Supporting Information

A Linear *trans*Bis(imido) Neptunium(V) Actinyl Analog: Np^V(NDipp)₂(^tBu₂bipy)₂Cl (Dipp = 2,6-ⁱPr₂C₆H₃)

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Experimental Details: Caution! All neptunium chemistry (using the ²³⁷Np isotope) was conducted inside specialist radiological facilities designed for the safe handling and manipulation of high specific-activity α -particle emitting radionuclides. Multiple levels of containment were utilized when appropriate for safety reasons.

General: All reactions were performed under anaerobic and anhydrous conditions inside a high purity helium atmosphere drybox. All solvents were purchased in anhydrous grade and dried over a mixture of 3 Å and 4 Å sieves for several days before use. 4,4'-ditertbutyl-2,2'-bipyridine (^tBu₂bipy) and lithium 2,6-diisopropyl-phenylamide (LiNH(Dipp))¹ were purchased from commercial suppliers or synthesized according to previously published procedures, as can be found from reference 17 cited in the actual communication text of this contribution.

¹H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to external SiMe₄ using the residual protio solvent peaks as internal standards. Solution-phase electronic absorption spectra of **1** were collected in quartz cuvettes at room temperature using a Varian Cary 6000i UV-vis-NIR spectrophotometer with a 0.3 nm spectral bandwidth. Approximately 0.5 mg of compound **1** was dissolved in approximately 1 mL of solvent. The solid-phase diffuse reflectance electronic absorption spectrum was collected using a Varian Cary 6000i UV-vis-NIR spectrophotometer with an installed Internal Diffuse Reflectance Accessory. The sample consisted of groundup crystalline **1** (thus offering random orientations to the beam – orientation dependent spectra were not obtained) placed inside a cut-down glass 4 mL vial with PTFE plug insert sealed to the glass with wax. Raman spectra were collected using a ThermoFisher DXR SmartRaman spectrometer with a 12817.33 cm⁻¹ Raman laser frequency.

Synthesis of Np(NDipp)₂(^tBu₂bipy)₂Cl (1):

Method A: used to obtain initial crystal structure determination: ¹Bu₂bipy (0.010 g, 0.038 mmol) was dissolved in THF (1.5 mL) and added to solid NpCl₄(DME)₂ (0.021 g, 0.038 mmol) with stirring at ambient temperature for 10 min resulting in a vibrant pink solution. LiNH(Dipp) (0.014 g, 0.075 mmol) was dissolved in THF (1.5 mL) and added dropwise to the Np-containing solution where the reaction mixture became a very deep red colored solution over the course of several seconds. Stirring was continued overnight at ambient temperature. Volatiles were removed in vacuo to give a dark colored residue. Hexanes (2 mL) was added to the residue, with stirring, resulting in moderate solubility of the residue. The solution was passed through a glass fiber filter circle and the deep red filtrate stored in the drybox freezer at -35 °C resulting in deposition of X-ray quality crystals of **1** over the course of a few days. Given the small scale, and small amount of product that was isolated, no % yield was determined for this particular synthetic method. ¹H NMR (THF-*d*₈, 25 °C, 400 MHz, ppm): δ -19.49 (br s, 4 H, aryl CH), -19.02 (br s, 4 H, aryl CH), -12.76 (br s, 4 H, aryl CH), -9.67 (br s, 4 H, aryl CH), -6.28 (s, 18 H, -C(CH₃)₃), -5.90 (s, 18 H, -C(CH₃)₃), 12.06 (br s, 24 H, -CH(CH₃)₂), 18.07 (s, 2 H, aryl CH), 68.42 (br s, 4H, aryl CH or -CH(CH₃)₂).

Method B: employing a higher stoichiometry of reagents to Np (Two equiv of ¹Bu₂bipy and four equiv of amide) –a unit cell determination was utilized to verify that the structure of the crystals obtained from this method were identical to those obtained from method A: ¹Bu₂bipy (0.0087 g, 0.032 mmol) was dissolved in THF (2 mL) and added to solid NpCl₄(DME)₂ (0.0090 g, 0.016 mmol) with stirring at ambient temperature for ~10 min resulting in a

vibrant pink solution. LiNH(Dipp) (0.012 g, 0.065 mmol) was dissolved in THF (1.5 mL) and added dropwise to the Np-containing solution and the resulting deep red solution stirred at ambient temperature for ~24 h. Volatiles were removed in vacuo to result in a dark colored residue. Hexanes (4 mL) was added to the residue and with stirring, the solution was gently heated (30-35 °C) for ~5 min to promote maximum extraction of **1**. The solution was then passed through a glass fiber filter circle and the deep red filtrate stored in the drybox freezer at -35 °C. Deposition of X-ray quality crystals occurred over several days on which a unit cell determination was performed. The crystals were crystallographically identical to those isolated in method A, and again no % yield was determined. ¹H NMR (THF-*d*₈, 25 °C, 400 MHz, ppm): δ -19.66 (br s, 4 H, aryl CH), -19.16 (br s, 4 H, aryl CH), -12.91 (br s, 4 H, aryl CH), -9.77 (br s, 4 H, aryl CH), -6.32 (s, 18 H, -C(CH_3)_3), -5.95 (s, 18 H, -C(CH_3)_3), 12.19 (br s, 24 H, -CH(CH_3)_2), 18.15 (s, 2 H, aryl CH), 68.80 (br s, 4H, aryl CH or -C*H*(CH₃)₂). UV-vis-NIR (solution-phase, THF, 25 °C, nm): 1191, 1096 (sh), 1059, 1023 (sh), 931, 846. Diffuse reflectance UV-vis-NIR (solid-state, neat, 25 °C, nm): 1198, 1133 (sh), 1099, 1045, 1003, 924. Raman (solid-state, neat, 25 °C, cm⁻¹): 702, 899, 1002, 1013, 1045, 1317, 1551, 1581, 1605.

