Thorium Triamidoamine Complexes: Synthesis of an Unusual Dinuclear Tuck-In-Tuck-Over Thorium Metallacycle Featuring the Longest Known Thorium- σ -Alkyl Bond

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Abstract

*We report the synthesis and characterization of a range of thorium(IV)-halide, -amide, and -alkyl complexes supported by a sterically demanding triamidoamine ligand. The reaction of $[\text{ThCl}_4(\text{THF})_{3.5}]$ with $[\text{Li}_3(\text{Tren}^{\text{DMBS}})(\text{THF})_3]$ $[\text{Tren}^{\text{DMBS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_3]$ gave $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{Cl})(\text{THF})]$ (**1**), which was converted to $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{I})]$ (**2**), with concomitant elimination of Me_3SiCl , by treatment with Me_3SiI . Treatment of **2** with $[\text{LiNEt}_2]$ afforded $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{NEt}_2)]$ (**3**), or treatment with $[\text{PhCH}_2\text{K}]$ produced the dimeric tuck-in-tuck-over alkyl complex $[\text{Th}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMeBu}^t-\mu\text{-CH}_2)\}]_2$ (**4**), which is notable as it features the longest reported Th- σ -alkyl bond distance of 2.875(9) Å. Reaction of **4** with $[\text{Et}_3\text{NH}][\text{BPh}_4]$ to give the putative separated ion pair complex $[\text{Th}(\text{Tren}^{\text{DMBS}})][\text{BPh}_4]$ resulted in an intractable product mixture which resisted all attempts to isolate crystalline material. In order to furnish a greater understanding of the latter reaction the solvent separated ion pair complex $[\text{U}(\text{Tren}^{\text{DMBS}})(\text{NCMe})_2][\text{BPh}_4]$ (**5**) was prepared from the monomeric uranium analogue of **4**, $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMeBu}^t-\mu\text{-}$*

$\text{CH}_2\text{)}\}\text{]} \text{ (I)}$, to provide a related model complex and to examine potential routes to useful $\text{Tren}^{\text{DMBS}}$ -actinide precursors. The nascent reactivity of **4** is suggested by the isolation of a small quantity of the oxo-insertion product $[\text{Th}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t\text{CH}_2-\mu\text{-O})\}]_2$ (**6**) when **4** is stored in diethyl ether. The complexes reported herein have been variously characterized by single crystal X-ray diffraction, NMR spectroscopy and FTIR spectroscopies, Evans method solution magnetic moment determination, and CHN elemental analyses.

Introduction

By virtue of their high charge density, versatile steric and electronic qualities, synthetic flexibility, and relative ease of preparation, amide (NR_2^-) ligands have provided widespread utility in the stabilization of electropositive metal centers.¹ Many advances have featured metal-amide linkages as a pivotal structural feature. Indeed, the broader field of organometallic and metal-organic amide chemistry enjoys a strong and enduring association with Professor Michael F. Lappert FRS, whose contributions by way of research articles and reviews to this area were nothing short of prolific.²

The study of f-element amide complexes has shown them to be effective at stabilizing a significant number of novel M-E linkages, promote novel small molecule reactivity patterns, and many such complexes demonstrate complex magnetic properties.³ Some recent studies by us have focused on f-element triamidoamine $[(\text{R}_3\text{NCH}_2\text{CH}_2)_3\text{N}]$ – or Tren – systems; these have enabled the synthesis of terminal uranium-nitride, -imide and -phosphinidene functionalities,⁴ supported single molecule magnetism and uranium-metal bonds,⁵ demonstrated unusual photochemistry⁶ and enabled small molecule activation and reactivity that contrasts with their traditional counterparts, that is to say a collection of several monoanionic amides at a metal center rather than one polyamide

ligand, which require significant (and perhaps energy-intensive) reorganization of the ligand environment during reactions.⁷

It was over a decade ago that Scott and co-workers reported a number of Tren-uranium systems, including an unusual dinitrogen adduct of uranium(III) as well as a highly strained uranium(IV) metallacycle $[U\{N(CH_2CH_2NSiMe_2Bu^t)_2(CH_2CH_2NSiMe_2Bu^tCH_2)\}]$ (**I**) and several thorium(IV) complexes including the thorium(IV) analogue of **I**.⁸ Tuck-in and tuck-over actinide metallacycles have often taken the form of metallocene derivatives with much utility demonstrated as useful entry points to a range of chemical reactivity,⁹ although we have shown that a dinuclear cyclometallated tuck-in-tuck-over tuck-over Tren derivative can access unexpected chemistry of the BPh_4^- anion.¹⁰ Our more recent efforts in the field of f-element Tren^{TIPS} $[Tren^{TIPS} = \{N(CH_2CH_2N(SiPr^i)_3)\}^{3-}]$ chemistry have demonstrated divergent reactivity patterns for closely comparable uranium and thorium systems, the origin of which has been shown to be a consequence of the increased ability for uranium to form covalent interactions that stabilize transition states thus encouraging reactions that might have *a priori* been predicted to be less favorable;¹¹ with this in mind it seemed desirable to us to investigate the contrast between the inherent reactivity profile of uranium and thorium utilizing Tren ligands with varying steric demands to further probe these findings. To this end we targeted a range of Tren^{DMBS} $[Tren^{DMBS} = \{N(CH_2CH_2N(SiMe_2Bu^t)_3)\}^{3-}]$ complexes of thorium(IV) to compare to the uranium(IV) analogues already reported in the primary literature and provide structural characterization for the former, which is currently lacking.^{8h}

Results and Discussion

Synthesis and Structural Analysis

Scheme 1 – Experimental synthesis of thorium complexes 1–5.

