Electronic Supporting Information

Neptunium and plutonium complexes with a sterically encumbered triamidoamine (TREN) scaffold

Jessie L. Brown,[a] Andrew J. Gaunt,*[a] David M. King,[b] Stephen T. Liddle,*[b] Sean D. Reilly,[a] Brian L. Scott,[c] and Ashley J. Wooles[b]

[a]Chemistry, [c]Materials Physics and Applications Divisions, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

[b]School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

Additional Experimental Details:

Caution! All neptunium and plutonium chemistry (using ^{237}Np and ^{239}Pu isotopes) 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. As a consequence of the radiological hazards, it is not possible to have elemental analyses performed on compounds by a third-party micro-analytical laboratory.

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. $NpCl_4(DME)_2$, $PuCl_4(DME)_2$ and $Li_3(TREN^{TIPS})$ were prepared as previously described (refs S1-S2).

^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (setting the residual protio resonance in C_6D_6 to 7.16 ppm). Solution-phase electronic absorption spectra were collected in screw-capped quartz cuvettes (loaded in a transuranic drybox using parafilm during the loading procedure to wrap and protect the exterior surface of the cuvette and cap from radioactive contamination) at room temperature using a Varian Cary 6000i UV-vis-NIR spectrophotometer. The solid-phase diffuse reflectance electronic absorption spectra of **1** and **2** were collected using a Varian Cary 6000i UV-vis-NIR spectrophotometer with an installed Internal Diffuse Reflectance Accessory. The sample consisted of ground-up crystalline **1** and **2** (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 (again with exterior surfaces of the sample holder wrapped in parafilm during the loading procedure inside the drybox to protect from radioactive material contamination).

Reduction of 1 over a potassium mirror to form putative Np^{III}[TREN^{TIPS}] and preliminary observations from oxidative addition scoping reactions: Np^{IV}[TREN^{TIPS}]Cl (**1**) was prepared using the same method as described in the manuscript communication text, except with different reagent amounts: $NpCl_4(DME)_2$ (0.0138 g, 0.025 mmol) and Li_3TREN^{TIPS} (0.0157 g, 0.025 mmol). Furthermore, because the intent was to minimize material loss associated with these small-scale reactions, in this particular experiment compound **1** was not isolated prior to the reduction procedure – instead, a solution of **1** formed in situ in toluene was subjected to vacuum to remove volatiles, the residue dissolved in hexanes (2 mL) at 50 °C, filtered through Celite supported on a glass fiber filter circle, and the red-orange filtrate stirred at ambient temperature over a K mirror (excess) for 4 days, resulting in a distinct color change to a more vibrant red (red-wine color). The cloudy solution was filtered through Celite supported on a glass fiber filter circle, volatiles removed *in vacuo*, and the red residue dissolved in C_6D_6 for ^{1}H NMR analysis. ^{1}H NMR (in C_6D_6, 400 MHz): δ 0.05 (d, 54H, CH(CH_3)$_2$), 4.43 (s, br, 9H, CH(CH$_3$)$_2$), 18.11 (m, 6H, CH_2), 18.75 (m, 6H, CH_2) (Fig S3).

Attempts to crystallize or precipitate the reduced product in powder form were thwarted by the combination of the small transuranic reaction scales and the much increased solubility of $Np^{III}[TREN^{TIPS}]$ compared to $Np^{IV}[TREN^{TIPS}]Cl$. For this reason, preliminary investigations of oxidative addition chemistry utilized in situ solutions of putative $Np^{III}[TREN^{TIPS}]$ – treatment of the Np(III) species in toluene with 1 equiv of either Me_3NO or TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) resulted in color changes from red to orange/yellow. Attempts at crystallization from these solution were unfruitful but ^1H NMR spectra confirmed disappearance of the Np(III) species with the emergence of new resonances (which were different to the Np(IV) compound **1**). Future full investigations of reactivity may require a consideration of larger scale reactions, which may be feasible in our laboratory to some extent with ^{237}Np, but less so with ^{239}Pu due to local considerations regarding building isotope inventory limits and prudent use of these limits, coupled with safety considerations.