Method C: used to obtain reported yield of 1 (^hH NMR spectroscopy was utilized to confirm that the crystals obtained from this method were identical to those obtained from method A and method B): ^bBu₂bipy (0.014 g, 0.052 mmol) was dissolved in THF (1.5 mL) and added to solid NpCl₄(DME)₂ (0.015 g, 0.027 mmol) with stirring at ambient temperature for ~10 min resulting in a vibrant pink solution. LiNH(Dipp) (0.020 g, 0.11 mmol) was dissolved in THF (1.5 mL) and added dropwise to the Np-containing solution. Excess CH₂Cl₂ (3 drops, ~200 µL) was added to the reaction mixture (note, in the corresponding uranium chemistry, halide abstraction is implicated in the formation mechanism of the U(V) bis(imido) species, meaning that deliberate addition of CH_2Cl_2 might be anticipated to drive the Np reaction and increase the yield of 1). The reaction mixture was stirred at ambient temperature for ~ 4 h. Volatiles were removed in vacuo, and the residue extracted into hexanes (3.5 mL) with stirring and gentle heating (30-35 °C). The hexanes solution was filtered through a glass fiber filter circle and the volume reduced in vacuo to 2 mL. Excess CH₂Cl₂ was then added (3 drops, ~200 µL) to the deep red solution; no color change was observed. Storage of this solution in the drybox freezer at -35 °C resulted in the deposition of crystalline 1 over a few days. The crystalline material was isolated, washed with cold hexanes and dried in vacuo (0.0070 g, 17 % yield). ¹H NMR (THF-d₈, 25 °C, 400 MHz, ppm): δ -19.25 (br s, 4 H, aryl CH), -18.77 (br s, 4 H, aryl CH), -12.59 (br s, 4 H, aryl CH), -9.50 (br s, 4 H, aryl CH), -6.21 (s, 18 H, -C(CH₃)₃), -5.82 (s, 18 H, -C(CH₃)₃), 12.06 (br s, 24 H, -CH(CH₃)₂), 17.95 (s, 2 H, aryl CH), 67.96 (br s, 4H, aryl CH or -CH(CH₃)₂). ¹H NMR (C₆D₆, 25 °C, 400 MHz, ppm): δ -19.55 (br s, 4 H, aryl CH), -18.69 (br s, 4 H, aryl CH), -13.22 (br s, 4 H, aryl CH), -9.20 (br s, 4 H, aryl CH), -6.57 (s, 18 H, -C(CH₃)₃), -5.83 (s, 18 H, -C(CH₃)₃), 12.60 (br s, 24 H, -CH(CH₃)₂), 18.23 (s, 2 H, aryl CH), 68.28 (br s, 4H, aryl CH or $-CH(CH_3)_2$). UV-vis-NIR (solution-phase, toluene, 25 °C, nm): 1200, 1112 (sh), 1098 (sh), 1063, 1018 (sh), 929, 856.

X-ray Diffraction Collection Details: Np-containing single-crystals of $1 \cdot 2(H_2N(Dipp)) \cdot O(C_4H_8)$ were coated in paratone-N oil and mounted inside a 0.5 mm capillary tube, which was sealed with hot capillary wax. The capillary was coated with a thin film of acrylic in ethyl acetate (Hard as Nails[®]) to provide structural integrity and additional containment. The capillary was placed on a Bruker Platform diffractometer with 1k CCD, and cooled to 140 K using a Bruker Kryoflex cryostat. The instrument was equipped with a sealed, graphite monochromatized MoK α X-ray source (λ = 0.71073 Å). Data collection and initial indexing and cell refinement were handled using SMART software (version 5.632, **2005**, Bruker AXS, Inc., Madison, Wisconsin 53719). Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software (version 6.45, **2003**, Bruker AXS, Inc., Madison, Wisconsin 53719). The data were corrected for absorption using the SADABS program (version 2.05, **2002**, George Sheldrick, University of Göttingen, Germany). Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Hydrogen atoms were idealized. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, and materials for publication were performed using SHELXTL software (version 6.10, **2001**, Bruker AXS, Inc., Madison, Wisconsin 53719).

