Hz, 3H, *CH* of side rings), 7.45 (t, *J* = 7.7 Hz, 3H, *CH* of side rings), 3.87 (br s, 9H, Ad), 3.62 (m, 4H, *α*-*CH*₂ of THF), 3.45 (s, 24H, 18-crown-6), 1.78 (m, 4H, *β*-*CH*₂ of THF), 0.66 (s, 9H, Ad), 0.54 (m, 9H, Ad), 0.09 (m, 9H, Ad), -0.16 (d, *J* = 6.4 Hz, 3H, *CH* of side rings), -10.60 (br s, 9H, Ad), -73.25 (s, 3H, *CH* of the anchor ring). Anal. (%): Calcd. for C₆₉H₉₀KN₃O_{6.75}U, M_w = 1346.62, as in the formula of [K(C₁₂H₂₄O₆)(C4H₈O)_{0.75}][(1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)U]: C, 61.54; H, 6.74; N, 3.12. Found: C, 61.14; H, 7.12; N, 2.84. The solution-state magnetism measurement by the Evans method could not be done due to the low solubility of the isolated crystalline sample. FTIR (KBr) $\tilde{\nu}$, cm⁻¹: 429 (w), 743 (m), 839 (w), 964 (m), 1075 (m), 1106 (s), 1141 (m), 1181 (m), 1250 (w), 1286 (w), 1308 (w), 1354 (m), 1385 (w), 1457 (m), 1508 (m), 1578 (w), 1601 (w), 2850 (m), 2903 (s).

1.2.7. Synthesis of [K(18-crown-6)(THF)2][(AdTPBN3)UNAd] (6)

A 25 mL Schlenk tube was charged with **4** (30.0 mg, 0.019 mmol) and THF (5 mL). The brownish red solution was heated at 80 °C and stirred for five days. The resulting brownish yellow suspension was transferred to a 20 mL vial, layered with Et₂O (5 mL), and stored at -35 °C for one week. The product precipitated out from the solution, and was washed with cold Et₂O (3 mL) and dried under reduced pressure to yield **6** as a greenish yellow solid (20.8 mg, 71%). Single crystals of **6** suitable for X-ray crystallography were grown from a THF solution at 25 °C. ¹H NMR (500 MHz, C4D₈O, 298 K) δ , ppm: 83.56 (m, 6H, N_{imide}–*Ad*), 66.31 (s, 3H, C*H* of the anchor ring), 38.87 (s, 3H, N_{imide}–*Ad*), 4.54 (s, 27H, 18-crown-6 (24H) & C*H* of side rings (3H)), – 8.92 (s, 3H, C*H* of side rings), –11.22 (s, 18H, N_{amide}–*Ad*), –16.04 (s, 9H, N_{amide}–*Ad*), –37.05 (s, 3H, C*H* of side rings), –59.41 (br s, 9H, N_{amide}–*Ad*). A peak (9H) belonging to the Ad groups of the (^{Ad}TPBN₃)^{3–} ligand was not found in the range of –500 to +500 **10** / **110**

ppm, probably due to signal broadening. Anal. (%): Calcd. for $C_{84}H_{115}KN_4O_8U$, $M_w = 1585.99$, as in the formula of $[K(C_{12}H_{24}O_6)(C_4H_8O)_2][(1,3,5-[2-(1-AdN)C_6H_4]_3C_6H_3)UN(1-Ad)]$: C, 63.61; H, 7.31; N, 3.53. Found: C, 63.25; H, 7.34; N, 3.27. The solution-state magnetism measurement by the Evans method could not be done due to low solubility of the isolated crystalline sample. FTIR (KBr) \tilde{v} , cm⁻¹: 438 (w), 480 (w), 588 (m), 742 (m), 841 (w), 893 (w), 961 (w), 1075 (m), 1107 (m), 1142 (w), 1181 (w), 1249 (w), 1308 (w), 1355 (w), 1384 (m), 1451 (w), 1467 (w), 1511 (w), 1536 (w), 1579 (w), 1602 (w), 2848 (m), 2903 (s).

1.2.8. Synthesis of (AdTPBN₃)UNAd (7)

NMR scale: **6** (9.6 mg, 6.1 µmol, 1.0 equiv) was suspended in THF-*d*₈ (0.6 mL) in a vial and transferred to a J. Young tube. To the J. Young tube, was added an excess amount of AgI (3.0 mg, 12.8 µmol, 2.1 equiv). The J. Young tube was shaken at room temperature for mixing. The reaction mixture turned from greenish yellow to brownish black within seconds. After kept undisturbed for 10 min, the mixture was measured by ¹H NMR spectroscopy (C₄D₈O, 500 MHz, 298 K). The generation of free 18-crown-6 was observed and a set of new peaks assigned to 7 could be identified as follows (δ , ppm): 30.54, 19.56, 15.99, 14.46, 11.70, 3.43, -3.85, -11.78, -21.57. However, the baseline correction and the peak integration could not be reliably done due to significant signal broadening.

Preparative scale: 6 (30.4 mg, 0.019 mmol, 1.0 equiv) and AgI (9.6 mg, 0.041 μ mol, 2.2 equiv) were weighted in a vial, suspended in THF (3 mL), and stirred at room temperature for 10 min. The resulting suspension was filtered through a Celite pad and washed with THF. The volatiles of the filtrate were removed under reduced pressure, and the remaining solid was extracted thoroughly into toluene followed by filtration through a Celite pad. The filtrate was concentrated to ca. 1.5 mL, layered with hexanes (3 mL), and kept undisturbed at -35 °C overnight. The product precipitated out from the solution, and was washed with cold *n*-pentane and dried under reduced pressure to yield 7 as a black solid (14.4 mg, 66%). Single crystals of 7 suitable for X-ray crystallography were grown from a THF solution layered with hexanes at -35 °C. ¹H 11 / 110

NMR spectroscopic characterization and the solution-state magnetism measurement by the Evans method could not be done due to the low solubility of the isolated sample. Anal. (%): Calcd. for C₇₁H₈₃N₄U, M_w = 1230.50, as in the formula of (1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)UN(1-Ad): C, 69.30; H, 6.80; N, 4.55. Found: C, 69.63; H, 6.41; N, 4.27. FTIR (KBr) \tilde{v} , cm⁻¹: 428 (w), 474 (w), 495 (m), 612 (w), 638 (w), 658 (w), 712 (w), 727 (m), 743 (m), 763 (w), 783 (w), 796 (w), 809 (w), 844 (m), 859 (w), 884 (m), 928 (w), 1043 (w), 1065 (s), 1094 (m), 1130 (s), 1181 (w), 1198 (m), 1208 (m), 1273 (w), 1299 (m), 1342 (w), 1352 (w), 1384 (m), 1399 (w), 1441 (s), 1466 (w), 1590 (w), 2847 (m), 2901 (s).

1.2.9. Reaction of 1 with PhCH₂N₃ (*NMR scale*)

1 (8.2 mg, 8.3 µmol, 1.0 equiv) was dissolved in C_6D_6 (0.5 mL) in a vial. A small amount of $C_6H_3(OMe)_3$ in C_6D_6 was added to the vial as an internal standard. After mixing, the solution was transferred to a J. Young tube and measured by ¹H NMR spectroscopy (C_6D_6 , 400 MHz, 298 K). The J. Young tube was then taken back to the glove box, added PhCH₂N₃ (1.5 µL, 1.6 mg, 12.0 µmol, 1.3 equiv) at the topmost space of the tube to avoid mixing. After cooled at 0 °C for 5 min, the J. Young tube was shaken to mix the reactants. The reaction mixture immediately turned red, and measured by ¹H NMR spectroscopy as soon as possible. The ¹H NMR spectrum showed the formation of **3** as the major product along with ca. 0.2 equiv of 1,2-diphenylethane and other unidentified minor by-products. No intermediate species could be observed under these conditions (Figure S31).

1.2.10. Reaction of 1 with Ph₃CN₃ (NMR scale)

1 (7.2 mg, 7.3 μ mol, 1.0 equiv) was dissolved in C₆D₆ (0.5 mL) in a vial. A small amount of C₆H₃(OMe)₃ in C₆D₆ was added to the vial as an internal standard. After mixing, the solution was transferred to a J. Young tube and measured by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). The J. Young tube was then taken back to the glove box, added a C₆D₆ solution (0.2 mL) of Ph₃CN₃ (2.4 mg, 8.4 μ mol, 1.2 equiv) at room temperature, and shaken for mixing. The reaction mixture immediately turned red, and measured by ¹H NMR spectroscopy as soon as possible. The ¹H NMR spectrum showed the quantitative formation of **3** and the Gomberg's dimer¹²⁻¹⁴ in a 2:1 molar ratio. No intermediate species was observed under these conditions (Figure S32).

1.2.11. Reaction of 1 with Me₃SnN₃ (*NMR scale*)

1 (9.2 mg, 9.3 µmol, 1.0 equiv) was dissolved in C_6D_6 (0.6 mL) in a vial. A small amount of C_6H_3 (OMe)₃ in C_6D_6 was added to the vial as an internal standard. After mixing, the solution was transferred to a J. Young tube and measured by ¹H NMR spectroscopy (C_6D_6 , 400 MHz, 298 K). The J. Young tube was then taken back to the glove box, added an excess amount of Me₃SnN₃ (2.0 mg, 17.1 µmol, 1.8 equiv), and shaken for mixing. The reaction mixture immediately turned red, and measured by ¹H NMR spectroscopy as soon as possible. The ¹H NMR spectrum showed the full conversion of **1**, and the formation of **3** and Me₆Sn₂ as the major products in a 10:3 molar ratio. Notably, an unidentified uranium-containing species (ca. 0.1 equiv) with C_3 symmetry in solution could also be observed at the initial stage, but gradually converted to **3** and Me₆Sn₂ in 36 hours at room temperature (Figure S33).

1.2.12. Reaction of 1 with Me₃SiN₃

NMR scale: **1** (11.4 mg, 12 µmol, 1.0 equiv) was dissolved in C₆D₆ (0.6 mL) in a vial. A small amount of C₆H₃(OMe)₃ in C₆D₆ was added to the vial as an internal standard. After mixing, the solution was transferred to a J. Young tube and measured by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). The J. Young tube was then taken back to the glove box, added an excess amount of Me₃SiN₃ (1.8 mg, 2.0 µL, 15 µmol, 1.3 equiv), and shaken for mixing. ¹H NMR spectrum showed no obvious change after 10 min at room temperature. The J. Young tube was then heated at 80 °C in an oil bath, and regularly monitored by ¹H NMR spectroscopy (Figure S35). The ¹H NMR spectra showed the full conversion of **1** and the formation of **3** and Me₆Si₂ (molar ratio \approx 1:0.1) in 48 hours at 80 °C, along with (^{Ad}TPBN₃)UNSiMe₃ (**8**) as a minor product. The molar ratio of **3** to **8** in the final mixture was determined to be about 3:1 based on the ratio of the integrations of characteristic ¹H NMR peaks in the range of –0.8 to –1.7 ppm (for

3) and in the range of -2.5 to -3.1 ppm (for **8**), respectively.

In addition, another monitoring experiment with the reaction temperature set at room temperature showed the full conversion of **1** and the formation of **3**, Me₆Si₂, and **8** over three months, yielding a 5:1 mixture of **3** and **8** (Figure S34).

Preparative scale: 1 (55.0 mg, 0.056 mmol, 1.0 equiv) and Me₃SiN₃ (9.6 mg, 11.0 μ L, 0.083 mmol, 1.5 equiv) was dissolved in toluene (3.5 mL) and transferred to a 20 mL Schlenk tube. The mixture was heated at 110 °C and stirred for 48 hours. The ¹H NMR spectrum of the aliquot showed the molar ratio of **3** and **8** in the final mixture to be 1:2.5. The volatiles were removed under reduced pressure. The remaining solid was thoroughly extracted with Et₂O (6 mL) and filtered through glass fiber. The filtrate was concentrated to ca. 2 mL, and kept undisturbed at -35 °C. After three days, a black crystalline solid precipitated out from the solution, which was washed with cold Et₂O and dried under reduced pressure to yield 7 (26.6 mg, 44%). Single crystals of 8 Et₂O suitable for X-ray crystallography were grown from an Et₂O solution at -35 °C. ¹H NMR (400 MHz, C₆D₆, 298 K) δ, ppm: 28.01 (s, 3H, CH of the anchor ring), 20.83 (s, 9H, SiCH₃), 14.95 (s, 3H, CH of side rings), 3.18 (s, 3H, CH of side rings), 2.20 (s, 3H, CH of side rings), -2.74 (m, 18H, Ad), -2.93 (s, 9H, Ad), -10.23 (s, 3H, CH of side rings), -19.90 (br s, 18H, Ad). Anal. (%): Calcd. for C₅₇H₆₉N₄SiU, M_w = 1076.32, as in the formula of (1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)UNSiMe₃: C, 63.61; H, 6.46; N, 5.21. Found: C, 63.65; H, 6.45; N, 5.19. FTIR (KBr) \tilde{v} , cm⁻¹: 436 (w), 493 (w), 612 (w), 638 (w), 660 (w), 712 (w), 727 (w), 744 (m), 762 (w), 782 (w), 796 (w), 834 (m), 887 (w), 939 (w), 969 (s), 1072 (s), 1099 (w), 1116 (w), 1142 (w), 1181 (w), 1220 (m), 1240 (w), 1276 (w), 1301 (w), 1354 (w), 1384 (m), 1447 (m), 1466 (w), 1512 (w), 1591 (w), 2848 (m), 2903 (s).