Halide-exchange reaction of $Np^{IV}[TREN^{TIPS}]$-Cl (1) with Me_3Si-I and reactivity towards potassium benzyl: Initial attempts to react **1** with potassium benzyl (K-CH_2Ph) afforded solutions for which NMR analysis indicated only the presence of unreacted **1**. Therefore, swapping the chloride for iodide was attempted since iodide should be more labile than chloride and increase the rate of reaction with potassium benzyl. $Np^{IV}[TREN^{TIPS}]Cl$ (**1**) (0.0247 g, 0.028 mmol) was dissolved in toluene (2 mL) and the solution cooled to -35 °C in the drybox freezer. To the cold solution was added three drops (excess) of Me_3Si–I and the solution allowed to warm to ambient temperature with stirring followed by heating to 50 °C for 1 h with a slightly discernable shift in the orange-red color of the solution to red. After stirring at ambient temperature overnight (16 h) volatiles were removed in vacuo. The residue was triturated with hexanes (2 mL) and the volatiles were removed *in vacuo*. The procedure of Me_3Si–I addition through to hexanes trituration and removal of volatiles *in vacuo* was then repeated. The resultant orange-red solid residue was dissolved in toluene (2 mL) and 1 equiv of $K(CH_2Ph)$ added. After stirring for 16 h at ambient temperature and heating to 50 °C for 1 h, volatiles were removed in vacuo from the reaction solution, the residue dissolved in hexanes, and the orange-red solution layered with HMDSO and stored at -35 °C to afford several red-orange crystals that were dried in vacuo (too few to determine yield and one crystals was selected for X-ray structural determination which resulted in the disordered structure not of publishable quality). The crystals were dissolved in C_6D_6 to afford a 'fire-orange' solution. ^1H NMR (in C_6D_6, 400 MHz): δ 10.10 (s, 54H, CH(CH_3)$_2$), 9.17 (s, 9H, CH(CH_3)$_2$), 15.97 (s, 6H, CH_2), -37.75 (s, 6H, CH_2) (Fig S4). The NMR spectrum of the supernatant from which the crystals were grown was recorded by removing volatiles in *vacuo*, dissolving the resultant solution in C_6D_6 followed by filtration through a glass fiber circle. The observed resonances were consistent with those above – the major peaks assignable to putative $Np^{IV}[TREN^{TIPS}]I$ and a minor component of the parent $Np^{IV}[TREN^{TIPS}]Cl$ complex. In addition, there were a few other minor impurities that are unassigned but nothing to suggest that the supernatant contained any significant additional products.

Reduction of 2 over a potassium mirror to form putative $Pu^{III}[TREN^{TIPS}]$: $Pu^{IV}[TREN^{tips}]Cl$ (**2**) (0.0051 g, 0.0058 mmol) was dissolved in hexanes (4 mL) to afford a red solution, which was stirred over a potassium mirror (excess) for 3 d (a color change from red to green was evident after 1d). The solution was filtered through Celite supported on a glass fiber filter circle, volatiles removed in vacuo, and the residue dissolved in C_6D_6 for ^1H NMR analysis (Figs S6 and S7).