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empirical formula	$C_{88}H_{128}Cl_1N_8Np_1O_1$
crystal habit, color	block, red
crystal size (mm)	$0.3\times0.1\times0.1$
crystal system	orthorhombic
space group	P ben
vol (Å ³)	8672.7(8)
a (Å)	16.8964(9)
b (Å)	21.2575(12)
c (Å)	24.1461(13)
α (deg.)	90
β (deg.)	90
γ (deg.)	90
Z	4
fw (g/mol)	1586.43
density (calcd) (Mg/m ³)	1.215
abs coeff (mm ⁻¹)	1.276
F ₀₀₀	3320
total no. reflections	96337
unique reflections	10442
R _{int}	0.0510
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0441, wR_2 = 0.0946$
largest diff peak and hole $(e^{-}A^{-3})$	1.941 and -3.850
GOF	1.138

 $Np^{V}(NDipp)_{2}(^{t}Bu_{2}bipy)Cl \cdot 2(H_{2}N(Dipp)) \cdot O(C_{4}H_{8})$

Table S1. X-ray crystallographic data for complex $1 \cdot 2(H_2N(Dipp)) \cdot O(C_4H_8)$. The identification code for $1 \cdot 2(H_2N(Dipp)) \cdot O(C_4H_8)$ is apx1823s.

¹H NMR Spectroscopic Studies:



Figure S1. ¹H NMR spectrum (full) in THF- d_8 of complex 1 isolated from method A. The resonances observed at -20.83, -11.98, -10.32, -8.36, 20.04 and 69.71 ppm are unidentified minor products.



Figure S2. ¹H NMR spectrum (partial) in THF- d_8 of complex **1** isolated from method A. The resonances at 1.20, 2.96, 4.14, 6.57 and 6.88 ppm are assignable to H₂N(Dipp). The resonances at 1.37, 7.31, 8.50 and 8.56 ppm are assignable to ^tBu₂bipy. The resonances at 0.88 and 1.29 ppm and, 2.30 and 7.05 – 7.21 ppm, are assignable to hexanes and toluene, respectively. Two unidentified peaks are observed at 0.96 and 2.24 ppm.



Figure S3. ¹H NMR spectrum (full) in THF- d_8 of complex 1 isolated from method B. The resonances observed at -20.50, -8.25 and 20.02 ppm are unidentified minor products.



Figure S4. ¹H NMR spectrum (partial) in THF- d_8 of complex **1** isolated from method B. The resonances at 1.20, 2.96, 4.14, 6.57 and 6.88 ppm are assignable to H₂N(Dipp). The resonances at 1.37, 7.31, 8.50 and 8.56 ppm are assignable to ^tBu₂bipy. The resonances at 0.88 and 1.29 ppm and, 2.30 and 7.05 – 7.20 ppm, are assignable to hexanes and toluene, respectively. Three unidentified peaks are observed at 1.15, 1.49 and 2.24 ppm.



Figure S5. ¹H NMR spectrum (full) in THF- d_8 of complex 1 isolated from method C. The resonances observed at -20.13, -11.86, -10.22, -8.12, and 19.82 ppm are unidentified minor products.



Figure S6. ¹H NMR spectrum (partial) in THF- d_8 of complex **1** isolated from method C. The resonances at 1.21, 2.96, 4.12, 6.57 and 6.88 ppm are assignable to H₂N(Dipp). The resonances at 1.37, 7.32, 8.50 and 8.56 ppm are assignable to ^tBu₂bipy. The resonances at 0.86 and 1.28 ppm and, 2.30 and 7.04 – 7.20 ppm, are assignable to hexanes and toluene, respectively. The resonances at 1.11 and 3.37 ppm, and 5.50 ppm are assignable to diethyl ether and dichloromethane, respectively. The resonance at 0.96 ppm is an unidentified product.



Figure S7. ¹H NMR spectrum (full) in C_6D_6 of complex **1** isolated from method C. Note, the resonances attributed to the paramagnetic impurities observed in the ¹H NMR spectra recorded in THF- d_8 are *not* observed.



Figure S8. ¹H NMR spectrum (partial) in C_6D_6 of complex **1** isolated from method C. The resonances at 1.14, 2.64, 3.19, 6.89 and 7.04 ppm are assignable to $H_2N(Dipp)$. The resonances at 0.87 and 1.24 ppm, and 2.11 ppm, are assignable to hexanes and toluene, respectively, while dichloromethane is observed at 4.30 ppm.



Figure S9. ¹H NMR spectrum in C_6D_6 of the hexanes *supernatant* following isolation of complex 1 from method C. The resonances observed in this spectrum are attributed primarily to $H_2N(Dipp)$ and ^tBu₂bipy. The resonance at -2.31 ppm is an unidentified product. Note, complex 1 is *not* observed in this spectrum.



Figure S10. ¹H NMR spectrum in THF- d_8 of the hexanes *insoluble fraction* following extraction of complex 1 from method C. The resonances observed in this spectrum are attributed primarily to H₂N(Dipp) and ^tBu₂bipy. Note, complex 1 is *not* observed in this spectrum.