Note: The attempted preparation of **8** at 80 °C in toluene was not successful due to the difficulty in separating **3** and **8**. The best attempt led to the isolation of a binary mixture in a 73% yield (referenced to **1**) with a molar ratio of 1.5:1 for **3** and **8**, as determined by ¹H NMR spectroscopy and CHN elemental analysis. It seems that the molar ratio of **3** and **8** in the final mixture is dependent on the reaction temperature:

room temperature, 5:1; 80 °C, 3:1; 110 °C, 1:2.5.

1.2.13. Reaction of [K(crypt)][(^{Ad}TPBN₃)U] with Me₃SiN₃ (NMR scale)

[K(crypt)][(^{Ad}TPBN₃)U]² (**5-crypt**, 10.2 mg, 7.3 μ mol, 1.0 equiv) was dissolved in THF-*d*₈ (0.5 mL) in a vial. A small amount of C₆H₃(OMe)₃ in THF-*d*₈ was added to the vial as an internal standard. After mixing, the solution was transferred to a J. Young tube and measured by ¹H NMR spectroscopy (THF-*d*₈, 400 MHz, 298 K). The J. Young tube was then taken back to the glove box, added an excess amount of Me₃SiN₃ (1.3 mg, 1.5 μ L, 11 μ mol, 1.5 equiv), and shaken for mixing. The ¹H NMR spectrum showed the quantitative formation of [K(crypt)][(^{Ad}TPBN₃)UN₃] (**9-crypt**) and Me₆Si₂ in a 2:1 molar ratio in 10 min. No intermediate species was observed under these conditions (Figure S39).

1.2.14. Synthesis of [M][(^{Ad}TPBN₃)UN₃] (M = K(crypt), 9-crypt; M = K(18-crown-6)(THF)₂, 9)

[K(crypt)][(^{Ad}TPBN₃)UN₃] (9-crypt) from 1 and KN₃. 1 (50 mg, 0.051 mmol, 1.0 equiv) and KN₃ (4.9 mg, 0.060 mmol, 1.2 equiv) were weighed in a vial. 2.2.2-Cryptand (20 mg, 0.053 mmol, 1.0 equiv) was dissolved in another vial with THF (5 mL). Both vials were cooled at -78 °C for 15 min. The THF solution was added to the vial containing 1 and KN₃, and the resulting suspension was stirred at room temperature for 4 h. The mixture was filtered through a Celite pad. Then the filtrate was concentrated to ca. 2 mL, layered with Et₂O (1 mL) and hexanes (0.5 mL), and stored at -35 °C overnight. A small amount of pale yellow/white solid (excess KN₃) precipitated out from the solution. The supernatant was filtered through a Celite pad again. The filtrate was layered with cold Et₂O (0.5 mL) and cold hexanes (0.5 mL), and kept undisturbed at 25 °C for 4 days. The product precipitated out from the solution, and was washed with cold hexanes and *n*-pentane and dried under reduced pressure to yield 9-crypt as a black crystalline solid (57 mg, 78%). Single crystals of 9-crypt THF suitable for X-ray crystallography were grown from a THF solution layered with Et₂O and hexanes at 25 °C. ¹H NMR (400 MHz, C₄D₈O, 298 K) δ , ppm: 15.21 (s, 3H, CH of side rings), 11.61 (s, 3H, *CH* of side rings), 9.99 (s, 3H, *CH* of the anchor ring), 8.44 (d, J = 6.6 Hz, 3H, *CH* of side rings), 6.13 (br s, 9H, Ad), 5.51 (br s, 9H, Ad), 4.92 (t, J = 7.1 Hz, 3H, *CH* of side rings), 3.57 (s, 12H, OCH₂CH₂O of crypt), 3.50 (m, 12H, OCH₂CH₂N of crypt), 2.87 (s, 9H, Ad), 2.50 (m, 12H, OCH₂CH₂N of crypt), 2.09 (m, 9H, Ad), 1.93 (m, 9H, Ad). Anal. (%): Calcd. for C₇₆H₁₀₄KN₈O₇U, M_w = 1518.84, as in the formula of [K(C₁₈H₃₆N₂O₆)][(1,3,5-[2-(1-AdN)C₆H₄]₃C₆H₃)UN₃]·C₄H₈O (THF): C, 60.10; H, 6.90; N, 7.38. Found: C, 60.18; H, 6.87; N, 7.17. μ_{eff} (Evans method, C₄D₈O, 298 K): 1.91 μ_{B} . FTIR (KBr) $\tilde{\nu}$, cm⁻¹: 607 (w), 662 (w), 741 (m), 845 (w), 949 (m), 1079 (m), 1103 (s), 1133 (m), 1181 (w), 1239 (m), 1259 (m), 1286 (m), 1301 (m), 1355 (m), 1446 (m), 1510 (w), 1580 (w), 1995 (w), 2062 (s, azide stretch), 2847 (m), 2901 (s).

[K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UN₃] (9) from 5 and Me₃SiN₃. To a stirring cold suspension of 5 (16.5 mg, 0.012 mmol, 1.0 equiv) in THF (1 mL), pre-cooled Me₃SiN₃ (1.8 mg, 2.1 μ L, 0.016 mmol, 1.3 equiv) was added via a pipette. The resulting brownish red solution was stirred at room temperature for 5 min. The mixture was filtered via glass fiber filter and washed with cold THF (0.5 mL). The filtrate was layered with cold hexanes (1.5 mL) and *n*-pentane (0.5 mL), and stored at -35 °C overnight. Black rod-like crystals precipitated out from the solution, which were washed with cold hexanes (3 mL) and dried under reduced pressure to yield 9 (12.5 mg, 70%). ¹H NMR (400 MHz, C₄D₈O, 298 K) δ, ppm: 15.18 (s, 3H, CH of side rings), 11.80 (s, 3H, CH of side rings), 10.40 (s, 3H, CH of the anchor ring), 8.33 (d, J = 5.2Hz, 3H, CH of side rings), 6.51 (br s, 9H, Ad), 6.00 (br s, 9H, Ad), 4.94 (t, J = 6.9 Hz, 3H, CH of side rings), 3.54 (s, 24H, 18-crown-6), 2.97 (s, 9H, Ad), 2.16 (m, 9H, Ad), 2.00 (m, 9H, Ad). Single crystals of 9 suitable for X-ray crystallography were grown from a THF solution layered with Et₂O and hexanes at 25 °C. Anal. (%): Calcd. for $C_{74}H_{100}KN_6O_8U$, $M_w = 1478.78$, as in the formula of $[K(C_{12}H_{24}O_6)(C_4H_8O)_2][(1,3,5-$ [2-(1-AdN)C₆H₄]₃C₆H₃)UN₃]: C, 60.10; H, 6.82; N, 5.68. Found: C, 60.11; H, 6.94; N, 5.64.

2. X-ray Crystallography

 $(^{Ad}TPBN_3)U(\gamma - N_3Ad)$ (2) (CCDC No. 2351606)



Figure S1. Representation of **2** with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity. The occupancies for two sets of N₃Ad groups (caused by disorder) are 0.69 and 0.31, respectively. Selected distances (Å) and angles (°): U1–N1 2.3086(41), U1–N2 2.3201(49), U1–N3 2.3299(44), U1–N4 1.9859(37), U1–C1 2.8949(49), U1–C2 2.9194(46), U1–C3 2.9220(42), U1–C4 2.9256(44), U1–C5 2.8877(49), U1–C6 2.8965(50), U1–C_{centroid} 2.5483(5), U1–3N_{plane} +0.0915(6), N4–N5 1.3342(87), N4–N5A 1.3331(250), N5–N6 1.2639(124), N5A–N6A 1.2584(320), N6–C55 1.4855(117), N6A–C55A 1.5671(388), C1–C2 1.3836(78), C2–C3 1.4123(77), C3–C4 1.3782(81), C4–C5 1.4168(77), C5–C6 1.4006(77), C6–C1 1.4114(83); N1–U1–N2 120.622(147), N2–U1–N3 118.871(151), N3–U1–N1 120.044(146), N4–U1–C_{centroid} 178.264(123), U1–N4–N5 170.614(490), U1–N4–N5A 170.315(1136), N4–N5–N6 115.019(759), N4–N5A–N6A 116.653(2064), N5–N6–C55 110.479(708), N5A–N6A–C55A 105.116(2203).

Single crystals suitable for X-ray crystallography were grown from a toluene solution. A total of 71280 reflections ($-48 \le h \le 45$, $-16 \le k \le 14$, $-26 \le l \le 27$) were collected

at T = 180.00(10) K with $2\theta_{\text{max}} = 50.054^{\circ}$, of which 11017 were unique. The residual peak and hole electron density were 2.63 and -1.70 eÅ^{-3} . The least-squares refinement converged normally with residuals of $R_1 = 0.0404$ and GOF = 1.063. Crystal and refinement data for **2**: formula C₆₄H₇₅N₆U, space group C2/c, a = 41.0293(7) Å, b = 13.6280(2) Å, c = 23.2572(3) Å, $\beta = 106.526(2)^{\circ}$, V = 12467.0(3) Å³, Z = 8, $\mu = 2.644$ mm⁻¹, F(000) = 4744.0, $R_1 = 0.0578$ and $wR_2 = 0.0994$ (based on all data).

(^{Ad}**TPBN**₃)**UN**₃ (**3**) (CCDC No. 2351601)



Figure S2. Representation of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.3369(24), U1–N2 2.2897(23), U1–N3 2.2942(24), U1–N4 2.2714(26), U1–C1 2.9134(32), U1–C2 2.9266(33), U1–C3 2.9222(31), U1–C4 2.9369(33), U1–C5 2.9179(32), U1–C6 2.9292(32), U1–C_{centroid} 2.5675(4), U1–3N_{plane} +0.0796(4), N4–N5 1.1514(39), N5–N6 1.1660(63), C1–C2 1.3838(43), C2–C3 1.4111(47), C3–C4 1.3986(44), C4–C5 1.4002(42), C5–C6 1.3981(46), C6–C1 1.4105(45); N1–U1–N2 119.861(87), N2–U1–N3 120.244(84), N3–U1–N1 119.540(81), N4–U1–C_{centroid} 178.783(63), U1–N4–N5 170.145(231), N4–N5–N6 177.264(403).

Single crystals suitable for X-ray crystallography were grown from an *n*-pentane solution. A total of 59157 reflections ($-27 \le h \le 22$, $-14 \le k \le 14$, $-26 \le l \le 26$) were collected at T = 180.00(10) K with $2\theta_{max} = 58.972^{\circ}$, of which 11317 were unique. The residual peak and hole electron density were 1.72 and -1.02 eÅ^{-3} . The least-squares refinement converged normally with residuals of $R_1 = 0.0326$ and GOF = 1.038. Crystal and refinement data for **3**: formula C₅₄H₆₀N₆U, space group $P2_1/c$, a = 20.3775(5) Å, b = 10.9395(3) Å, c = 19.6244(5) Å, $\beta = 95.369(2)^{\circ}$, V = 4355.5(2) Å³, Z = 4, $\mu = 3.772$ mm⁻¹, F(000) = 2072.0, $R_1 = 0.0496$ and $wR_2 = 0.0763$ (based on all data).



Figure S3. Representation of $3 \cdot 1.5Et_2O$ with thermal ellipsoids set at 35% probability. Hydrogen atoms and lattice solvent (Et₂O) molecules are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.3098(31), U1–N2 2.3156(31), U1–N3 2.3036(31), U1–N4 2.2728(32), U1–C1 2.8763(38), U1–C2 2.9078(37), U1–C3 2.9116(37), U1–C4 2.9188(35), U1–C5 2.8880(36), U1–C6 2.8900(38), U1–C_{centroid} 2.5401(5), U1–3N_{plane} +0.0639(5), N4–N5 1.1737(52), N5–N6 1.1381(65), C1–C2 1.3910(56), C2–C3 1.3927(51), C3–C4 1.4159(50), C4–C5 1.3783(54), C5–C6 1.4133(51), C6–C1 1.3903(50); N1–U1–N2 117.743(108), N2–U1–N3 121.093(111), N3–U1–N1 120.937(107), N4–U1–C_{centroid} 177.709(83), U1–N4–N5 160.710(306), N4–N5–N6 178.929(500).

Single crystals suitable for X-ray crystallography were grown from a Et₂O solution. A total of 62223 reflections ($-35 \le h \le 32$, $-33 \le k \le 33$, $-24 \le l \le 22$) were collected at T = 179.99(10) K with $2\theta_{max} = 59.058^{\circ}$, of which 14104 were unique. The residual peak and hole electron density were 1.27 and -0.47 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.0359$ and GOF = 1.040. Crystal and refinement data for $3 \cdot 1.5Et_2O$: formula C₆₀H₇₅N₆O_{1.5}U, space group *Pbcn*, *a* = 25.8962(7) Å, *b* = 24.3659(6) Å, *c* = 17.3181(5) Å, *V* = 10927.4(5) Å³, *Z* = 8, μ = 3.016 mm⁻¹, *F*(000) = 4648.0, $R_1 = 0.0699$ and $wR_2 = 0.0856$ (based on all data).