X-ray Diffraction Collection Details: Neptunium (**1**) and plutonium (**2**) containing single-crystals 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. In the case of **1**, the capillary was placed on a Bruker AXS SMART APEX II charge-coupled-device diffractometer. In the case of **2**, the capillary was placed on a Bruker D8 Quest diffractometer with a CMOS detector. The instruments were equipped with a sealed, graphite monochromatized MoKα 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).
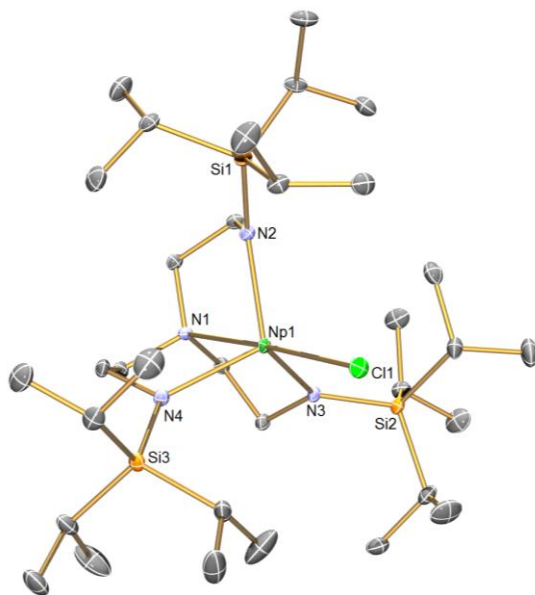
Figure S1. Thermal ellipsoid plot (at the 50% probability level) of the solid-state structure of $Np^{IV}[TREN^{TIPS}]Cl$ (**1**). Hydrogen atoms are omitted for clarity.
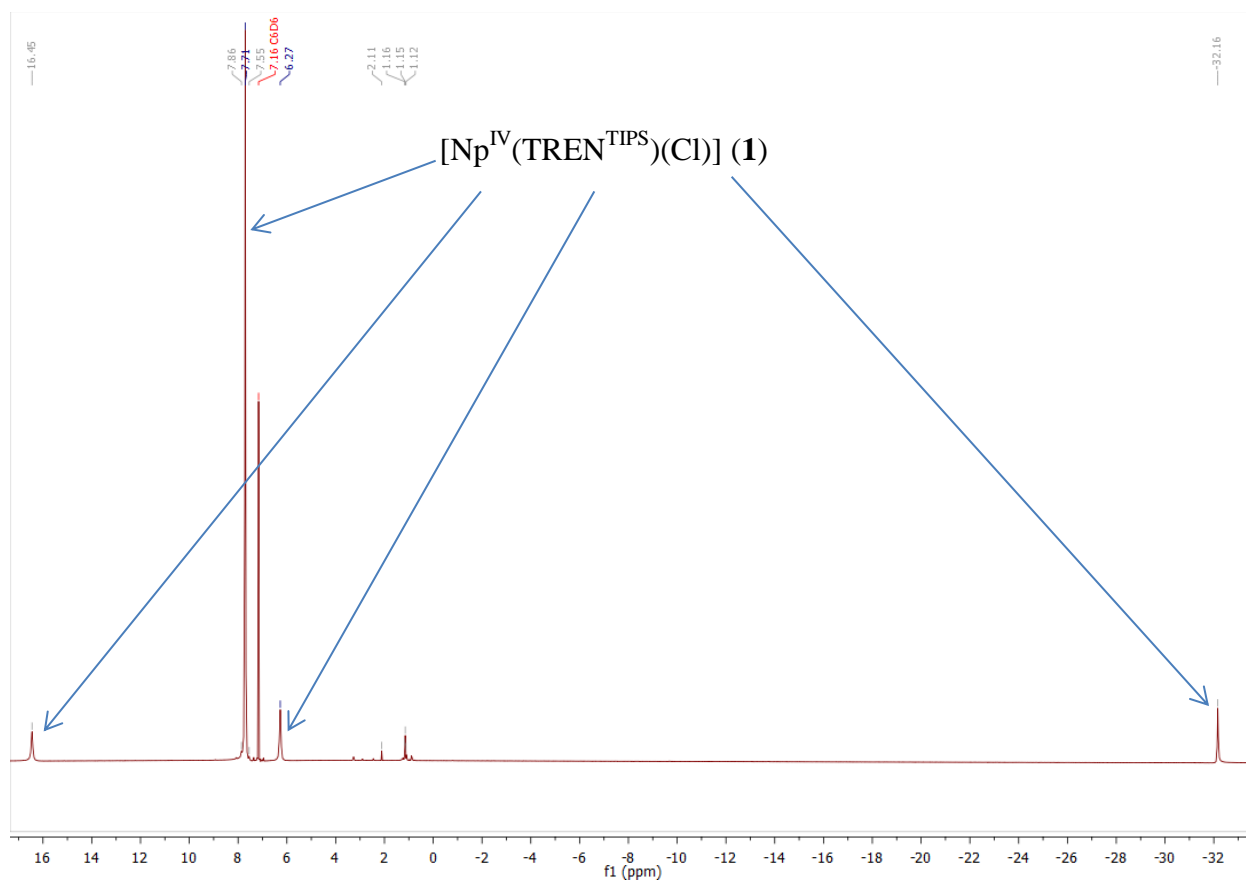
¹H NMR Spectroscopic Studies:

Figure S2. ^{1}H NMR spectrum of **1** dissolved in C_6D_6.

Putative "[Np^{III}(TREN^{TIPS})]"

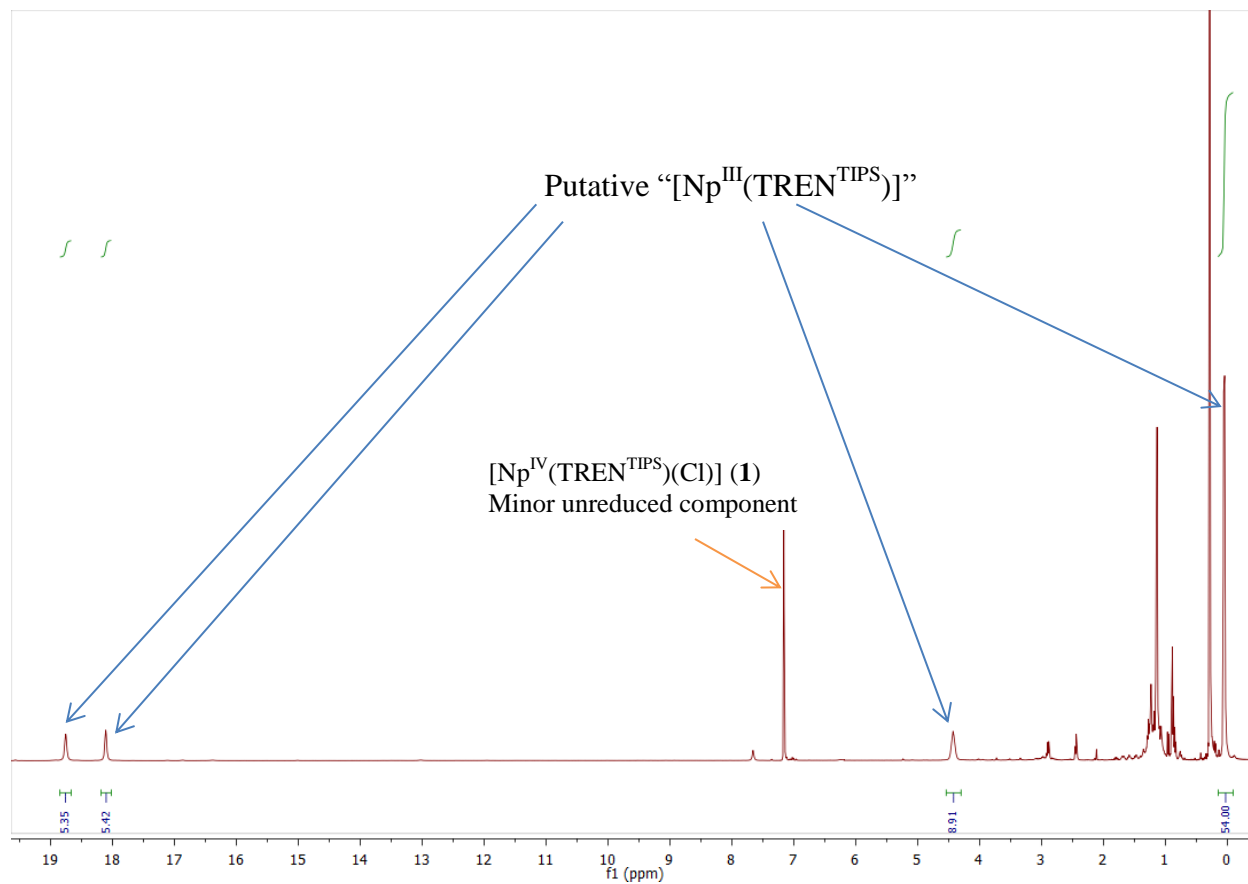[Np^{IV}(TREN^{TIPS})(Cl)] (**1**)
Minor unreduced component