Figure S11. ¹H NMR spectrum (full) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *one* equiv of ¹Bu₂bipy and *two* equiv of LiNH(Dipp) in THF. The resonances at -19.32, -18.47, -13.07, -9.09, -6.51, -5.77, 12.48, 18.12 and 67.79 ppm are assignable to complex **1**.

Experimental details: To stirring NpCl₄(DME)₂ (0.0045 g, 0.0080 mmol) a THF solution of ^tBu₂bipy (0.0022 g, 0.0082 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0029 g, 0.016 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. The solution was allowed to stir at RT for ~2.5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S12. ¹H NMR spectrum (partial) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *one* equiv of ^tBu₂bipy and *two* equiv of LiNH(Dipp) in THF. The resonances at 1.14, 2.67, 3.19, 6.89 and 7.04 ppm are assignable to H₂N(Dipp). The resonances at 8.62 and 9.03 ppm are assignable to ^tBu₂bipy. Both H₂N(Dipp) and ^tBu₂bipy have overlapping resonances at 1.14 ppm. The resonances at 0.87 and 1.20 ppm, and 2.11 ppm are assignable to hexanes and toluene, respectively, while dichloromethane is observed at 4.29 ppm.

Experimental details: To stirring NpCl₄(DME)₂ (0.0045 g, 0.0080 mmol) a THF solution of ¹Bu₂bipy (0.0022 g, 0.0082 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0029 g, 0.016 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. The solution was allowed to stir at RT for ~2.5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S13. ¹H NMR spectrum (full) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *two* equiv of ^tBu₂bipy and *four* equiv of LiNH(Dipp) in THF. In conjunction with peaks assignable to complex **1**, there are numerous other unidentified products observed.

Experimental details: To stirring NpCl₄(DME)₂ (0.0046 g, 0.0082 mmol) a THF solution of ^tBu₂bipy (0.0044 g, 0.016 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0061 g, 0.033 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. The solution was allowed to stir at RT for ~5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S14. ¹H NMR spectrum (partial) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *two* equiv of ^tBu₂bipy and *four* equiv of LiNH(Dipp) in THF. The resonances at 1.13, 2.65, 3.20, 6.88 and 7.03 ppm are assignable to H₂N(Dipp). The resonances at 0.87 and 2.11 ppm are assignable to hexanes and toluene, respectively, while dichloromethane is observed at 4.32 ppm.

Experimental details: To stirring NpCl₄(DME)₂ (0.0046 g, 0.0082 mmol) a THF solution of ^tBu₂bipy (0.0044 g, 0.016 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0061 g, 0.033 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. The solution was allowed to stir at RT for ~5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S15. ¹H NMR spectrum (full) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *two* equiv of ^tBu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (three drops) in THF. The resonances at -19.37, -18.48, -13.06, -9.04, -6.51, -5.76, 12.51, 18.12 and 67.79 ppm are assignable to complex **1**. There are several other unidentified products also observed.

Experimental details: To stirring NpCl₄(DME)₂ (0.0048 g, 0.0086 mmol) a THF solution of ^tBu₂bipy (0.0044 g, 0.016 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0063 g, 0.034 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. Excess CH₂Cl₂ (three drops, ~200 μ L) was added; no color change was observed. The solution was allowed to stir at RT for ~4.5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S16. ¹H NMR spectrum (partial) in C_6D_6 of the *crude* hexane soluble fraction formed by reaction of NpCl₄(DME)₂ with *two* equiv of ^tBu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (three drops) in THF. The resonances at 1.15, 2.65, 3.19, 6.89 and 7.04 ppm are assignable to H₂N(Dipp). The resonances at 6.93, 8.61 and 9.02 ppm are assignable to ^tBu₂bipy. Both H₂N(Dipp) and ^tBu₂bipy have overlapping resonances at 1.15 ppm. The resonances at 0.87 and 2.12 ppm are assignable to hexanes and toluene, respectively, while dichloromethane is observed at 4.30 ppm.

Experimental details: To stirring NpCl₄(DME)₂ (0.0048 g, 0.0086 mmol) a THF solution of ^tBu₂bipy (0.0044 g, 0.016 mmol) was added dropwise, resulting in a vibrant pink solution. After ~5 min a THF solution of LiNH(Dipp) (0.0063 g, 0.034 mmol) was added dropwise. A color change to deep red was observed immediately during the addition. Excess CH₂Cl₂ (three drops, ~200 μ L) was added; no color change was observed. The solution was allowed to stir at RT for ~4.5 h. All volatiles were removed in vacuo, the resulting residue was extracted into hexanes (1.5 mL) and the solution passed through a glass fiber filter circle. All volatiles from the hexanes filtrate were removed in vacuo, the residue dissolved fully into C₆D₆ (0.5 mL) and the ¹H NMR spectrum was recorded.



Figure S17. ¹H NMR spectrum (full) in THF- d_8 of the *in situ* reaction between NpCl₄(DME)₂ and *two* equiv of ¹Bu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (five drops). The resonances at -19.41, -18.98, -12.86, -9.77, -6.28, -5.94, 12.02, 18.10 and 68.17 ppm are assignable to complex **1**. There are a few unidentified minor products also observed.