Figure S4. Representation of 4 with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity. The occupancies for two sets of N₃Ad groups (caused by disorder) are 0.60 and 0.40, respectively. Selected distances (Å) and angles (°): U1–N1 2.4070(26), U1–N2 2.4175(23), U1–N3 2.3975(19), U1–N4 2.0230(25), U1–C1 2.9389(27), U1–C2 2.9504(25), U1–C3 2.9330(27), U1–C4 2.9439(29), U1–C5 2.9461(28), U1–C6 2.9718(30), U1–C_{centroid} 2.5950(3), U1–3N_{plane} +0.1836(3), N4–N5 1.3168(91), N4–N5A 1.3347(154), N5–N6 1.2267(100), N5A–N6A 1.2120(158), N6–C55 1.5171(104), N6A–C55A 1.5301(161), C1–C2 1.3876(41), C2–C3 1.4034(38), C3–C4 1.3850(33), C4–C5 1.4142(42), C5–C6 1.3843(36), C6–C1 1.4123(33); N1–U1–N2 118.738(79), N2–U1–N3 119.397(79), N3–U1–N1 120.137(78), N4–U1–C_{centroid} 178.804(67), U1–N4–N5 167.555(393), U1–N4–N5A 170.480(604), N4–N5–N6 117.077(723), N4–N5A–N6A 117.340(995), N5–N6–C55 108.372(617), N5A–N6A–C55A 108.629(982).

Single crystals suitable for X-ray crystallography were grown from a THF/hexanes solution. A total of 63634 reflections ($-19 \le h \le 19$, $-20 \le k \le 15$, $-28 \le 1 \le 30$) were collected at T = 180.00(10) K with $2\theta_{max} = 59.092^{\circ}$, of which 22152 were unique. The residual peak and hole electron density were 1.34 and -0.81 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.0330$ and GOF = 1.051. Crystal and refinement data for 4: formula C₈₄H₁₁₅KN₆O₈U, space group *P*–1, *a* = 14.1622(2) Å, *b* = 14.7733(2) Å, *c* = 22.4211(3) Å, *a* = 98.1000(10)°, *β* = 103.2850(10)°, *γ* = 100.6780(10)°, *V* = 4403.07(11) Å³, *Z* = 2, μ = 1.943 mm⁻¹, *F*(000) = 1672.0, R_1 = 0.0422 and wR_2 = 0.0859 (based on all data).

[K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (5) (CCDC No. 2351611)



Unit	avg. U–N	avg. U–C _{anchor}	U–C _{centroid}	U–3N _{plane} *	avg. C–C _{anchor}
U1	2.43(2)	2.58(2)	2.1628(8)	-0.3110(8)	1.41(3)
U2	2.40(2)	2.57(2)	2.1543(8)	-0.3286(8)	1.41(3)
U3	2.45(2)	2.57(2)	2.1484(9)	-0.3385(9)	1.41(3)
U4	2.41(2)	2.57(2)	2.1439(8)	-0.3135(8)	1.42(3)

All distances in Å. *uranium out-of-plane (defined by three N atoms) shift

Figure S5. Representation of **5** (formula: $[K(18-crown-6)(THF)_2][K_{0.5}(18-crown-6)_{0.5}(THF)]_2[K(18-crown-6)]_2[(^{Ad}TPBN_3)U]_4)$ with thermal ellipsoids set at 20% probability, and a summary of key metrical parameters. Hydrogen atoms are omitted for clarity. Occupancy of some disordered oxygen atoms of 18-crown-6 are shown in the brackets. The arrangement of cations and anions in the unit cell is shown in Figure S6.

Single crystals suitable for X-ray crystallography were grown from a THF solution. A total of 169933 reflections ($-46 \le h \le 45$, $-31 \le k \le 46$, $-23 \le l \le 23$) were collected at T = 180.00(10) K with $2\theta_{max} = 50.054^{\circ}$, of which 53333 were unique. The residual peak and hole electron density were 5.84 and -1.46 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.1098$ and GOF = 1.052. Crystal and refinement data for **5**: formula C₇₀H₉₂KN₃O₇U, space group *P*2₁2₁2, *a* = 39.2324(6) Å,

b = 39.2407(8) Å, c = 19.6235(4) Å, V = 30210.5(10) Å³, Z = 16, $\mu = 2.251$ mm⁻¹, F(000) = 11200.0, $R_1 = 0.1583$ and $wR_2 = 0.2848$ (based on all data, $I \ge 2\sigma$ (I)).



Figure S6. Representation (view along the b-axis on the unit cell) of **5** with thermal ellipsoids set at 20% probability. Only potassium, uranium, and carbon of the anchoring arene are shown. Only atoms inside or close to the edges of a unit cell are shown.



Figure S7. Representation of **6** with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.4741(40), U1–N2 2.4796(48), U1–N3 2.4470(51), U1–N4 1.9768(56), U1–C1 3.0731(60), U1–C2 3.0835(72), U1–C3 3.0858(79), U1–C4 3.0849(76), U1–C5 3.0848(65), U1–C6 3.0862(56), U1–C_{centroid} 2.7492(4), U1–3N_{plane} +0.3330(3), N4–C55 1.4436(87), C1–C2 1.3848(76), C2–C3 1.3968(70), C3–C4 1.3855(72), C4–C5 1.4037(76), C5–C6 1.4146(70), C6–C1 1.3874(42); N1–U1–N2 117.191(180), N2–U1–N3 118.294(162), N3–U1–N1 119.137(161), N4–U1–C_{centroid} 179.476(129), U1–N4–C55 178.363(372).

Single crystals suitable for X-ray crystallography were grown from a THF solution. A total of 44745 reflections ($-16 \le h \le 16$, $-16 \le k \le 16$, $-25 \le 1 \le 29$) were collected at T = 179.99(10) K with $2\theta_{max} = 50.044^{\circ}$, of which 14175 were unique. The residual peak and hole electron density were 4.90 and -1.24 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.0454$ and GOF = 1.080. Crystal and refinement data for **6**: formula C₈₄H₁₁₅KN₄O₈U, space group P-1, a = 13.91330(10) Å, b = 14.2338(2) Å, c = 24.3755(6) Å, $a = 87.235(2)^{\circ}$, $\beta = 73.7820(10)^{\circ}$, $\gamma = 60.7700(10)^{\circ}$, V = 4022.55(12) Å³, Z = 2, $\mu = 2.124$ mm⁻¹, F(000) = 1644.0, $R_1 = 0.0490$ and $wR_2 = 0.1246$ (based on all data).

(^{Ad}**TPBN**₃)**UNAd** (7) (CCDC No. 2351604)



Figure S8. Representation of 7 with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.3349(76), U1–N2 2.3536(77), U1–N3 2.3173(72), U1–N4 1.9368(50), U1–C1 3.0369(67), U1–C2 3.0492(71), U1–C3 3.0547(75), U1–C4 3.0558(76), U1–C5 3.0324(76), U1–C6 3.0469(66), U1–C_{centroid} 2.7062(3), U1–3N_{plane} +0.2180(3), N4–C55 1.4798(80), C1–C2 1.3884(146), C2–C3 1.3947(128), C3–C4 1.4084(114), C4–C5 1.380(11), C5–C6 1.4133(108), C6–C1 1.4047(113); N1–U1–N2 118.022(264), N2–U1–N3 119.488(268), N3–U1–N1 119.905(237), N4–U1–C_{centroid} 179.277(149), U1–N4–C55 178.813(421).

Single crystals suitable for X-ray crystallography were grown from a THF/hexanes solution. A total of 71299 reflections ($-14 \le h \le 14$, $-30 \le k \le 29$, $-22 \le l \le 22$) were collected at T = 179.99(10) K with $2\theta_{max} = 50.054^{\circ}$, of which 10824 were unique. The residual peak and hole electron density were 1.83 and -3.82 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.0593$ and GOF = 1.155. Crystal and refinement data for 7: formula C₆₄H₇₅N₄U, space group $P2_1/n$, a = 12.5539(2) Å, b = 25.8395(7) Å, c = 18.9196(3) Å, $\beta = 90.9520(10)^{\circ}$, V = 6136.4(2) Å³, Z = 4, $\mu = 2.683$ mm⁻¹, F(000) = 2316.0, $R_1 = 0.0726$ and $wR_2 = 0.1384$ (based on all data).

(^{Ad}TPBN₃)UNSiMe₃·C₄H₁₀O (8·Et₂O) (CCDC No. 2351598)



Figure S9. Representation of $8 \cdot Et_2O$ with thermal ellipsoids set at 35% probability. Hydrogen atoms and co-crystallized solvent (Et₂O) molecules were omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.3315(45), U1–N2 2.2995(48), U1–N3 2.3370(35), U1–N4 1.9793(41), U1–C1 2.9853(52), U1–C2 2.9815(48), U1–C3 2.9626(47), U1–C4 2.9806(42), U1–C5 2.9680(42), U1–C6 2.9852(45), U1–C_{centroid} 2.6276(3), U1–3N_{plane} +0.1624(3), N4–Si1 1.6914(44), C1–C2 1.3960(73), C2–C3 1.4181(62), C3–C4 1.3796(65), C4–C5 1.4154(71), C5–C6 1.3744(62), C6–C1 1.4161(69); N1–U1–N2 118.142(160), N2–U1–N3 120.143(137), N3–U1–N1 120.262(140), N4–U1–C_{centroid} 179.234(120), U1–N4–Si1 177.620(265).

Single crystals suitable for X-ray crystallography were grown from a Et₂O solution. A total of 29230 reflections ($-12 \le h \le 13$, $-17 \le k \le 16$, $-19 \le 1 \le 19$) were collected at T = 179.99(10) K with $2\theta_{max} = 50.044^{\circ}$, of which 9287 were unique. The residual peak and hole electron density were 4.61 and -1.24 eÅ^{-3} . The least-squares refinement converged normally with residuals of $R_1 = 0.0446$ and GOF = 1.057. Crystal and refinement data for **8**·**Et**₂**O**: formula C₆₁H₇₉N₄OSiU, space group *P*-1, *a* = 11.6457(3) Å, *b* = 14.4084(5) Å, *c* = 16.0175(5) Å, *a* = 99.122(3)°, *β* = 96.481(3)°, *γ* = 92.891(2)°, V = 2630.32(14) Å³, Z = 2, $\mu = 3.153$ mm⁻¹, F(000) = 1174.0, $R_1 = 0.0543$ and $wR_2 = 0.1101$ (based on all data).



Figure S10. Representation of **9-crypt·THF** with thermal ellipsoids set at 35% probability. Hydrogen atoms and lattice solvent (THF) molecules are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.4261(27), U1–N2 2.4527(27), U1–N3 2.4130(29), U1–N4 2.4193(27), U1–C1 2.7841(26), U1–C2 2.7896(24), U1–C3 2.7978(24), U1–C4 2.8116(29), U1–C5 2.8133(33), U1–C6 2.8167(31), U1–C_{centroid} 2.4265(3), U1–3N_{plane} –0.0045(3), N4–N5 1.1509(50), N5–N6 1.1484(59), C1–C2 1.4129(42), C2–C3 1.3967(42), C3–C4 1.4088(52), C4–C5 1.3867(43), C5–C6 1.4169(42), C6–C1 1.3885(50); N1–U1–N2 119.610(89), N2–U1–N3 121.124(90), N3–U1–N1 119.265(86), N4–U1–C_{centroid} 176.748(74), U1–N4–N5 174.519(308), N4–N5–N6 178.029(515).

Single crystals suitable for X-ray crystallography were grown from a THF/Et₂O/hexanes solution. A total of 44306 reflections $(-11 \le h \le 17, -17 \le k \le 18, -23 \le 1 \le 23)$ were collected at T = 180.00(10) K with $2\theta_{max} = 52.744^{\circ}$, of which 14506 were unique. The residual peak and hole electron density were 1.59 and -0.97 eÅ⁻³. The least-squares refinement converged normally with residuals of $R_1 = 0.0356$ and GOF = 1.016. Crystal and refinement data for **9-crypt**·**THF**: formula C₇₆H₁₀₄KN₈O₇U, space group *P*-1, *a* = 13.8942(4) Å, *b* = 14.6035(5) Å, *c* = 19.0556(6) Å, *a* = 68.468(3)°, $\beta = 89.387(2)^{\circ}$, $\gamma = 80.974(2)^{\circ}$, V = 3547.5(2) Å³, Z = 2, $\mu = 2.406$ mm⁻¹, *F*(000) = 1566.0, $R_1 = 0.0489$ and $wR_2 = 0.0740$ (based on all data).