Figure S3. ^{1}H NMR spectrum of **1**, reduced over a potassium mirror in hexanes, volatiles removed *in vacuo* and residue dissolved in C$_6$D$_6$. Impurities are identified as hexanes, grease from the glass stopper/seal, and a minor component of unreduced **1**. Major resonances are assigned and integrate well for the reduced Np^{III}[TREN^{TIPS}] product.
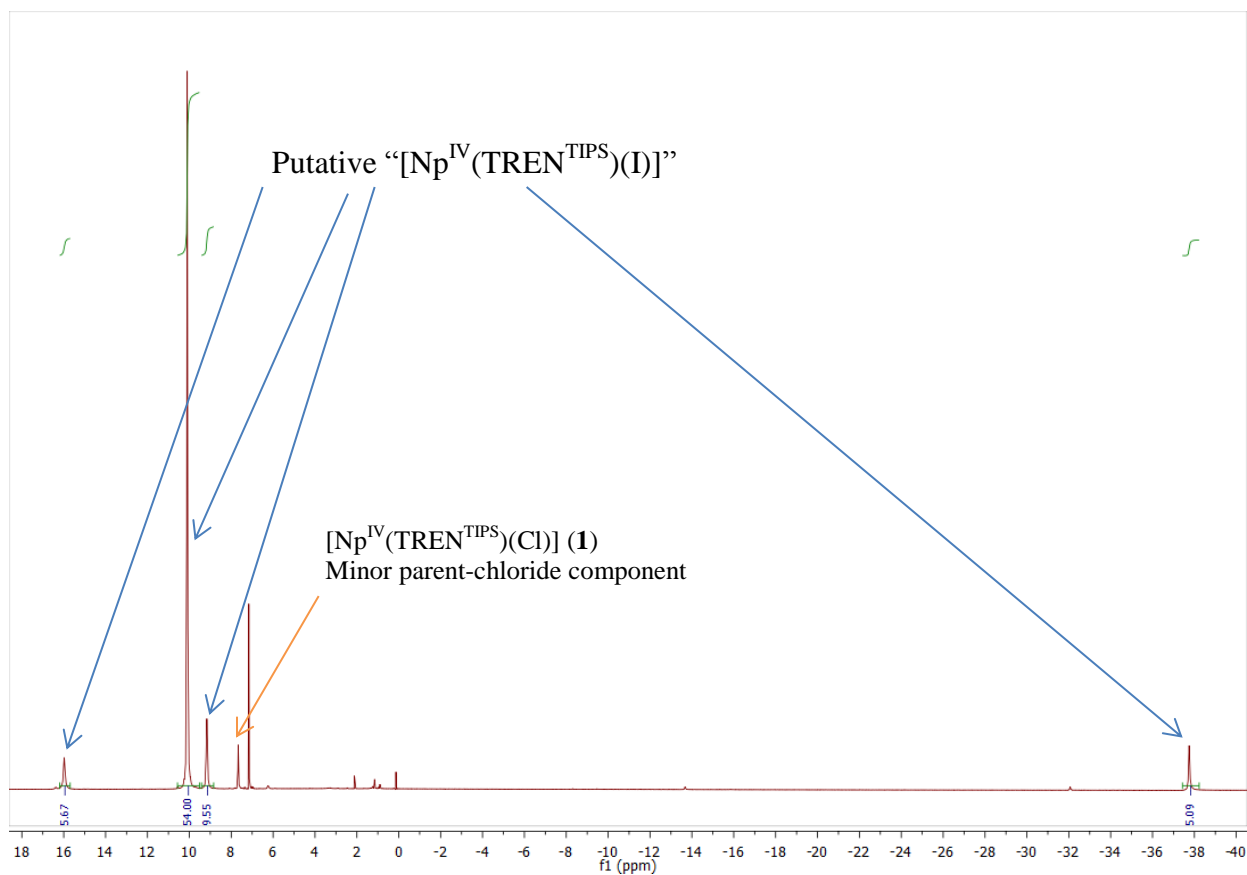
Figure S4. ^{1}H NMR spectrum of **1** after treatment with Me$_3$Si-I and K-benzyl, product dissolved in C$_6$D$_6$. The four resonances that integrate for 54, 9, 6, and 6 protons are tentatively assigned to the putative halide swapped product "Np^{IV}[TREN^{TIPS}]-I" based on the following observation: The only other significant resonances in the ^{1}H NMR spectrum above can be assigned to the parent chloride, Np^{IV}[TREN^{TIPS}]-Cl (**1**) and solvents, there are no remaining peaks that would indicate the presence of a benzyl substituent or cyclometallated product, although without structural verification and alternative product cannot be completely ruled out.
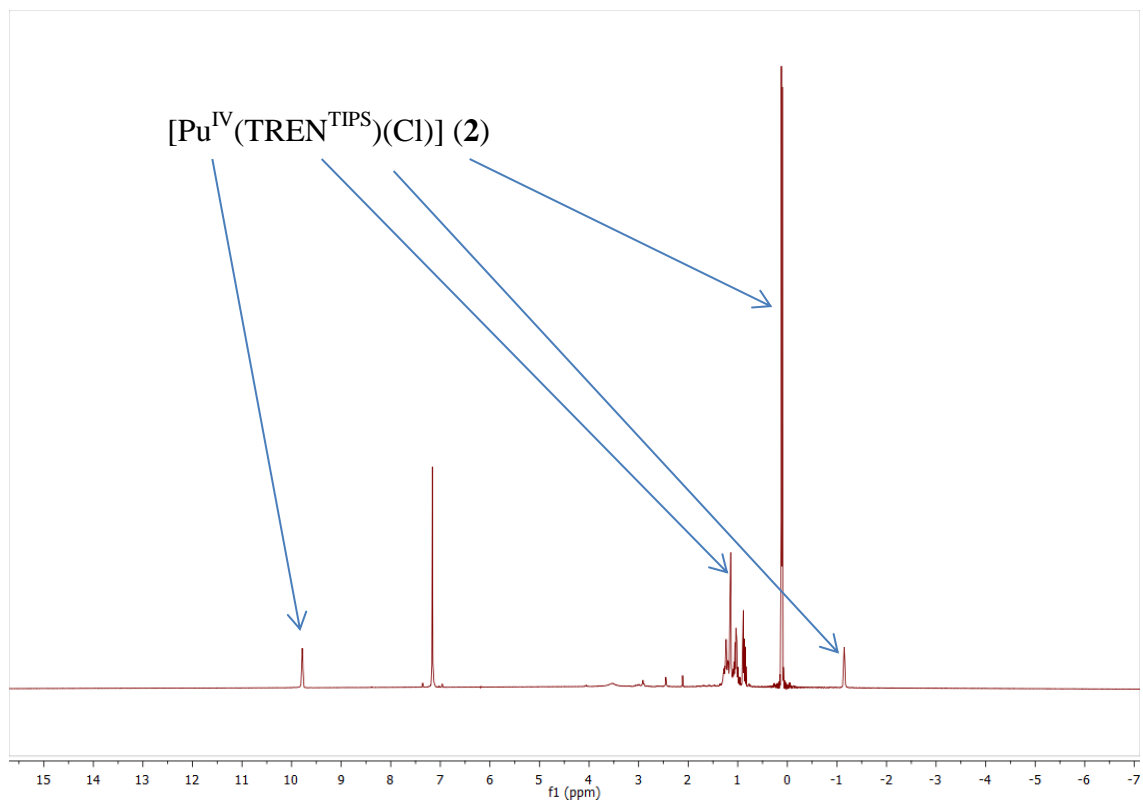
Figure S5. ^{1}H NMR spectrum of **2** dissolved in C$_6$D$_6$. The spectrum is complicated by the presence of uncoordinated TREN^{TIPS} ligand that arises from a coating of supernatant solution on the crystals – the small transuranic reaction scales, low yield, and very high solubility of the product, **2**, preventing practicable crystal washing.
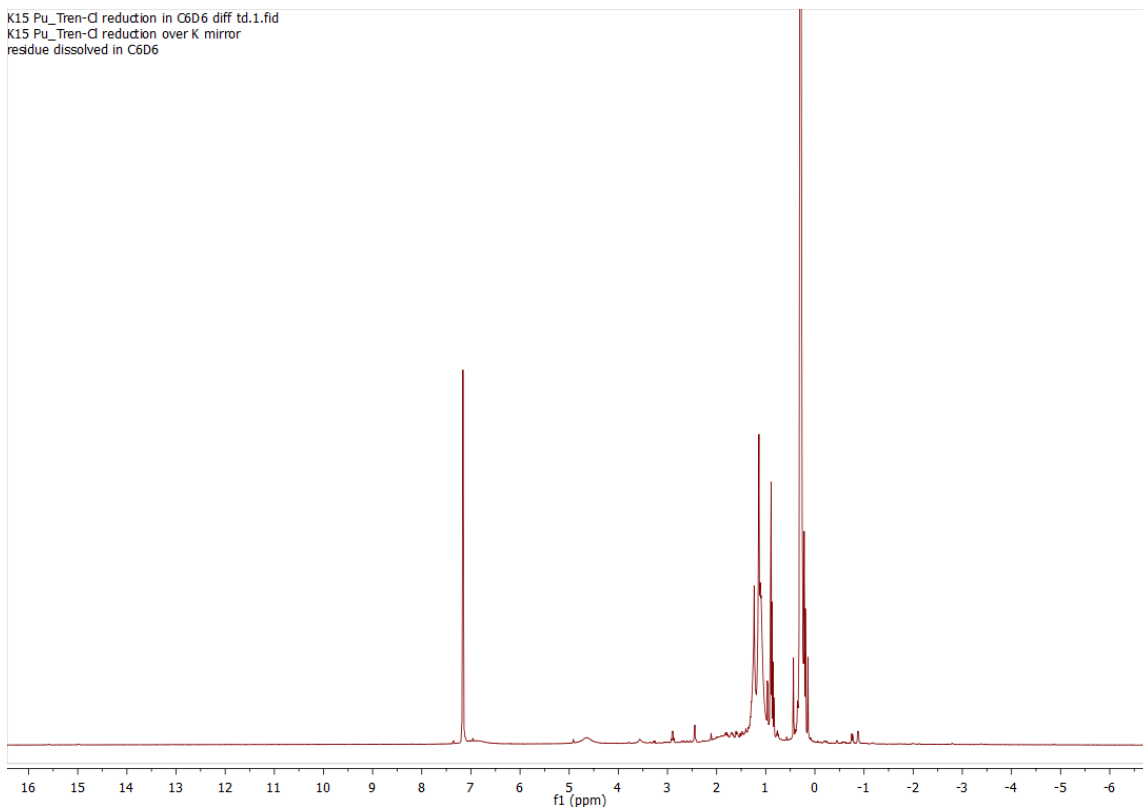
K15 Pu_Tren-Cl reduction in C6D6 diff td.1.fid
K15 Pu_Tren-Cl reduction over K mirror
residue dissolved in C6D6