Experimental details: To a stirring THF- d_8 solution of NpCl₄(DME)₂ (0.0044 g, 0.0079 mmol), was added ¹Bu₂bipy (0.0042 g, 0.016 mmol) as a solid, resulting in a vibrant pink solution. After ~5 min, LiNH(Dipp) (0.0060 g, 0.033 mmol) was added to the solution as a solid. A color change to deep red was observed immediately during the addition. Excess CH₂Cl₂ (five drops, ~325 µL) was added; no color change was observed. The solution was allowed to stir at RT for ~5 h. The solution was then transferred to a Teflon liner, inserted into an NMR 7mm tube and the ¹H NMR spectrum was recorded.



Figure S18. ¹H NMR spectrum (partial) in THF- d_8 of the *in situ* reaction between NpCl₄(DME)₂ and *two* equiv of ^tBu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (five drops). The resonances at 1.18, 2.94, 4.09, 6.55 and 6.87 ppm are assignable to H₂N(Dipp). The resonances at 1.35, 7.30 and 8.50 ppm are assignable to ^tBu₂bipy. Dichloromethane is observed at 5.48 ppm, while several other unidentified products are observed at 1.10, 3.26 and 3.42 ppm.

Experimental details: To a stirring THF- d_8 solution of NpCl₄(DME)₂ (0.0044 g, 0.0079 mmol), was added ¹Bu₂bipy (0.0042 g, 0.016 mmol) as a solid, resulting in a vibrant pink solution. After 5 min, LiNH(Dipp) (0.0060 g, 0.033 mmol) was added to the solution as a solid. A color change to deep red was observed immediately during the addition. CH₂Cl₂ (5 drops, ~325 µL) was added; no color change was observed. The solution was allowed to stir at RT for ~5 h. The solution was then transferred to a Teflon liner, inserted into an NMR 7mm tube and the ¹H NMR spectrum was recorded.



Figure S19. ¹H NMR spectrum (full) in C_6D_6 of the *in situ* reaction between NpCl₄(DME)₂ and *two* equiv of ¹Bu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (five drops). The resonances at -19.64, -19.07, -13.34, -9.75, -6.57, -6.08, 12.39, 18.39 and 68.64 ppm are assignable to complex **1**.

Experimental details: To a stirring C_6D_6 solution of NpCl₄(DME)₂ (0.0042 g, 0.0075 mmol), was added ¹Bu₂bipy (0.0041 g, 0.015 mmol) as a solid, resulting in a vibrant pink solution. After ~5 min, LiNH(Dipp) (0.0055 mg, 0.030 mmol) was added to the solution as a solid. A color change to deep red was observed immediately during the addition. Excess CH₂Cl₂ (five drops, ~325 µL) was added; no color change was observed. The solution was allowed to stir at RT for ~5 h. The solution was then transferred to a Teflon liner, inserted into an NMR 7mm tube and the ¹H NMR spectrum was recorded.



Figure S20. ¹H NMR spectrum (partial) in C_6D_6 of the *in situ* reaction between NpCl₄(DME)₂ and *two* equiv of ^tBu₂bipy, *four* equiv of LiNH(Dipp) and excess CH₂Cl₂ (five drops). The resonances at 1.12, 2.64, 3.22, 6.81 and 7.00 ppm are assignable to H₂N(Dipp). The resonances at 8.57 and 8.88 ppm are assignable to ^tBu₂bipy. Both H₂N(Dipp) and ^tBu₂bipy have overlapping resonances at 1.12 ppm.

Experimental details: To a stirring C_6D_6 solution of NpCl₄(DME)₂ (0.0042 g, 0.0075 mmol), was added ^tBu₂bipy (0.0041 g, 0.015 mmol) as a solid, resulting in a vibrant pink solution. After ~5 min, LiNH(Dipp) (0.0055 g, 0.030 mmol) was added to the solution as a solid. A color change to deep red was observed immediately during the addition. Excess CH₂Cl₂ (five drops, ~325 µL) was added; no color change was observed. The solution was allowed to stir at RT for ~5 h. The solution was then transferred to a Teflon liner, inserted into an NMR 7mm tube and the ¹H NMR spectrum was recorded.

Discussion of ¹H NMR Spectroscopic Studies:

As shown in Figures S1 and S3, dissolution of single crystals of **1** in THF- d_8 results in complicated ¹H NMR spectra. However, complex **1** is readily identified by the diagnostic proton resonances of the bipyridyl's ¹Bu substituents observed at -5.90 and -6.28 ppm, while the ¹Pr protons of the imido ligands are observed at 12.06 ppm (Figure S1). There are also several broad peaks upfield at -9.67, -12.76, -19.02 and -19.49 ppm and two resonances downfield at 18.07 and 68.42 ppm. All of these resonances are consistently observed from batch to batch in both relative shift and integration regardless of what method is used to synthesize complex **1** (Figures S1, S3 and S5); therefore, we are confident in attributing these resonances to **1**. However, it is evident that several other paramagnetically shifted and broadened resonances are present in the ¹H NMR spectra. These resonances are likely assignable to one or more, as of yet, unidentified Np-containing products. It should be noted that in the diamagnetic region (Figures S2, S4 and S6) free ^tBu₂bipy is also observed, in conjunction with the expected two equiv of H₂N(Dipp) (as indicated by the solid-state molecular structure of **1**, *vide supra*). The presence of ^tBu₂bipy and H₂N(Dipp) may not be unexpected based on the ¹H NMR spectrum (in THF- d_8) of the U(V) bis(imido) analogue, U(NDipp)₂(¹Bu₂bipy)₂Cl.² This spectrum is also fairly complicated exhibiting several unidentified paramagnetically shifted and broadened resonances in conjunction with the observation of both free ^tBu₂bipy and H₂N(Dipp). It is clear that the use of THF- d_8 as a solvent medium causes partial dissociation of pure **1** upon dissolution.

Because of the complicated ¹H NMR spectra of complex **1** (when recorded in THF- d_8), we investigated its solution-phase behavior in non-coordinating solvents. Specifically, we probed a single batch of crystals of **1** by ¹H NMR spectroscopy in both THF- d_8 and C₆D₆ (Figures S5 and S7, respectively). As expected, the ¹H NMR spectrum recorded in THF- d_8 resembles Figures S1-S4 regarding the shifts of **1** and the common impurities. Interestingly, the ¹H NMR spectrum of **1** is remarkably cleaner when recorded in C₆D₆, where many of the paramagnetic impurities are not observed (Figure S7). To explain this difference in solution-phase behavior, we propose the bipyridyl co-ligands may be undergoing exchange with the strongly-coordinating THF solvent molecules. This is likely the case in the analogous U(V) bis(imido) complex as well, although further studies are needed. The important point here is that using C₆D₆ as the NMR solvent verifies that the NMR profile of **1** is consistent with the solid-state structure obtained from single-crystal X-ray diffraction, including correct integration for the two molecules of free aniline, H₂N(Dipp) that are present in the lattice.

Upon harvesting crystals of 1 we probed the remaining hexanes supernatant by ¹H NMR spectroscopy in C₆D₆ in an attempt to better understand whether solubility was a contributing factor to the low yields of 1 (Figure S9). Surprisingly, the ¹H NMR spectrum is dominated by free ¹Bu₂bipy and H₂N(Dipp) and complex 1 is not observed (Figure S9). It should also be noted that the bulk reaction mixture contains a hexanes insoluble fraction. According to ¹H NMR spectroscopy (in THF-*d*₈; Figure S10) this fraction also consists primarily of free ¹Bu₂bipy and H₂N(Dipp). Several factors could explain these observations, the most obvious being that over the course of time of the initial reaction in THF and/or the time needed to grow single crystals, significant amounts of product have undergone ligand re-arrangement and/or solution-phase decomposition. It also cannot be discounted that protons are carried through from the Np(IV)/HCl stock solution that is utilized to synthesize the NpCl₄(DME)₂ starting material, despite washing and drying *in vacuo*. However, the variability in the amount of free H₂N(Dipp) that is observed in the reaction mixture as a function of other variables (reagent stoichiometry, presence of CH₂Cl₂) (see below) would not support residual proton presence as the major mechanism to account for the low conversion of starting material to **1**.

To further investigate the reaction we performed the synthesis of **1** using the previously described methods A-C (*vide supra*) and promptly obtained the ¹H NMR spectrum (in C_6D_6) of the *crude* hexanes soluble fraction. Surprisingly, using deficient stoichiometric amounts of ^tBu₂bipy and LiNH(Dipp) (method A; Figures S11 and S12), complex **1** is readily observed after only 2.5 h, where none of the common paramagnetic impurities are present. In contrast, when the proper stoichiometric amounts of ^tBu₂bipy and LiNH(Dipp) are employed (method B; Figures S13 and S14), a very complicated reaction mixture is observed. In conjunction with the formation of **1**, there are

significant amounts of unidentified products, likely assignable to one or more putative Np-containing species. Interestingly, using the proper stoichiometric amounts of ${}^{t}Bu_{2}bipy$ and LiNH(Dipp) and adding CH₂Cl₂ to the reaction mixture (method C; Figures S15 and S16), the spectrum becomes substantially cleaner than when CH₂Cl₂ is not employed (i.e. method B). While there are still several minor impurities present, the addition of CH₂Cl₂ seems to promote the formation of 1 as the dominant Np-containing product, similar to what was observed in the analogous uranium chemistry.² However, it should be noted that in all three methods the ¹H NMR spectra exhibit significant amounts of free ${}^{t}Bu_{2}bipy$ and $H_{2}N(Dipp)$. In addition to the postulation above regarding the possibility of proton 'carry-through' in the starting material, another possible explanation is that the use of THF as a solvent medium in the synthesis of 1 may be contributing to aniline formation and/or out-competing the ${}^{t}Bu_{2}bipy$ co-ligands. To probe these possibilities, we followed the *in situ* formation of 1 in both THF- d_8 and C₆D₆ by ¹H NMR spectroscopy, using two equiv of ^tBu₂bipy, four equiv of LiNH(Dipp) and excess CH₂Cl₂ (five drops). The ¹H NMR spectra recorded in THF- d_8 and C₆D₆ from these studies are shown in Figures S17 and S19, respectively. As expected, the ¹H NMR spectrum recorded in C₆D₆ is noticeably cleaner with respect to the absence of paramagnetic impurities but more importantly, only three equiv of aniline are observed. In contrast, nearly ten equiv of aniline are observed in the ¹H NMR spectrum recorded in THF- d_8 . These observations demonstrate that HCl is not a common contaminant (and thus not a source of protons for aniline formation) and that THF may be playing an, as of yet, unknown role in the formation of larger than desired quantities of ^tBu₂bipy and aniline.