Figure S11. Representation of **9** with thermal ellipsoids set at 35% probability. Hydrogen atoms and the disordered counterparts of THF are omitted for clarity. Selected distances (Å) and angles (°): U1–N1 2.4012(43), U1–N2 2.3992(42), U1–N3 2.4023(46), U1–N4 2.3675(36), U1–C1 2.8069(49), U1–C2 2.7933(52), U1–C3 2.7841(51), U1–C4 2.8001(44), U1–C5 2.8056(45), U1–C6 2.8223(45), U1–C_{centroid} 2.4202(3), U1–3N_{plane} –0.0084(4), N4–N5 1.2102(65), N5–N6 1.1532(83), C1–C2 1.4101(76), C2–C3 1.4020(75), C3–C4 1.4335(79), C4–C5 1.3975(74), C5–C6 1.4378(76), C6–C1 1.3932(83); N1–U1–N2 120.600(129), N2–U1–N3 120.211(142), N3–U1–N1 119.185(141), N4–U1–C_{centroid} 177.735(99), U1–N4–N5 154.980(383), N4–N5–N6 176.155(666).

Single crystals suitable for X-ray crystallography were grown from a THF/Et₂O/hexanes solution. A total of 35524 reflections ($-13 \le h \le 13$, $-14 \le k \le 14$, $-28 \le 1 \le 28$) were collected at T = 179.99(10) K with $2\theta_{max} = 48.808^{\circ}$, of which 11367 were unique. The residual peak and hole electron density were 1.58 and -3.20 eÅ^{-3} . The least-squares refinement converged normally with residuals of $R_1 = 0.0486$ and GOF = 1.019. Crystal and refinement data for **9**: formula C₇₄H₁₀₀KN₆O₈U, space group P-1, a = 11.3731(2) Å, b = 12.7468(2) Å, c = 24.8086(5) Å, $a = 97.311(2)^{\circ}$, $\beta = 95.515(2)^{\circ}$, $\gamma = 101.804(2)^{\circ}$, V = 3464.10(11) Å³, Z = 2, $\mu = 2.462 \text{ mm}^{-1}$, F(000) = 1522.0, $R_1 = 0.0623$ and $wR_2 = 0.1069$ (based on all data).



Figure S12. Evaluation of the steric hindrance of $(^{Ad}TPBN_3)^{3-}$ in the X-ray structure of $(^{Ad}TPBN_3)U(1)^2$ by the buried volume calculation using SambVca 2.1,¹⁵⁻¹⁷ as well as the ligand solid angles calculation (to reflect the ligand shielding) using Solid-G program,¹⁸ both with default settings. All views are from the entrance of the coordination pocket and along the C_3 axis (defined as z-axis). The computation results and the reactivity of the uranium(III) complex are compared with Meyer's $((ArO)_3 tacn)^{3-}$ system (right column).¹⁹

	2	3	4	6	7	9-crypt
U oxidation states	V	IV	IV	IV	V	III
avg. U–N _{amido}	2.320(5)	2.307(2)	2.407(3)	2.467(5)	2.335(8)	2.431(3)
U-C _{centroid} ^a	2.548(1)	2.568(1)	2.595(1)	2.749(1)	2.706(1)	2.427(1)
avg. C–Carene	1.400(8)	1.400(5)	1.398(4)	1.395(8)	1.398(14)	1.402(5)
avg. U–Carene	2.908(5)	2.924(3)	2.947(3)	3.083(8)	3.046(8)	2.802(3)
U-3N _{plane} ^b	0.092(1)	0.080(1)	0.184(1)	0.333(1)	0.218(1)	-0.005(1)
U–N _{axial}	1.986(4)	2.271(3)	2.023(3)	1.977(6)	1.937(5)	2.419(3)

Table S1. Selected metrical parameters of 2, 3, 4, 6, 7, and 9-crypt.

Note: All distances in Å. ^a $C_{centroid}$ = geometrical center of six carbon atoms of the anchoring arene; ^b U–3N_{plane} is defined as the distance of the uranium ion to the plane of the three nitrogen atoms (positive values for above the plane and negative values for below the plane).

3. IR Spectra

All IR spectra are given in the range of 4000–400 cm⁻¹.



Figure S13. IR spectrum of (^{Ad}TPBN₃)U(γ -N₃Ad) (**2**) in KBr, $\tilde{\nu}$ / cm⁻¹: 612 (w), 639 (w), 729 (w), 743 (m), 844 (w), 889 (w), 937 (w), 1074 (m), 1099 (w), 1142 (w), 1181 (w), 1222 (m), 1277 (w), 1303 (w), 1355 (w), 1384 (w), 1448 (m), 1466 (w), 1511 (w), 1590 (w), 2087 (w, N=N stretch), 2848 (m), 2903 (s).



Figure S14. IR spectrum of (^{Ad}TPBN₃)UN₃ (**3**) in KBr, \tilde{v} / cm⁻¹: 613 (w), 645 (w), 666 (w), 714 (w), 743 (m), 797 (w), 843 (w), 892 (w), 936 (w), 1068 (m), 1099 (w), 1118 (w), 1159 (w), 1221 (m), 1277 (w), 1305 (w), 1357 (m), 1384 (w), 1448 (m), 1466 (w), 1510 (w), 1591 (w), 2086 (s, azide stretch), 2848 (m), 2904 (s).



Figure S15. IR spectrum of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ -N₃Ad)] (4) in KBr, $\tilde{\nu}$ / cm⁻¹: 743 (m), 839 (w), 962 (w), 1109 (s), 1181 (w), 1250 (w), 1285 (w), 1308 (w), 1355 (m), 1408 (w), 1451 (m), 1510 (m), 1580 (m), 1602 (w), 2074 (w, N=N stretch), 2849 (s), 2903 (s).



Figure S16. IR spectrum of [K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (**5**) in KBr, $\tilde{\nu}$ / cm⁻¹: 429 (w), 743 (m), 839 (w), 964 (m), 1075 (m), 1106 (s), 1141 (m), 1181 (m), 1250 (w), 1286 (w), 1308 (w), 1354 (m), 1385 (w), 1457 (m), 1508 (m), 1578 (w), 1601 (w), 2850 (m), 2903 (s).



Figure S17. IR spectrum of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6) in KBr, \tilde{v} / cm⁻¹: 438 (w), 480 (w), 588 (m), 742 (m), 841 (w), 893 (w), 961 (w), 1075 (m), 1107 (m), 1142 (w), 1181 (w), 1249 (w), 1308 (w), 1355 (w), 1384 (m), 1451 (w), 1467 (w), 1511 (w), 1536 (w), 1579 (w), 1602 (w), 2848 (m), 2903 (s).



Figure S18. IR spectrum of (^{Ad}TPBN₃)UNAd (7) in KBr, \tilde{v} / cm⁻¹: 428 (w), 474 (w), 495 (m), 612 (w), 638 (w), 658 (w), 712 (w), 727 (m), 743 (m), 763 (w), 783 (w), 796 (w), 809 (w), 844 (m), 859 (w), 884 (m), 928 (w), 1043 (w), 1065 (s), 1094 (m), 1130 (s), 1181 (w), 1198 (m), 1208 (m), 1273 (w), 1299 (m), 1342 (w), 1352 (w), 1384 (m), 1399 (w), 1441 (s), 1466 (w), 1590 (w), 2847 (m), 2901 (s).


Figure S19. IR spectrum of (^{Ad}TPBN₃)UNSiMe₃ (**8**) in KBr, $\tilde{\nu}$ /cm⁻¹: 436 (w), 493 (w), 612 (w), 638 (w), 660 (w), 712 (w), 727 (w), 744 (m), 762 (w), 782 (w), 796 (w), 834 (m), 887 (w), 939 (w), 969 (s), 1072 (s), 1099 (w), 1116 (w), 1142 (w), 1181 (w), 1220 (m), 1240 (w), 1276 (w), 1301 (w), 1354 (w), 1384 (m), 1447 (m), 1466 (w), 1512 (w), 1591 (w), 2848 (m), 2903 (s).



Figure S20. IR spectrum of [K(crypt)][(^{Ad}TPBN₃)UN₃] (**9-crypt**) in KBr, $\tilde{\nu}$ / cm⁻¹: 607 (w), 662 (w), 741 (m), 845 (w), 949 (m), 1079 (m), 1103 (s), 1133 (m), 1181 (w), 1239 (m), 1259 (m), 1286 (m), 1301 (m), 1355 (m), 1446 (m), 1510 (w), 1580 (w), 1995 (w), 2062 (s, azide stretch), 2847 (m), 2901 (s).

4. NMR Spectra



Figure S21. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of (^{Ad}TPBN₃)U(γ -N₃Ad) (**2**), δ, ppm: 21.35 (s, 3H, CH of the anchor ring), 13.59 (s, 9H, N₃Ad (6H) & CH of side rings (3H)), 7.92 (s, 3H, N₃Ad), 6.80 (s, 3H, N₃Ad), 5.92 (s, 3H, N₃Ad), 3.92 (s, 3H, CH of side rings), 2.34 (s, 3H, CH of side rings), -0.55 (s, 18H, UNAd), -1.12 (s, 9H, UNAd), -7.11 (s, 3H, CH of side rings), -12.30 (s, 9H, UNAd), -14.34 (br s, 9H, UNAd). The region between 0.5 and 7.5 ppm is enlarged for clarification.



Figure S22. Monitoring the stability of **2** in the presence of $C_6H_3(OMe)_3$ (internal standard) at room temperature by ¹H NMR spectroscopy (C_6D_6 , 400 MHz, 298 K). From bottom to top: <10 min, 14 d, 28 d, 42 d, 56 d, and 70 d at room temperature. The ¹H NMR spectra show that (^{Ad}TPBN₃)UN₃ (**3**) is the sole paramagnetic product at the end of the reaction. The ¹H NMR yield of **3** is determined to be ca. 57% based on the integration of characteristic peaks at –9.2 ppm for **3** and –7.1 ppm for **2** compared to that of $C_6H_3(OMe)_3$. The peaks of aliphatic by-products and the Ad groups of the free ligand $H_3(^{Ad}TPBN_3)$ are highlighted by a red box in the top spectrum. The peaks in this region could not be clearly assigned to any simple Ad containing compounds, such as AdH and Ad₂. In addition, the pattern of these peaks suggests the formation of low-symmetry species, which may be resulted from bond cleavage and/or skeleton rearrangement of 1-adamantyl radical.^{20, 21}



Figure S23. Monitoring the stability of **2** in the presence of $C_6H_3(OMe)_3$ (internal standard) at 80 °C by ¹H NMR spectroscopy (C_4D_8O , 400 MHz, 298 K). From bottom to top: t = 0, 1 h, 4 h, 14 h, 38 h, 108 h, and 275 h at 80 °C. After heating for 1 h, **2** was fully consumed along with the formation of (^{Ad}TPBN₃)UN₃ (**3**) and other minor uranium containing species, the latter of which gradually decomposed to NMR inactive species after prolong heating. Finally, **3** is the sole paramagnetic product at the end of the reaction observed by ¹H NMR spectroscopy. The ¹H NMR yield of **3** is determined to be ca. 67% at t = 1 h based on the integration of characteristic peaks at –9.1 ppm for **3** and –7.3 ppm for **2** compared to that of $C_6H_3(OMe)_3$. The ¹H NMR yield of **3** remained at ca. 66% at t = 275 h, indicating high thermal stability of **3** at elevated temperature.



Figure S24. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of (^{Ad}TPBN₃)UN₃ (**3**), δ , ppm: 15.07 (s, 3H, *CH* of the anchor ring), 13.45 (d, *J* = 7.6 Hz, 3H, *CH* of side rings), 3.64 (t, *J* = 7.0 Hz, 3H, *CH* of side rings), 3.37 (t, *J* = 7.2 Hz, 3H, *CH* of side rings), -0.98 (s, 9H, Ad), -1.62 (m, 18H, Ad), -9.12 (d, *J* = 8.3 Hz, 3H, *CH* of side rings), -12.36 (s, 9H, Ad), -17.42 (br s, 9H, Ad). The region between 0.5 and 7.5 ppm is enlarged for clarity.



Figure S25. ¹H NMR (C₄D₈O, 400 MHz, 298 K) spectrum of **3**, Cp₂Co, and 2.2.2cryptand as the products of the reaction between [K(crypt)][(^{Ad}TPBN₃)UN₃] (**9-crypt**) and [Cp₂Co][PF₆]. For **3**, δ , ppm: 15.17 (s, 3H, *CH* of the anchor ring), 13.66 (d, *J* = 7.8 Hz, 3H, *CH* of side rings), 3.66 (t, *J* = 7.1 Hz, 3H, *CH* of side rings), 3.43 (t, *J* = 7.4 Hz, 3H, *CH* of side rings), -1.06 (s, 9H, Ad), -1.64 (m, 18H, Ad), -9.10 (d, *J* = 8.3 Hz, 3H, *CH* of side rings), -12.23 (s, 9H, Ad), -17.56 (br s, 9H, Ad). The region between 1.7 and 4.0 ppm is enlarged to show the concomitant formation of free 2.2.2-cryptand.