Figure S6. ^{1}H NMR spectrum of **2**, reduced over a potassium mirror in hexanes, volatiles removed *in vacuo* and residue dissolved in C_6D_6. The resonances for **2** decrease and then disappear during the reduction process but it is difficult to assign resonances conclusively to the reduced Pu(III) daughter molecule with the resonance for silicone grease dominating the spectrum – however, the emergence of broad features at 6.87, 4.61, 1.88 and 1.11 ppm, which overlap with residual solvent peaks and other minor impurities are likely attributable to the daughter Pu(III) molecule, Pu^{III}[TREN^{TIPS}] (see expanded view in Fig S7). Despite the ambiguity in peaks assignments, the main conclusion that **2** is reduced by the potassium mirror is unambiguous.
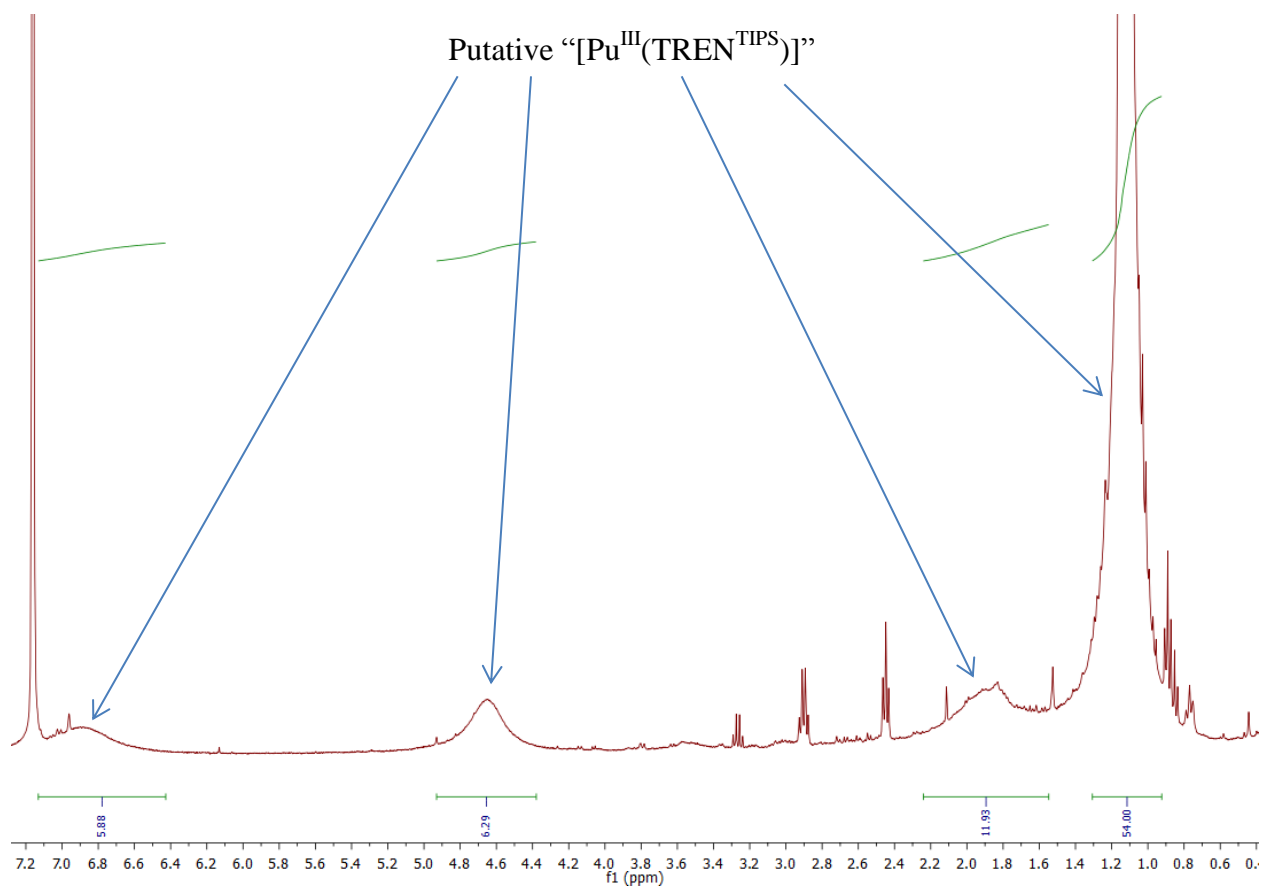
Putative "[Pu^{III}(TREN^{TIPS})]"