Regardless of the complicated ¹H NMR spectroscopic studies described above, the synthesis and isolation of **1** is reproducible under a variety of reaction conditions as determined by X-ray crystallography and by both ¹H NMR and UV-vis-NIR spectroscopies. Furthermore, complex **1** can be isolated in pure form, as crystals, in amounts suitable for full characterization including determination of its solid-state molecular structure and extensive studies involving ¹H NMR and Raman spectroscopies and both solid-state and solution-phase UV-vis-NIR spectroscopy. In order to expand this chemistry to other systems and isolate further examples of novel transuranic terminal imido species, we are actively trying to understand the effects of solvent and advantageous oxidant, the impact of the bipyridine co-ligands, and lastly, the effect and influences of the amide employed. For transuranic elements, such as neptunium, the need for higher yields is driven by the fact that most research institutions performing synthetic chemistry with high specific-activity radioisotopes are usually restricted to reaction scales of tens of milligrams due to both radiological/contamination considerations and availability of isotopes. We hope to identify the appropriate conditions that promote higher yields of Np(V) bis-imido species (and therefore allow subsequent reactivity studies), which will be presented as a full paper in the future.

UV-vis-NIR Spectroscopic Studies:



Figure S21. Overlay of solution-phase UV-vis-NIR spectra of 1 in toluene (blue line) and in THF (red line).



Figure S22. Diffuse reflectance UV-vis-NIR spectrum of **1** (neat, solid-state, in a glass diffuse reflectance cell with Teflon plug).



Figure S23. Solution-phase UV-vis-NIR spectrum of U(NDipp)₂(^tBu₂bipy)₂Cl in THF.

Raman Spectroscopic Studies:



Figure S24. Raman spectrum of the Np(V) complex 1 (blue) compared with the U(V) analog (red), highlighting the region of interest for comparison with the computed Raman lines. The Raman spectrometer parameter readings indicated a resolution of '2-4 cm⁻¹', meaning that the U(V) and Np(V) frequencies are only marginally different from a statistical perspective when accounting for spectral resolution.



Figure S25. Overlay of full Raman spectra of complex 1 (neat, solid-state, in a glass diffuse reflectance cell with Teflon plug; red spectrum), the U(V) analog (green spectrum) and the blank Teflon plug (blue spectrum).

Computational Details and Data:

All calculations were performed with unrestricted density functional theory (UDFT) with the hybrid functional B3LYP3,^{3,4} as implemented in Gaussian 09.⁵ U and Np were modelled with the small core Stuttgart relativistic effective core potential with its associated basis set (with the most diffuse functions removed).⁶⁻⁸ All other atoms were modelled using a Pople style double- ζ 6-31G(d',p') basis set with polarization functions optimized for heavy atoms.^{9,10} NBO version 6.0 was utilized.¹¹



Figure S26. Analog compound used for theoretical modeling.

Excited States of Uranium(V) complex:

Excited states for the U(V) bis(imido) bis(bipy) complex: The three lowest excited states of the uranium(V) complex consists of f-f transitions for the single occupied f orbital into the f_{ϕ} [y (3x²-y²)] orbital, f_{δ} [z(x2-y2)] and f_{ϕ} [x(x2-3y2)] orbitals (see Figure S27). The TDDFT computed energy of these three excitations are 25,752, 14,383, and 4,849 nm, respectively. The 4th excited state was computed at 958 nm and it corresponds to a transition into the f_{σ} -N(p) antibonding orbital. Similarly, the 5th, 6th, and 7th excitations, computed at 950, 834, and 820 nm, respectively, correspond to excitation of the U(5f) electron into the U(f_{π})-N(p) antibonding orbitals with significant mixing of the bipy π orbital.



Figure S27. Excited states for the U(V) bis(imido) bis(bipy) complex. The lowest three excitations (f-f) were found below 4849 nm, and the excitations into the U(5f)-N(p) antibonding orbitals were computed to be above 950 nm of energy.



Figure S28. Natural Orbital showing the unpaired spin density in the uranium(V) complex, as a $5f_{\delta}$.



Figure S29. Natural Orbital showing the unpaired spin density in the neptunium(V) complex, as a 5 $f_{\delta}f_{\phi}$.