Figure S26. (a) ¹H NMR (C₅D₅N, 400 MHz, 298 K) spectrum of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ-N₃Ad)] (**4**), δ, ppm: 53.80 (s, 3H, *CH* of the anchor ring), 37.98 (s, 6H, N₃Ad), 25.80 (s, 3H, *CH* of side rings), 17.99 (s, 3H, N₃Ad), 17.71 (d, J = 44 / 110

15.1 Hz, 3H, N₃*Ad*), 13.94 (d, J = 15.6 Hz, 3H, N₃*Ad*), 3.66 (m, 8H, OCH₂CH₂ of THF), 3.55 (s, 24H, 18-crown-6), 2.97 (s, 3H, C*H* of side rings), 1.62 (m, 8H, OCH₂CH₂ of THF), -2.76 (br s, 9H, UN*Ad*), -5.53 (s, 9H, UN*Ad*), -6.37 (s, 3H, C*H* of side rings), -8.95 (s, 9H, UN*Ad*), -31.04 (s, 3H, C*H* of side rings), -39.38 (br s, 9H, UN*Ad*). A peak (9H) belonging to the Ad groups of the (^{Ad}TPBN₃)^{3–} ligand was not found in the range of -500 to +500 ppm, probably due to signal broadening. (b) Two representative regions (+60 to +12 ppm, 0 to -50 ppm) of the ¹H NMR spectrum (C₅D₅N, 400 MHz, 298 K) of **4** without baseline correction were enlarged for clarification.



Figure S27. Monitoring the stability of **4** in solution at room temperature by ¹H NMR spectroscopy (C_5D_5N , 400 MHz, 298 K). For clarity, only two regions (+95 to +8.5, and -4.5 to -70 ppm) are shown here. From bottom to top: 10 min, 12 h, 2 d, 4 d, 8 d, 12 d, and 18 d at room temperature. The ¹H NMR spectra show the clean transformation of **4** to [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (**5**). No formation of (^{Ad}TPBN₃)UN₃ (**3**) nor [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UN₃] (**9**) was observed under these conditions.



Figure S28. ¹H NMR (400 MHz, C₄D₈O, 298 K) spectrum of [K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (**5**), δ, ppm: 16.34 (d, J = 8.5 Hz, 3H, CH of side rings), 7.75 (t, J = 7.0 Hz, 3H, CH of side rings), 7.45 (t, J = 7.7 Hz, 3H, CH of side rings), 3.87 (br s, 9H, Ad), 3.62 (m, 4H, α-CH₂ of THF), 3.45 (s, 24H, 18-crown-6), 1.78 (m, 4H, β-CH₂ of THF), 0.66 (s, 9H, Ad), 0.54 (m, 9H, Ad), 0.09 (m, 9H, Ad), -0.16 (d, J = 6.4 Hz, 3H, CH of side rings), -10.60 (br s, 9H, Ad), -73.25 (s, 3H, CH of the anchor ring). The region between -0.5 and 1.0 ppm is enlarged for clarity.



Figure S29. ¹H NMR (C₄D₈O, 500 MHz, 298 K) spectrum of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6, saturated), δ , ppm: 83.56 (m, 6H, N_{imide}-Ad), 66.31 (s, 3H, CH of the anchor ring), 38.87 (s, 3H, N_{imide}-Ad or CH of side rings), 35.82 (s, 3H, CH of side rings or N_{imide}-Ad), 28.03 (m, 6H, N_{imide}-Ad), 4.54 (s, 27H, 18-crown-6 (24H) & CH of side rings (3H)), -8.92 (s, 3H, CH of side rings), -11.22 (s, 18H, N_{amide}-Ad), -16.04 (s, 9H, N_{amide}-Ad), -37.05 (s, 3H, CH of side rings), -59.41 (br s, 9H, Ad). A peak (9H) belonging to the Ad groups of the (^{Ad}TPBN₃)³⁻ ligand was not found in the range of -500 to +500 ppm, probably due to signal broadening.



Figure S30. ¹H NMR (C₄D₈O, 500 MHz, 298 K) spectrum of *in situ* formed (^{Ad}TPBN₃)UNAd (7, saturated), δ , ppm: 30.54, 19.56, 15.99, 14.46, 11.70, 3.43, -3.85, -11.78, -21.57. No other peak was observed in the range of -500 to +500 ppm. The baseline correction and the peak integration could not be reliably done due to signal broadening, preventing detailed assignment of peaks.



Figure S31. Monitoring the reaction of $(^{Ad}TPBN_3)U(1)$ with an equivalent of PhCH₂N₃ in C₆D₆ in the presence of C₆H₃(OMe)₃ as an internal standard by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). Bottom: $1 + C_6H_3(OMe)_3$; Next to top: $1 + C_6H_3(OMe)_3 + PhCH_2N_3$ after 5 min (0–5 °C) and a day at room temperature. The ¹H NMR spectra show that (^{Ad}TPBN₃)UN₃ (**3**) is the major product with the concomitant formation of PhCH₂CH₂Ph (0.2 equiv).



Figure S32. Monitoring the reaction of 1 with an equivalent of Ph_3CN_3 in C_6D_6 in the presence of $C_6H_3(OMe)_3$ as an internal standard at room temperature by ¹H NMR spectroscopy (C_6D_6 , 400 MHz, 298 K). Bottom: $1 + C_6H_3(OMe)_3$; Top: $1 + C_6H_3(OMe)_3 + Ph_3CN_3$ after 5 min. The ¹H NMR spectra show the formation of 3 and the Gomberg's dimer in a 2:1 molar ratio. The region between 4.5 and 8.0 ppm is enlarged for clarity, and the characteristic peaks of the Gomberg's dimer are labelled with A, B, and C.



Figure S33. Monitoring the reaction of **1** with Me₃SnN₃ in C₆D₆ in the presence of C₆H₃(OMe)₃ (internal standard) by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). Bottom: **1** + C₆H₃(OMe)₃; Next to top: **1** + C₆H₃(OMe)₃ + Me₃SnN₃ at room temperature after 5 min, 1 h, 7 h, 24 h, 36 h, 48 h, respectively. The ¹H NMR spectra show that **3** and Me₆Sn₂ (at 0.25 ppm with ¹¹⁹Sn–¹H coupling) are the major products. In addition, a uranium-containing intermediate (marked with red arrows) formed at the early stage of the reaction, but gradually converted to the final product **3**.



Figure S34. Monitoring the reaction of **1** with Me₃SiN₃ in C₆D₆ in the presence of C₆H₃(OMe)₃ (internal standard) at room temperature by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). Only three regions (+30 to +8, -8 to -22, and 0.7 to -3.0 ppm) are shown for clarity. From bottom to top: 5 min, 2 d, 18 d, 60 d, 100 d. The ¹H NMR spectra show that (^{Ad}TPBN₃)UN₃ (**3**) and Me₆Si₂ form in a molar ratio of 1:0.15, along with a minor product (^{Ad}TPBN₃)UNSiMe₃ (**8**). ¹H NMR (400 MHz, C₆D₆, 298 K) assignment for **8** (δ , ppm): 27.85 (s, 3H, CH of the anchor ring), 20.67 (s, 9H, SiCH₃), 14.89 (s, 3H, CH of side rings), 3.21 (s, 3H, CH of side rings), 2.24 (s, 3H, CH of side rings), -19.79 (br s, 18H, Ad).

The molar ratio of **3** and **8** in the final mixture is determined to be 5:1 based on the ratio of the integrations of characteristic ¹H NMR peaks in the range of -0.8 to -1.7 ppm (for **3**) and in the range of -2.5 to -3.1 ppm (for **8**), respectively. Notably, the peaks of **3** and **1** could not be clearly identified until the full consumption of **1** (see Figure S37 for further confirmation). This might be attributed to an equilibrium between **1** and **3** and a dinuclear species (proposed to be $[(^{Ad}TPBN_3)U]_2(\mu-N_3))$, which leads to significant peak shifting and broadening. The region of 0.7 to -3.0 ppm of the stacked spectra clearly shows the gradual formation of **8** and the equilibrium (**3** + **1** \rightleftharpoons $[(^{Ad}TPBN_3)U]_2(\mu-N_3))$ steadily shifting toward **3**.



Figure S35. Monitoring the reaction of **1** with Me₃SiN₃ in C₆D₆ in the presence of C₆H₃(OMe)₃ (internal standard) at 80 °C by ¹H NMR spectroscopy (C₆D₆, 400 MHz, 298 K). Only three regions (+30 to +8, -8 to -22, and 0.7 to -3.0 ppm) are shown for clarity. From bottom to top: 25 °C for 5 min after mixing, and 80 °C for 2 h, 8 h, 20 h, 48 h. The ¹H NMR spectra show that **3** and Me₆Si₂ form in a molar ratio of 1:0.1, along with a minor product **8**. The molar ratio of **3** and **8** in the final mixture is determined to be 3:1 based on the ratio of the integrations of characteristic ¹H NMR peaks in the range of -0.8 to -1.7 ppm (for **3**) and in the range of -2.5 to -3.1 ppm (for **8**), respectively. Similar to Figure S34, the presence of the equilibrium (**3** + **1** \rightleftharpoons [(^{Ad}TPBN₃)U]₂(µ-N₃)) could be observed before the full consumption of **1**.



Figure S36. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of (^{Ad}TPBN₃)UNSiMe₃ (8), δ , ppm: 28.01 (s, 3H, CH of the anchor ring), 20.83 (s, 9H, SiCH₃), 14.95 (s, 3H, CH of side rings), 3.18 (s, 3H, CH of side rings), 2.20 (s, 3H, CH of side rings), -2.74 (m, 18H, Ad), -2.93 (s, 9H, Ad), -10.23 (s, 3H, CH of side rings), -19.90 (br s, 18H, Ad). The region between 1.0 and 3.3 ppm is enlarged for clarity. Less than 1 mol% (^{Ad}TPBN₃)UN₃ (3) could be identified in this spectrum.



Figure S37. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of a 1:1 (molar ratio) mixture of (^{Ad}TPBN₃)U (1) and (^{Ad}TPBN₃)UN₃ (3) in C₆D₆ without baseline correction (top). A higher-resolution spectrum of such a mixture could not be obtained due to the limited solubility of 1 and the extreme broadening of several peaks (note that the region between 5.0 and 16.0 ppm is enlarged in the upper left corner for clarification). The corresponding spectra of pure 1² (middle) and pure 3 (bottom) measured under the same conditions are also shown for comparison. The disappearance of peaks belonging to pure 1 and 3 and emergence of new broad peaks indicate the presence of an equilibrium: $3 + 1 \Rightarrow [(^{Ad}TPBN_3)U]_2(\mu-N_3).$



Figure S38. Monitoring the reaction of $[K(crypt)][(^{Ad}TPBN_3)U]$ (**5-crypt**) with an equivalent of Me₃SiN₃ in C₄D₈O in the presence of C₆H₃(OMe)₃ as an internal standard by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). Bottom: **5-crypt** + C₆H₃(OMe)₃; Top: **5-crypt** + C₆H₃(OMe)₃ + Me₃SiN₃ after 10 min, 3.5 h, and 18 h. The ¹H NMR spectra show that **5-crypt** is fully consumed and $[K(crypt)][(^{Ad}TPBN_3)UN_3]$ (**9-crypt**) and Me₆Si₂ form in a 2:1 molar ratio within 10 min at room temperature.



Figure **S39**. $^{1}\mathrm{H}$ NMR (400 MHz, C_4D_8O , 298 K) spectrum of [K(crypt)][(^{Ad}TPBN₃)UN₃] (9-crypt), δ, ppm: 15.21 (s, 3H, CH of side rings), 11.61 (s, 3H, CH of side rings), 9.99 (s, 3H, CH of the anchor ring), 8.44 (d, J = 6.6 Hz, 3H, CH of side rings), 6.13 (br s, 9H, Ad), 5.51 (br s, 9H, Ad), 4.92 (t, J = 7.1 Hz, 3H, CH of side rings), 3.57 (s, 12H, OCH₂CH₂O of crypt), 3.50 (m, 12H, OCH₂CH₂N of crypt), 2.87 (s, 9H, Ad), 2.50 (m, 12H, OCH₂CH₂N of crypt), 2.09 (m, 9H, Ad), 1.93 (m, 9H, Ad).



Figure S40. ¹H NMR (400 MHz, C₄D₈O, 298 K) spectrum of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UN₃] (**9**), δ , ppm: 15.18 (s, 3H, CH of side rings), 11.80 (s, 3H, CH of side rings), 10.40 (s, 3H, CH of the anchor ring), 8.33 (d, J = 5.2 Hz, 3H, CH of side rings), 6.51 (br s, 9H, Ad), 6.00 (br s, 9H, Ad), 4.94 (t, J = 6.9 Hz, 3H, CH of side rings), 3.54 (s, 24H, 18-crown-6), 2.97 (s, 9H, Ad), 2.16 (m, 9H, Ad), 2.00 (m, 9H, Ad). Based on the integration, less than 5 mol% free ligand H₃(^{Ad}TPBN₃) was present.