Figure S7. Expanded view of ^{1}H NMR spectrum of **2**, reduced over a potassium mirror in hexanes, volatiles removed *in vacuo* and residue dissolved in C$_6$D$_6$. This expanded view more clearly show the four broad resonances that emerge during the reduction process. The linewidth and peak overlap renders accurate integration an assignment difficult.
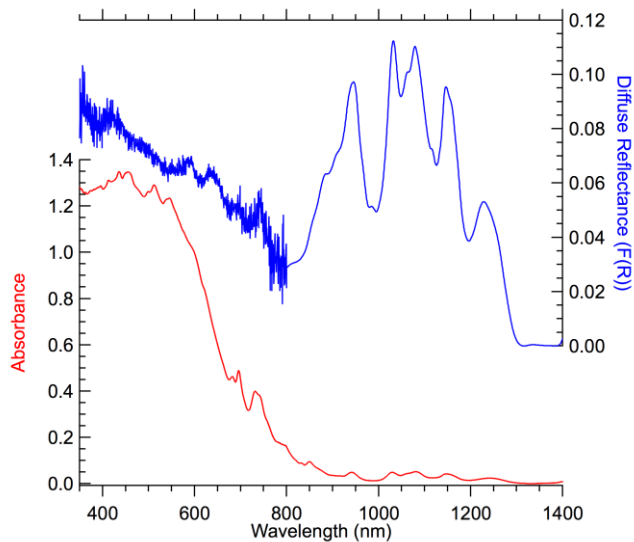
Electronic Absorption Spectroscopy:

Figure S8. Overlay of solid (right axis blue trace) and solution phase (left axis, red trace) vis/NIR spectra of Pu[TREN^TIPS]Cl (**2**).
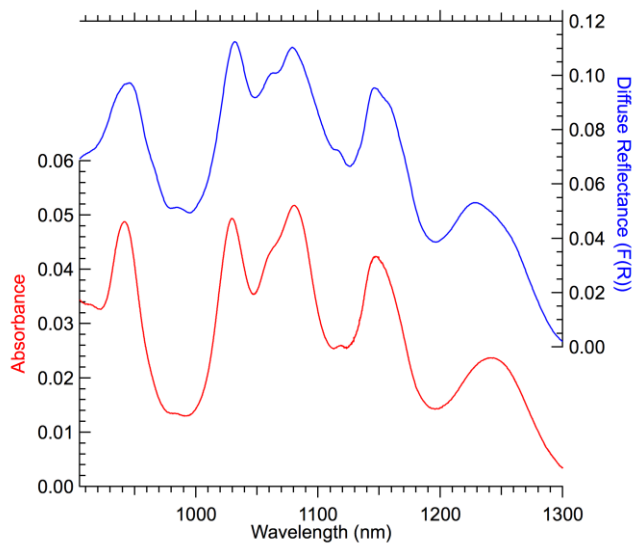