Figure S30. Energy level diagram for the imido fragments compared with the An core. Only the frontier orbitals are included up to the HOMO, and labeled are the metal and ligand orbitals with proper symmetry for mixing. We notice that the Np orbitals, even though more contracted, spatially can mix with the ligand orbitals due to better energy matching.



Figure S31. Computed Raman spectra in the vicinity of the modes coupling the N-An(V)-N stretch modes. A slight shift towards lower frequency is found in the Np complex relative to the U case.

Analysis of the antisymmetric displacement on the N-U-N and N-Np-N atoms

Because the antisymmetric displacement in a triatomic linear molecule is Raman active we looked for a Raman signal corresponding to the N-(U/Np)-N triad. A first visual inspection of the normal modes in the model molecules shows that this atomic displacement is not a normal mode of the molecule due to the strong coupling between the N atoms and the neighboring. Hence, none of the normal modes frequencies yield a signature for the antisymmetric displacement of the N-(U/Np)-N group. In order to quantify this coupling and to possibly identify a dominating normal mode that could describe this displacement, we projected the antisymmetric displacement onto the normal modes writing it as:

$$v(N-M-N) = \sum_{\text{all modes}} \alpha_i \chi_i$$

where χ_i are the normal mode vectors and α_i the expansion coefficients. For the Np complex the 10 largest contributions to this expansion are:

Mode #	freq(cm ⁻¹)) α	α2	cumulative α^2
100	944.6	0.562	0.32	0.32
148	1294.8	0.445	0.20	0.51
76	754.2	0.374	0.14	0.65
62	558.5	0.245	0.06	0.71
99	941.3	0.195	0.04	0.75
46	345.5	0.174	0.03	0.78
142	1274.8	0.160	0.03	0.81
141	1272.4	0.143	0.02	0.83
60	542.9	0.124	0.02	0.84
38	233.0	0.118	0.01	0.86

For the uranium complex as:

Largest 10 contributions

Mode #	freq(cm	·1) α	α^2	cumulative α^2
100	943.9	0.473	0.22	0.22
98	942.6	0.392	0.15	0.38
149	1301.5	0.365	0.13	0.51
76	755.5	0.358	0.13	0.64
148	1298.5	0.257	0.07	0.70

62	564.2	0.256	0.07	0.77
141	1277.6	0.252	0.06	0.83
129	1126.0	0.154	0.02	0.86
36	237.1	0.120	0.01	0.87
46	349.8	0.100	0.01	0.88

The slow convergence of this expansion is testimony to the coupling between the N-(U/Np)-N group and the rest of the ligand making it impossible to identify *the* peak in the spectrum that corresponds to this displacement. In order to represent 90% of the displacement more than 10 normal modes are needed.

For completeness we also list here a similar projection exercise for the symmetric displacement in the N-An-N mode, which also needs a large number of normal modes to be described, as evidence of the coupling referred above.

For the Np complex the 10 largest contributions to the symmetric mode are:

Mode #	freq(cm ⁻¹) α	α^2	cumulative α^2
93	924.8	0.500	0.25	0.25
75	741.1	0.403	0.16	0.41
145	1291.0	0.352	0.12	0.54
146	1291.6	0.243	0.06	0.59
95	927.7	0.214	0.05	0.64
61	550.6	0.209	0.04	0.68
59	539.9	0.197	0.04	0.72
142	1274.8	0.191	0.04	0.76
92	922.5	0.181	0.03	0.79
30	161.9	0.178	0.03	0.82
For the U complex:				

Mode #	freq(cm ⁻¹)) α	α^2	cumulative α^2
150	1315.9	0.500	0.25	0.25
97	939.9	0.480	0.23	0.48
75	751.1	0.364	0.13	0.61
98	942.6	0.298	0.09	0.70

61	558.3	0.252	0.06	0.77
100	943.9	0.196	0.04	0.80
142	1279.8	0.176	0.03	0.83
156	1345.4	0.175	0.03	0.87
130	1126.9	0.146	0.02	0.89
30	170.7	0.138	0.02	0.91

References

(1) Eckert, N. A.; Smith, J. M.; Lachicotte, R. M.; Holland, P. L. Inorg. Chem. 2004, 43, 3306.

(2) Jilek, R. E.; Spencer, L. P.; Lewis, R. A.; Scott, B. L.; Hayton, T. W.; Boncella, J. M. J. Am. Chem. Soc. 2012, 134, 9876.

(3) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

(4) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(5) Frisch, M. J. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, USA 2009.

(6) Fuentealba, P.; Preuss, H.; Stoll, H.; Von Szentpaly, L. A. Chem. Phys. Lett. 1982, 89, 418.

(7) Kuchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.

(8) Kuchle, W.; Dolg, M.; Stoll, H.; Preuss, H. J. Chem. Phys. 1994, 100, 7535.

(9) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Matzaris, J. J. Chem. Phys. 1988, 89, 2193.

(10) Petersson, G. A.; Al-Laham, M. A. J. Chem. Phys. 1991, 94, 6081.

(11) NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); http://nbo6.chem.wisc.edu/