Figure S41. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of a 1:1 (molar ratio) mixture of (^{Ad}TPBN₃)Ce⁴ and (^{Ad}TPBN₃)UN₃ (**3**) in C₆D₆ (bottom), as well as the spectra of pure (^{Ad}TPBN₃)Ce (top) and **3** (middle) for comparison. Only two regions (+25.0 to 7.0, and -0.7 to -25.0 ppm) are shown for the sake of clarity. The ¹H NMR spectrum of the mixture clearly showed two separate sets of peaks corresponding to (^{Ad}TPBN₃)Ce and **3**, indicating no equilibrium between the two compounds in C₆D₆.



Figure S42. ¹H NMR (C₆D₆, 400 MHz, 298 K) spectrum of a 1:1 (molar ratio) mixture of (^{Ad}TPBN₃)Pr⁴ and (^{Ad}TPBN₃)UN₃ (**3**) in C₆D₆ (bottom), as well as the spectra of pure (^{Ad}TPBN₃)Pr (top) and **3** (middle) for comparison. Only two regions (+35.0 to 7.0, and -0.5 to -45.0 ppm) are shown for the sake of clarity. The ¹H NMR spectrum of the mixture clearly showed two separate sets of peaks corresponding to (^{Ad}TPBN₃)Pr and **3**, indicating no equilibrium between the two compounds in C₆D₆.

5. Kinetic Studies

This section presents the results of kinetic studies on the conversion of $[K(18-crown-6)(THF)_2][(^{Ad}TPBN_3)U(\gamma-N_3Ad)]$ (4) to $[K(18-crown-6)(THF)_2][(^{Ad}TPBN_3)UNAd]$ (6) and dinitrogen in THF- d_8 .

Experiment details:

4 (8.7 mg, 5.4 µmol) was dissolved in THF- d_8 (500 µL), followed by the addition of 1.5 µL C₆H₃(OMe)₃/THF- d_8 stock solution (173.8 mg 1,3,5-C₆H₃(OMe)₃ dissolved in 500 µL THF- d_8) as an internal standard. The mixture was transferred to a J. Young tube, and measured by ¹H NMR spectroscopy regularly. The tube was kept at room temperature (23 °C ± 3 °C, determined by thermometer) during the whole monitoring process. The room temperature data were not taken into account for the solution of the Arrhenius equation (Figure S54) and the Eyring equation (Figure S55).

Given the slow kinetics of the transformation from **4** to **6**, it was not practical to perform *in situ* monitoring experiment inside the NMR spectrometer at elevated temperatures. Therefore, we conducted the following procedure as the alternative to minimize the error in heating time. The solution of **4** in THF- d_8 (8.9–9.2 mg, 500 µL THF- d_8) with the presence of C₆H₃(OMe)₃ was transferred to a J. Young tube and heated in stirring oil baths with temperature settings at 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C, respectively. The range of bath temperature is within ± 0.5 °C of the set temperature. The solution sample was estimated to equilibrate to the desired temperature within 5–10 min, and cooled to room temperature prior to measuring by ¹H NMR spectroscopy. The stacked spectra for each temperature (ca. 23 °C, and 40 °C, 50 °C, 60 °C, 70 °C, 80 °C) were displayed in Figures S44–S49.

Data processing details:

Given the paramagnetic nature of the mixture (5f² uranium(IV) complexes), a consistent and appropriate data processing procedure was necessary to eliminate the systematic error of integration as much as possible. For each ¹H NMR spectrum, after the phase correction, an Ablative method with default settings (points = 5, passes = 10) was applied for the baseline correction. The singlet of C_{Ar} –*H* (3H) of $C_{6}H_{3}(OMe)_{3}$

appearing at 6.04 ppm was selected as a reference peak. The integration of CH_2 (N₃Ad, 6H) peak at 37.6 ppm was used to calculate the concentration of **4**. The integration of the peak at 39.2 ppm (3H, from N_{imido}-Ad or CH of side rings) was used to calculate the concentration of **5**.

At the early stage of each monitoring experiment, a gradual increase of the concentration of **6** was observed. However, due to the very low solubility of **6** in THF- d_8 at room temperature, the integration of the characteristic peak of **6** stayed constant after **6** reached saturation in THF- d_8 solution. Therefore, only the concentration of **4** was used to calculate the kinetics of the transformation from **4** to **6**.

The plots of $\ln([U(IV)N_3Ad])$ (natural logarithm of the concentration of 4) versus cumulative reaction time at various temperatures (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C) were displayed in Figures S49–S53.

Parameter extraction details:

A first-order reaction fits the rate law: $rate = k \cdot c_t$, then $\ln(c_t) = -k \cdot t + \ln(c_0)$, where k is the rate constant, c_0 is the initial concentration of the reactant (at time 0), c_t is the concentration of the reactant at time t. Therefore, in the $\ln(c_t) - t$ plots (Figures S49–S53), k = - slope.

As the Arrhenius equation points out, $k = Ae^{\frac{-E_a}{RT}}$, then $\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A)$, where A is a factor, R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature in Kelvin (K), and E_a is the activation energy. Therefore, in the $\ln(k) - (\frac{1}{T})$ plots (Figure S54), $E_a = -\operatorname{slope} \times R$.

As the Eyring equation points out, $k = \frac{k_B T}{h} e^{-(\frac{\Delta H^{\ddagger}}{RT})} e^{(\frac{\Delta S^{\ddagger}}{R})}$, then $\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$, where k_B is the Boltzmann's constant (1.381 × 10⁻²³ J/K), h is Planck's constant (6.626 × 10⁻³⁴ J·s), ΔH^{\ddagger} is the enthalpy of activation, and ΔS^{\ddagger} is the entropy of activation. Therefore, in the $\ln(\frac{k}{T}) - (\frac{1}{T})$ plots (Figure S55), $\Delta H^{\ddagger} = -\text{slope} \times R$, $\Delta S^{\ddagger} = [\text{intercept} - \ln\left(\frac{k_B}{h}\right)] \times R$.



Figure S43. Monitoring the stability of **4** in solution at room temperature (ca. 23 °C) by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+60 to +13 ppm, +6.4 to -50 ppm) are shown here. From bottom to top: t = 0, 24 h, 72 h, 216 h, 440 h, 780 h, 1020 h, and 1443 h at room temperature. The ¹H NMR spectra show the gradual consumption of **4**. A brownish yellow precipitate was observed at the bottom of the J. Young tube. Notably, the peaks of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (**6**) were hardly observed with very low signal-to-noise ratio, probably due to the very low solubility of **6** in THF-*d*₈ at room temperature and a slow formation rate of **6** at room temperature. This scenario is in stark contrast to the stacked spectra for the stability monitoring experiment of **4** performed in pyridine-*d*₅, where the product **6** exhibits a noticeable solubility at room temperature (Figure S27). In addition, the conversion rate of **5** in THF-*d*₈ is much slower than that in pyridine-*d*₅ at room temperature.



Figure S44. Monitoring the stability of **4** in solution at 40 °C by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+60 to +13 ppm, +6.4 to -50 ppm) are shown here. From bottom to top: t = 0, 57 h, 115 h, 236 h, 310 h, 404 h, 451 h, 548 h, and 1541 h at 40 °C. The decrease of the concentration of the product **6** at the final stage of the monitoring process is attributed to the precipitation of **6** due to its low solubility.



Figure S45. Monitoring the stability of **4** in solution at 50 °C by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+90 to +13 ppm, +6.4 to -80 ppm) are shown here. From bottom to top: t = 0, 4 h, 8 h, 6 h, 21 h, 32 h, 44 h, 78 h, 125 h, and 200 h at 50 °C.



Figure S46. Monitoring the stability of **4** in solution at 60 °C by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+90 to +13 ppm, +6.4 to -80 ppm) are shown here. From bottom to top: t = 0, 55 min, 3 h, 6 h, 27 h, 33 h, 46 h, and 246 h at 60 °C. The decrease of the concentration of the product **6** at the final stage of the monitoring process is attributed to the precipitation of **6** due to its low solubility.



Figure S47. Monitoring the stability of **4** in solution at 70 °C by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+90 to +13 ppm, +6.4 to -80 ppm) are shown here. From bottom to top: t = 0, 1 h, 2 h, 5 h, 9 h, 20 h, 31 h, and 126 h at 70 °C. The decrease of the concentration of the product **6** at the final stage of the monitoring process is attributed to the precipitation of **6** due to its low solubility.



Figure S48. Monitoring the stability of **4** in solution at 80 °C by ¹H NMR spectroscopy (C₄D₈O, 400 MHz, 298 K). For clarity, only two regions (+90 to +13 ppm, +6.4 to -80 ppm) are shown here. From bottom to top: t = 0, 1 h, 2 h, 3 h, 4 h, 5 h, 6.5 h, and 55 h at 80 °C.



Figure S49. Natural logarithm (ln) of the concentration (mol/L) of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ -N₃Ad)] (4) *versus* time (h) plot for the conversion of 4 to [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6) in THF-*d*₈ at 40 °C (313.15 K). Linear fit parameters for ln[U(IV)N₃Ad] *versus* time: $R^2 = 0.99319$, intercept = -4.5159 ± 0.01353, slope = $-k_1 = -0.00134 \pm (4.18868 \times 10^{-5}) h^{-1}$, $k_1 = 3.72 \times 10^{-7} \pm (1.16352 \times 10^{-8}) s^{-1}$.



Figure S50. Natural logarithm of the concentration (mol/L) of 4 *versus* time (h) plot for the conversion of 4 to 6 in THF- d_8 at 50 °C (323.15 K). Linear fit parameters for ln[U(IV)N₃Ad] *versus* time: $R^2 = 0.97169$, intercept = -4.59824 ± 0.03402 , slope = $-k_1$ = $-0.00663 \pm (3.99445 \times 10^{-4})$ h⁻¹, $k_1 = 1.84 \times 10^{-6} \pm (1.10957 \times 10^{-7})$ s⁻¹.



Figure S51. Natural logarithm of the concentration (mol/L) of 4 *versus* time (h) plot for the conversion of 4 to 6 in THF- d_8 at 60 °C (333.15 K). Linear fit parameters for ln[U(IV)N₃Ad] *versus* time: $R^2 = 0.95658$, intercept = -4.61007 ± 0.03432, slope = $-k_1$ = -0.0167 ± 0.00145 h⁻¹, $k_1 = 4.64 \times 10^{-6} \pm (4.03 \times 10^{-7})$ s⁻¹.


Figure S52. Natural logarithm of the concentration (mol/L) of 4 versus time (h) plot for the conversion of 4 to 6 in THF- d_8 at 70 °C (343.15 K). Linear fit parameters for ln[U(IV)N₃Ad] versus time: $R^2 = 0.96605$, intercept = -4.62342 ± 0.04837 , slope = $-k_1$ = -0.04387 ± 0.00335 h⁻¹, $k_1 = 1.219 \times 10^{-5} \pm (9.3 \times 10^{-7})$ s⁻¹.



Figure S53. Natural logarithm of the concentration (mol/L) of 4 *versus* time (h) plot for the conversion of 4 to 6 in THF- d_8 at 80 °C (353.15 K). Linear fit parameters for ln[U(IV)N₃Ad] *versus* time: $R^2 = 0.95304$, intercept = -4.58252 ± 0.05251 , slope = $-k_1$ = -0.15609 ± 0.01409 h⁻¹, $k_1 = 4.3358 \times 10^{-5} \pm (3.914 \times 10^{-6})$ s⁻¹.



Figure S54. Natural logarithm of the rate constant (s⁻¹) versus T^{-1} (K⁻¹) plot for the conversion of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UN₃Ad] (4) to [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6) in THF- d_8 at 40, 50, 60, 70, 80 °C (313.15–353.15 K). Linear fit parameters: $R^2 = 0.99009$, intercept = 25.63536 ± 1.89889, slope = -12625.39659 ± 630.9046 K. Data extraction from the Arrhenius equation ($k = Ae^{\frac{-E_a}{RT}}$): $A = 1.359 \times 10^{11} \text{ s}^{-1}$, $E_a = 105.0 \pm 5.2 \text{ kJ/mol.}$



Figure S55. Natural logarithm of k/T (s⁻¹ K⁻¹) versus T^{-1} (K⁻¹) plot for the conversion of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ -N₃Ad)] (4) to [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6) in THF- d_8 at 40, 50, 60, 70, 80 °C (313.15–353.15 K). Linear fit parameters: $R^2 = 0.98953$, intercept = 18.82854 ± 1.90054, slope = -12293.13775 ± 631.45059 K. Data extraction from the Eyring equation ($k = \frac{k_BT}{h}e^{-(\frac{AH^{\ddagger}}{RT})}e^{(\frac{AS^{\ddagger}}{R})}$): $\Delta H^{\ddagger} = 102.2 \pm 5.2$ kJ/mol, $\Delta S^{\ddagger} = -41.0 \pm 15.8$ J mol⁻¹ K⁻¹.

6. UV-Vis-NIR Spectra



Figure S56. UV-Vis-NIR spectrum (320–1600 nm) of (^{Ad}TPBN₃)U(γ -N₃Ad) (**2**) in THF solution (3.9 mM) at room temperature with the NIR region (950–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. Broad bands over the range from 370 to 900 nm with ε of 1200–7000 M⁻¹·cm⁻¹. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 1130 (400), 1480 (130).