Figure S9. Overlay of solid (right axis blue trace) and solution phase (left axis, red trace) vis/NIR spectra of Pu[TREN^TIPS]Cl (**2**), showing only the 900-1300 nm region.
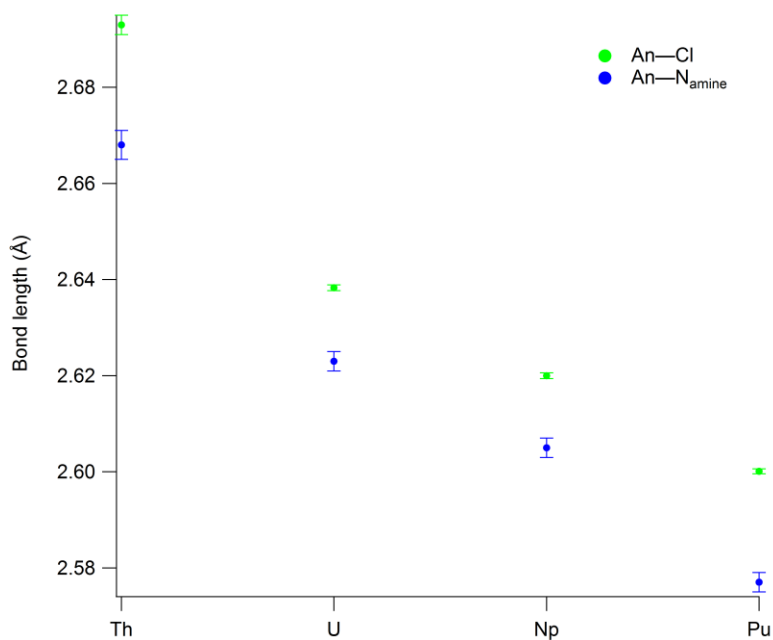
Figure S10. Plot of An-Cl and An-N(amine) bond distances, with error bars shown, across the An[TREN^{TIPS}]Cl (An = Th, U, Np, Pu) series of molecules.
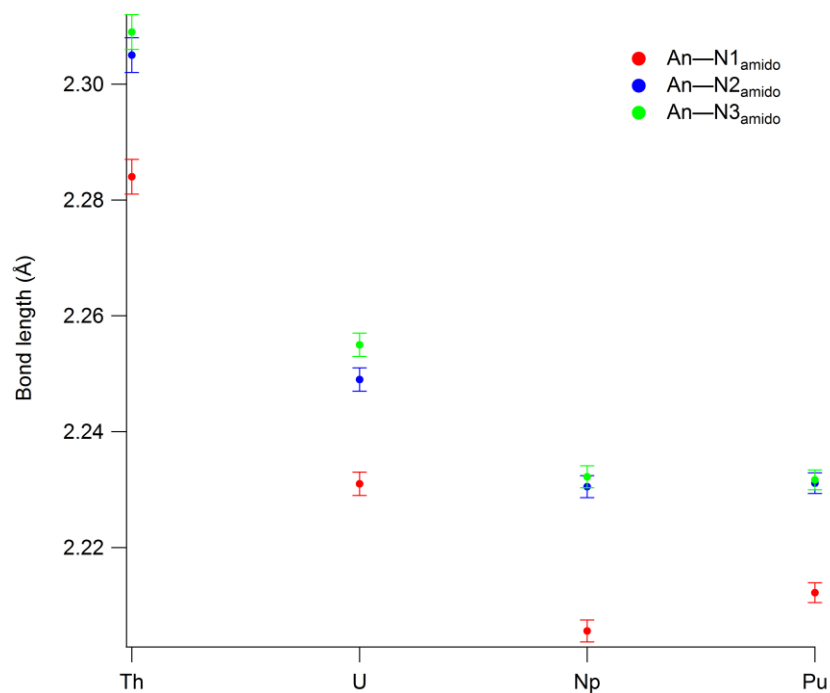

Figure S11. Plot of the three independent An-N(amide) bond distances, with error bars shown, across the An[TREN^{TIPS}]Cl (An = Th, U, Np, Pu) series of molecules.

References

S1. S. D. Reilly, J. L. Brown, B. L. Scott and A. J. Gaunt, *Dalton Trans.*, 2014, **43**, 1498.

S2. D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717.