Figure S57. UV-Vis-NIR spectrum (320–1600 nm) of (^{Ad}TPBN₃)UN₃ (**3**) in THF solution (4.5 mM) at room temperature with the NIR region (750–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. Broad bands over the range from 360 to 550 nm with ε of 1100–6000 M⁻¹·cm⁻¹. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 700 (70), 860 (30), 945 (34), 1037 (66), 1078 (51), 1115 (65), 1170 (106), 1211 (67), 1400 (65), 1450 (66).



Figure S58. UV-Vis-NIR spectrum (350–1600 nm) of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)U(γ -N₃Ad)] (4) in THF solution (3.8 mM) at room temperature with the NIR region (725–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. Broad bands over the range from 400 to 550 nm with ε of 1100–8000 M⁻¹·cm⁻¹. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 670 (440), 840 (170), 990 (150), 1065 (140), 1190 (100), 1325 (105), 1550 (60).



Figure S59. UV-Vis-NIR spectrum (320–1600 nm) of [K(18-crown-6)(THF)][(^{Ad}TPBN₃)U] (5) in THF solution (2.8 mM) at room temperature with the NIR region (650–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. $\lambda_{max} / nm (\varepsilon / M^{-1} \cdot cm^{-1})$: 390 (4100), 480 (2600), 570 (1670), 940 (160), 1380 (100). The characteristic absorption peaks are similar to those of [K(crypt)][(^{Ad}TPBN₃)U] (**5-crypt**).²



Figure S60. UV-Vis-NIR spectrum (260–1600 nm) of [K(18-crown-6)(THF)₂][(^{Ad}TPBN₃)UNAd] (6) in THF solution (0.47 mM) at room temperature with the NIR region (750–1300 nm) enlarged in the upper right corner. The solvent background was subtracted. $\lambda_{max} / nm (\varepsilon / M^{-1} \cdot cm^{-1})$: 313 (10100), 580 (90), 730 (55), 840 (50), 1180 (30), 1380 (100).



Figure S61. UV-Vis-NIR spectrum (250–1600 nm) of (^{Ad}TPBN₃)UNAd (7) in THF solution (2.1 mM) at room temperature with the NIR region (950–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 365 (6600), 470 (4500), 700 (2500), 1185 (50), 1465 (120), 1555 (140).



Figure S62. UV-Vis-NIR spectrum (250–1600 nm) of (^{Ad}TPBN₃)UNSiMe₃ (**8**) in THF solution (2.7 mM) at room temperature with the NIR region (950–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 370 (4600), 470 (3400), 720 (2100), 1050 (180), 1185 (25), 1470 (110).



Figure S63. UV-Vis-NIR spectrum (330–1600 nm) of [K(crypt)][(^{Ad}TPBN₃)UN₃] (**9-crypt**) in THF solution (4.0 mM) at room temperature with the NIR region (750–1600 nm) enlarged in the upper right corner. The solvent background was subtracted. λ_{max} / nm (ε / M⁻¹·cm⁻¹): 400–570 (4000–1000), 671 (465), 728 (380), 851 (308), 964 (313), 1010 (300), 1190 (200).

7. Density Functional Theory (DFT) Calculations

7.1. General Considerations

All DFT calculations were presented by Gaussian 16 A03.²² Single crystal structures were used as initial structure in geometry optimization with counter ions, disorder atoms, and lattice solvent molecules removed. Hybrid functional PBE0²³ and GD3BJ^{24, 25} dispersion correction were used in DFT calculations. For light atoms, all nitrogen atoms and carbon atoms in the anchoring ring were applied with 3-ζ basis set def2-TZVP, while other light atoms (C, H, N, Si) were applied with 2-ζ basis set def2-SVP.²⁶ For uranium atoms, MWB60 quasi-relativistic pseudo potential and standard basis set were used.²⁷ Default convergence threshold for SCF iteration and geometry optimization was adopted. All optimized structures showed no imaginary frequencies by frequency analysis, and wave functions were checked to be stable under perturbation by time-dependent DFT (TD-DFT) calculation (with the keyword 'stable=opt'). NBO 7.0 software was used in NLMO analysis.²⁸ Multiwfn was used in wave function analyses.²⁹

7.2. Comparison between Experimental and Calculated Optimized Structures

Selected distances [Å]			
and angles [°]	Exp.	Calc.	Diff.
U–N1	2.309(4)	2.293	-0.016
U–N2	2.320(5)	2.310	-0.010
U–N3	2.330(4)	2.302	-0.028
U–N4	1.986(4)	1.961	-0.025
U–C1	2.895(5)	2.906	0.011
U–C2	2.919(5)	2.921	0.002
U–C3	2.922(4)	2.911	-0.011
U–C4	2.926(4)	2.924	-0.002
U–C5	2.888(5)	2.908	0.020
U–C6	2.896(5)	2.919	0.023
U-Ccentroid	2.548(1)	2.558	0.010
U-3N _{plane}	+0.092(1)	+0.126	0.035
C1–C2	1.384(8)	1.384	0.000
C2–C3	1.412(8)	1.410	-0.002
C3–C4	1.378(8)	1.383	0.005
C4–C5	1.417(8)	1.410	-0.007
С5–С6	1.401(8)	1.384	-0.017
C6–C1	1.411(8)	1.410	-0.001
N4–N5	1.334(9)	1.309	-0.025
N5–N6	1.264(13)	1.246	-0.018
N6-Cbridgehead(Ad)	1.486(12)	1.461	-0.025
N1–U–N2	120.6(2)	119.55	-1.1
N2-U-N3	118.9(1)	119.15	0.3
N3-U-N1	120.0(1)	120.41	0.4
U-N4-N5	170.6(5)	172.28	1.7
N4-N5-N6	115.0(9)	116.77	1.8

Table S2. Selected structural parameters of $(^{Ad}TPBN_3)U(\gamma-N_3Ad)(2)$. Note: See the X-ray structure in Figure S1 for atom numbering; same for the following Tables.

	-		
Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.337(2)	2.324	-0.013
U–N2	2.290(2)	2.302	0.012
U–N3	2.294(2)	2.302	0.008
U–N4	2.271(3)	2.253	-0.018
U–C1	2.913(3)	2.865	-0.048
U–C2	2.927(3)	2.875	-0.052
U–C3	2.922(3)	2.869	-0.053
U–C4	2.937(3)	2.888	-0.049
U–C5	2.918(3)	2.878	-0.040
U–C6	2.929(3)	2.886	-0.043
U-Ccentroid	2.568(1)	2.515	-0.052
U–3N _{plane}	+0.080(1)	+0.069	-0.011
C1–C2	1.384(4)	1.387	0.003
C2–C3	1.411(5)	1.407	-0.004
C3–C4	1.399(4)	1.386	-0.013
C4–C5	1.400(4)	1.408	0.008
C5–C6	1.398(5)	1.386	-0.012
C6–C1	1.411(4)	1.407	-0.004
N4–N5	1.151(4)	1.192	-0.013
N5-N6	1.166(6)	1.137	0.012
N1-U-N2	119.9(1)	120.11	0.2
N2–U–N3	120.2(1)	120.06	-0.2
N3–U–N1	119.5(1)	119.56	0.0
U-N4-N5	170.1(2)	173.84	3.7
N4–N5–N6	177.3(4)	178.85	1.6

Table S3. Selected structural parameters of (^{Ad}TPBN₃)UN₃ (3).

Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.407(3)	2.392	-0.015
U–N2	2.397(2)	2.422	0.025
U–N3	2.418(2)	2.388	-0.030
U–N4	2.023(2)	2.027	0.004
U–C1	2.939(3)	2.906	-0.033
U–C2	2.950(3)	2.912	-0.038
U–C3	2.933(3)	2.919	-0.014
U–C4	2.944(3)	2.947	0.003
U–C5	2.946(3)	2.940	-0.006
U–C6	2.972(3)	2.942	-0.030
U-Ccentroid	2.595(1)	2.573	-0.022
U–3N _{plane}	+0.184(1)	+0.168	-0.016
C1–C2	1.388(4)	1.387	-0.001
C2–C3	1.403(4)	1.409	0.006
C3–C4	1.385(3)	1.385	0.000
C4–C5	1.414(4)	1.408	-0.006
C5–C6	1.384(4)	1.384	0.000
C6–C1	1.412(3)	1.408	-0.004
N4-N5	1.317(9)	1.291	-0.026
N5–N6	1.227(10)	1.262	0.035
N6-Cbridgehead(Ad)	1.517(11)	1.467	-0.050
N1–U–N2	119.4(1)	118.51	-0.9
N2-U-N3	120.1(1)	118.02	-2.1
N3-U-N1	118.7(1)	122.01	3.3
U-N4-N5	167.6(4)	171.70	4.1
N4N5N6	117.1(7)	117.76	0.7

Table S4. Selected structural parameters of $[(^{Ad}TPBN_3)U(\gamma-N_3Ad)]^-$ (the anion of 4).

Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.474(4)	2.453	-0.021
U–N2	2.480(5)	2.455	-0.025
U–N3	2.447(5)	2.449	0.002
U–N4	1.977(6)	1.956	-0.021
U–C1	3.073(6)	3.055	-0.018
U–C2	3.083(7)	3.086	0.003
U–C3	3.086(8)	3.080	-0.006
U–C4	3.085(8)	3.089	0.004
U–C5	3.085(6)	3.063	-0.022
U–C6	3.086(6)	3.067	-0.019
U-Ccentroid	2.749(1)	2.739	-0.010
U–3N _{plane}	+0.333(1)	+0.334	0.001
C1–C2	1.385(8)	1.385	0.000
C2–C3	1.397(7)	1.406	0.009
C3–C4	1.386(7)	1.384	-0.002
C4–C5	1.404(8)	1.406	0.002
C5–C6	1.415(7)	1.383	-0.032
C6–C1	1.387(7)	1.406	0.019
N4-Cbridgehead(Ad)	1.444(9)	1.429	-0.015
N1–U–N2	117.2(2)	116.47	-0.7
N2–U–N3	118.3(2)	118.09	-0.2
N3–U–N1	119.1(2)	119.97	0.9
U-N4-C _{bridgehead} (Ad)	178.4(4)	179.52	1.1

 Table S5. Selected structural parameters of [(^{Ad}TPBN₃)UNAd]⁻ (the anion of 6).

Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.335(8)	2.331	-0.004
U–N2	2.354(8)	2.331	-0.023
U–N3	2.317(7)	2.331	0.014
U–N4	1.937(5)	1.906	-0.031
U–C1	3.037(7)	3.014	-0.023
U–C2	3.049(7)	3.029	-0.020
U–C3	3.055(7)	3.014	-0.041
U–C4	3.056(8)	3.029	-0.027
U–C5	3.032(8)	3.014	-0.018
U–C6	3.047(7)	3.029	-0.018
U-Ccentroid	2.706(1)	2.680	-0.026
U–3N _{plane}	+0.218(1)	+0.227	0.009
C1–C2	1.389(15)	1.406	0.017
C2–C3	1.395(13)	1.383	-0.012
C3–C4	1.409(12)	1.406	-0.003
C4–C5	1.380(11)	1.383	0.003
C5–C6	1.413(11)	1.406	-0.007
C6–C1	1.405(12)	1.383	-0.022
N4-Cbridgehead(Ad)	1.480(8)	1.438	-0.042
N1–U–N2	118.0(2)	119.04	1.0
N2–U–N3	119.5(2)	119.10	-0.4
N3–U–N1	119.9(2)	119.04	-0.9
U-N4-C _{bridgehead} (Ad)	178.8(5)	179.92	1.1

 Table S6. Selected structural parameters of (^{Ad}TPBN₃)UNAd (7).

Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.332(4)	2.318	-0.014
U–N2	2.337(4)	2.317	-0.020
U–N3	2.300(5)	2.317	0.017
U–N4	1.979(4)	1.910	-0.069
U–C1	2.985(5)	3.002	0.017
U–C2	2.981(5)	2.987	0.006
U–C3	2.963(5)	3.001	0.038
U–C4	2.981(5)	2.987	0.006
U–C5	2.985(5)	3.001	0.016
U–C6	2.985(5)	2.987	0.002
U-Ccentroid	2.628(1)	2.649	0.021
U–3N _{plane}	+0.162(1)	+0.201	0.039
C1–C2	1.396(7)	1.383	-0.013
C2–C3	1.418(6)	1.407	-0.011
C3–C4	1.380(7)	1.383	0.003
C4–C5	1.415(7)	1.407	-0.008
C5–C6	1.374(6)	1.383	0.009
C6–C1	1.416(7)	1.407	-0.009
N4–Sil	1.691(4)	1.744	0.053
N1–U–N2	118.1(1)	119.23	1.1
N2-U-N3	120.1(1)	119.27	-0.8
N3-U-N1	120.3(1)	119.27	-1.0
U–N4–Sil	177.6(3)	179.97	2.4

 Table S7. Selected structural parameters of (^{Ad}TPBN₃)UNSiMe₃ (8).

Selected distances [Å] and angles [°]	Exp.	Calc.	Diff.
U–N1	2.426(3)	2.409	-0.017
U–N2	2.453(3)	2.409	-0.044
U–N3	2.413(3)	2.409	-0.004
U–N4	2.419(3)	2.384	-0.035
U–C1	2.784(3)	2.753	-0.031
U–C2	2.790(3)	2.764	-0.026
U–C3	2.798(2)	2.753	-0.045
U–C4	2.812(3)	2.764	-0.048
U–C5	2.813(3)	2.753	-0.060
U–C6	2.817(3)	2.764	-0.053
U-C _{centroid}	2.427(1)	2.376	-0.050
U–3N _{plane}	-0.005(1)	+0.012	0.007
C1–C2	1.413(4)	1.414	0.001
C2–C3	1.397(4)	1.389	-0.008
C3–C4	1.409(5)	1.414	0.005
C4–C5	1.387(4)	1.389	0.002
C5–C6	1.417(4)	1.414	-0.003
C6–C1	1.388(5)	1.389	0.001
N4-N5	1.151(5)	1.184	0.033
N5–N6	1.148(6)	1.147	-0.001
N1–U–N2	119.6(1)	120.00	0.4
N2–U–N3	121.1(1)	120.01	-1.1
N3-U-N1	119.3(1)	119.99	0.7
U-N4-N5	174.5(3)	179.83	5.3
N4N5N6	178.0(5)	179.99	2.0

 Table S8. Selected structural parameters of [(^{Ad}TPBN₃)UN₃]⁻ (the anion of 9/9-crypt).

7.3. Calculated Bond Orders

Compound	OS*	U–N _{axial}	U–N _{amido}	U-C _{ring} **	C-C _{ring} **
(^{Ad} TPBN ₃)UN ₃ Ad (2)	V	2.368	1.195	0.244	1.473
(^{Ad} TPBN ₃)UN ₃ (3)	IV	1.180	1.168	0.258	1.471
$[(^{Ad}TPBN_3)UN_3Ad]^-(4^-)$	IV	2.071	0.943	0.237	1.479
[(^{Ad} TPBN ₃)UNAd] ⁻ (6 ⁻)	IV	2.644	0.873	0.180	1.494
(^{Ad} TPBN ₃)UNAd (7)	V	2.866	1.160	0.203	1.485
(^{Ad} TPBN ₃)UNSiMe ₃ (8)	V	2.838	1.172	0.213	1.481
[(^{Ad} TPBN ₃)UN ₃] ⁻ (9 ⁻)	III	0.935	0.939	0.361	1.454

 Table S9. Wiberg bond index of the selected bonds.

*: Uranium oxidation states

**: Average bond index

7.4. Population Analysis

Cpd.	Uranium oxidation state	U	N _{axial}	avg. N _{amido}	The anchor ring (C / C+H)
2	V	+0.721	-0.581	-0.647	-0.972 / -0.368
3	IV	+0.877	-0.734	-0.658	-0.970 / -0.356
4-	IV	+0.912	-0.730	-0.697	-1.016 / -0.449
6-	IV	+1.151	-0.904	-0.728	-1.166 / -0.543
7	V	+1.015	-0.731	-0.674	-1.125 / -0.462
8	V	+1.052	-0.852	-0.667	-1.075 / -0.436
9-	III	+0.861	-0.642	-0.678	-1.067 / -0.500

 Table S10. Calculated Mulliken atomic charges.

 Table S11. Calculated Mulliken spin population on uranium.

Cpd.	Uranium oxidation state	Spin population on uranium
2	V	1.399
3	IV	2.188
4-	IV	2.214
6-	IV	2.196
7	V	1.330
8	V	1.276
9-	III	2.923

Cpd.	Uranium oxidation state	U	N _{imido}	avg. N _{amido}	The anchor ring (C / C+H)
2	V	+1.048	-0.525	-0.676	-0.647 / +0.202
3	IV	+1.151	-0.502	-0.735	-0.676 / +0.463
4-	IV	+1.122	-0.640	-0.735	-0.723 / +0.114
6-	IV	+1.418	-1.010	-0.776	-0.774 / +0.024
7	V	+1.349	-0.797	-0.717	-0.696 / +0.123
8	V	+1.350	-0.710	-1.217	-0.681 / +0.147
9-	III	+0.912	-0.234	-0.369	-0.504 / -0.084

 Table S12. Calculated natural charges.

 Table S13. Calculated natural spin densities on uranium.

Cpd.	Uranium oxidation state	Spin population
2	V	1.329
3	IV	2.081
4-	IV	2.111
6-	IV	2.108
7	V	1.267
8	V	1.213
9-	III	2.771

7.5. Composition Analysis of Kohn-Sham Orbitals

MO	Energy (eV)	U (%)	N4 (%)	N5 (%)	N6 (%)
264a	-5.74	17.1	p 10.9	22.7	17.1
		(<i>d</i> 5.7 <i>f</i> 10.3)		(s 6.9 p 15.4)	(s 3.1 p 13.1)
263α	-6.19	88.3	/	/	/
		(<i>d</i> 2.7 <i>f</i> 85.6)			
262a	-6.53	13.6	<i>p</i> 33.0	<i>p</i> 3.5	<i>p</i> 19.4
		(d 5.7 f 7.9)			

Table S14. Composition analysis of the MOs of $(^{Ad}TPBN_3)U(\gamma-N_3Ad)$ (2).



264a

262a



263α (singly occupied)

Figure S64. Kohn-Sham orbitals (isosurface = 0.05) of the MOs of $(^{Ad}TPBN_3)U(\gamma - N_3Ad)$ (2). All hydrogens were omitted for clarity.

МО	Energy (eV)	U (%)	N4 (%)	N5 (%)	N6 (%)
268α	-2.00	47.0	p 7.6	<i>p</i> 4.3	p 3.5
		(<i>d</i> 0.7 <i>f</i> 46.0)			
267a	-2.13	47.1	<i>p</i> 10.1	7.3	4.5
		(<i>d</i> 2.3 <i>f</i> 44.1)		(s 1.3 p 4.8)	(s 0.8 p 3.4)
266a	-2.34	59.4	<i>p</i> 14.8	11.4	5.8
		(<i>d</i> 4.3 <i>f</i> 54.2)		(s 3.8 p 6.5)	(s 0.9 p 4.7)
266β	-2.19	9.7	p 28.7	21.7	10.0
		(<i>d</i> 3.0 <i>f</i> 6.7)		(s 7.3 p 13.6)	(s 1.7 p 8.0)
262a	-3.30	13.3	p 37.1	p 2.5	p 28.5
		(<i>d</i> 5.2 <i>f</i> 7.4)			
262β	-3.28	8.4	p 38.8	p 2.3	<i>p</i> 30.3
		(d 4.2 f 3.7)			

Table S15. Composition analysis of the MOs of $[(^{Ad}TPBN_3)U(\gamma-N_3Ad)]^-(4^-)$.



262a

262β

Figure S65. Kohn-Sham orbitals (isosurface = 0.05) of the MOs of $[(^{Ad}TPBN_3)U(\gamma - N_3Ad)]^-$ (4⁻). All hydrogens were omitted for clarity.

MO	Energy (eV)	U (%)	N4 (%)
261a	-1.65	f70.4	/
260a	-1.77	85.4	/
		(<i>d</i> 1.5 <i>f</i> 83.6)	
256α	-2.99	18.2	p 47.0
		(<i>d</i> 10.5 <i>f</i> 7.2)	
255α	-2.99	20.4	p 47.5
		(<i>d</i> 10.2 <i>f</i> 9.5)	

Table S16. Composition analysis of the MOs of [(^{Ad}TPBN₃)UNAd]⁻ (6⁻).



256α ohn-Sham orbitals (isosu

255a

Figure S66. Kohn-Sham orbitals (isosurface = 0.05) of the MOs of [(^{Ad}TPBN₃)UNAd]⁻ (6⁻). All hydrogens were omitted for clarity.

MO	Energy (eV)	U (%)	N4 (%)
257α	-5.99	85.1	/
		(<i>d</i> 1.9 <i>f</i> 82.8)	
256a	-6.41	17.7	p 34.3
		(<i>d</i> 7.5 <i>f</i> 10.0)	
255a	-6.41	17.8	<i>p</i> 34.3
		(<i>d</i> 7.5 <i>f</i> 10.0)	

 Table S17. Composition analysis of the MOs of (^{Ad}TPBN₃)UNAd (7).



257α (singly occupied)



Figure S67. Kohn-Sham orbitals (isosurface = 0.05) of the MOs of (^{Ad}TPBN₃)UNAd (7). All hydrogens were omitted for clarity.

MO	Energy (eV)	U (%)	N4 (%)
240α	-6.11	81.4	/
		(<i>d</i> 1.8 <i>f</i> 79.3)	
239a	-6.71	11.1	p 28.8
		(d 5.5 f 5.5)	
238a	-6.71	11.2	<i>p</i> 29.0
		$(d \ 5.5 f \ 5.5)$	

Table S18. Composition analysis of the MOs of (^{Ad}TPBN₃)UNSiMe₃ (8).



240α (singly occupied)



Figure S68. Kohn-Sham orbitals (isosurface = 0.05) of the MOs of (^{Ad}TPBN₃)UNSiMe₃ (8). All hydrogens were omitted for clarity.

7.6. Natural Localized Molecular Orbital (NLMO) Analysis

NLMO	U (%)	N4 (%)	N5 (%)	N6 (%)
σ(86α)	17.5 (s 1.6 <i>d</i> 9.7 <i>f</i> 6.2)	81.6 (s 53.1 p 28.4)	/	/
$\pi_1(261\alpha)$	34.3 (<i>d</i> 7.7 <i>f</i> 26.6)	p 63.7	/	/
$\pi_2(262\alpha)$	20.3 (<i>d</i> 6.2 <i>f</i> 14.1)	p 68.5	p 5.4	p 4.8

Table S19. NLMO contributions for U–N interactions in (^A	AdTPBN3)U(y-N ₃ Ad)	(2)).
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σ(86α)



 $\pi_1(261\alpha) \qquad \qquad \pi_2(262\alpha)$ Figure S69. NLMOs (isosurface = 0.05) for U–N interactions in (^{Ad}TPBN₃)U(γ -N₃Ad) (2).

NLMO	U (%)	N4 (%)	N5 (%)	N6 (%)
σ(87α)	15.7 (s 1.6 <i>d</i> 8.9 <i>f</i> 5.1)	83.4 (s 54.2 p 29.1)	/	/
$\pi_1(262\alpha)$	25.3 (<i>d</i> 8.9 <i>f</i> 16.4)	<i>p</i> 71.8	/	/
$\pi_2(263\alpha)$	12.3 (<i>d</i> 5.8 <i>f</i> 6.5)	<i>p</i> 70.0	p 9.3	p 6.8

Table S20. NLMO contributions for U–N interactions in $[(^{Ad}TPBN_3)U(\gamma-N_3Ad)]^-(4^-)$.







Figure S70. NLMOs (isosurface = 0.05) for U–N interactions in $[(^{Ad}TPBN_3)U(\gamma - N_3Ad)]^- (4^-)$.

NLMO	U (%)	N4 (%)
σ(93α)	15.4 (s 1.0 <i>d</i> 10.1 <i>f</i> 5.6)	83.9 (s 48.0 p 35.7)
$\pi_1(94\alpha)$	21.9 (<i>d</i> 9.6 <i>f</i> 12.3)	p 75.4
$\pi_2(95\alpha)$	22.0 (<i>d</i> 9.6 <i>f</i> 12.3)	p 75.3

Table S21. NLMO contributions for U–N interactions in [(^{Ad}TPBN₃)UNAd]⁻ (6⁻).



σ(93α)



Figure S71. NLMOs (isosurface = 0.05) for U–N interactions in [(^{Ad}TPBN₃)UNAd]⁻ (6⁻).

NLMO	U (%)	N4 (%)
σ(89α)	16.6 (s 1.0 <i>d</i> 9.4 <i>f</i> 6.1)	82.7 (s 47.5 p 35.1)
$\pi_1(90\alpha)$	29.7 (<i>d</i> 8.3 <i>f</i> 21.4)	p 68.4
$\pi_2(91\alpha)$	29.7 (<i>d</i> 8.3 <i>f</i> 21.4)	p 68.4

 Table S22. NLMO contributions for U–N interactions in (^{Ad}TPBN₃)UNAd (7).



σ(89α)



Figure S72. NLMOs (isosurface = 0.05) for U–N interactions in (^{Ad}TPBN₃)UNAd (7).

NLMO	U (%)	N4 (%)
σ(91α)	17.9 (s 0.7 <i>d</i> 8.9 <i>f</i> 8.1)	81.1 (s 45.5 p 35.5)
$\pi_1(92\alpha)$	25.7 (<i>d</i> 7.8 <i>f</i> 17.9)	<i>p</i> 72.1
$\pi_2(93\alpha)$	25.7 (<i>d</i> 7.8 <i>f</i> 17.9)	<i>p</i> 72.1

Table S23. NLMO contributions for U–N interactions in (^{Ad}TPBN₃)UNSiMe₃ (8).



σ(91α)



 $\pi_1(92\alpha)$



Figure S73. NLMOs (isosurface = 0.05) for U–N interactions in (^{Ad}TPBN₃)UNSiMe₃ (8).

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