Treatment of colorless $[\text{ThCl}_4(\text{THF})_{3.5}]$ with one equivalent of $[\text{Li}_3(\text{Tren}^{\text{DMBS}})(\text{THF})_3]$ (Scheme 1) in THF yielded a pale yellow suspension, which after work-up and crystallization from pentane afforded colorless crystals of **1** suitable for an X-ray diffraction (XRD) study. The molecular structure of **1** is shown in Figure 1 with selected bond lengths and angles.

Figure 1 – Left: molecular structure of **1** with displacement ellipsoids set at 30% probability. One of the four crystallographically independent molecules is shown and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Th1–Cl1, 2.735(3); Th1–N1, 2.294(11); Th1–N2, 2.330(10); Th1–N3, 2.350(12); Th1–N4, 2.665(11); Th1–O1, 2.648(9); N3–Th1–O1, 172.5(3); N4–Th1–Cl1, 161.9(2). Right: molecular structure of **2** with displacement ellipsoids set at 30% probability, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Th1–I1, 3.1685(12); Th1–N1, 2.261(15); Th1–N2, 2.285(14); Th1–N3, 2.279(13); Th1–N4, 2.677(13); N4–Th1–I1, 177.9(3).

All four of the independent molecules of **1** present in the unit cell are generally quite similar with only very minor variations in bond lengths and angles so we limit our discussion to one of the unique molecules in the X-ray diffraction structure of **1**. The Th center in **1** is six-coordinate, adopting a distorted octahedral geometry. As expected the chloride atom resides *trans* to the amine center [N4–Th1–Cl1 = 161.9(2)°] with the datively bound oxygen atom of a THF molecule thus located *trans* to an anionic amide [N3–Th1–O1 = 172.5(3)°]. The bond lengths and angles in **1** are unremarkable, with Th–

N_{amide}, Th–N_{amine}, Th–Cl and Th–O bond lengths of 2.325(11) (av.), 2.665(11), 2.735(3) and 2.648(9) Å, respectively, typical of Th(IV)–N_{amide}, Th(IV)–N_{amine}, Th(IV)–Cl and Th(IV)–O bond distances.¹² Prepared analogously, the uranium congener of **1** is known to be THF-free in the solid state^{8d} arising from the smaller ionic radius of U(IV) (89 pm) vs. Th(IV) (94 pm);¹³ however, careful heating of **1** at 60 °C at 10^{–5} mbar over eight hours produced the ether-free complex [Th(Tren^{DMBS})(Cl)] as a virtually pure white solid, as ascertained by ¹H NMR spectroscopy (see the Experimental section for full details).

The iodide derivative of **1** was targeted since the elimination of iodide from actinide centers is frequently easier to accomplish than for chloride, thus ameliorating the requirement for potentially deleterious heating of reaction mixtures.^{8a, 10, 14} Accordingly, a solution of **1** in hexanes was treated with a slight excess of iodotrimethylsilane to afford [Th(Tren^{DMBS})(I)] (**2**), eliminating Me₃SiCl (Scheme 1). Work up and crystallization afforded **2** as colorless crystals suitable for a single crystal X-ray diffraction study. The molecular structure of **2** is illustrated in Figure 1 with selected bond lengths and angles. The thorium center in **2** is five-coordinate, adopting a distorted trigonal bipyramidal geometry with the N4 and I1 centers occupying the axial sites [N4–Th1–I1 = 177.9(3)°]. The bond lengths and angles in **2** are unexceptional, with Th–N_{amide}, Th–N_{amine} and Th–I bond lengths of 2.275(14) (av.), 2.677(13) and 3.1685(12) Å, respectively, typical of Th(IV)–N_{amide}, Th(IV)–N_{amine} and Th(IV)–I bond distances.¹²

Recent studies of organometallic actinide chemistry supported by quadridentate amide ligands by us have focused on the construction of novel actinide-transition metal bonds *via* a variety of methods that circumvent the requirement for halide metathesis,^{5c,d,15} which can prove to be sluggish and problematic. One such route is *via* elimination of an amine, a strategy requiring suitable actinide amide precursors for reaction with metal

hydrides.^{5c,d,16} Alternatively, incorporating a counteranion within the precursor that does not coordinate to the actinide center of the form $[L_xAn(S)_y][A]$ (An = actinide, S = solvent, A = non-coordinating anion) is often a desirable approach where a salt elimination methodology is appropriate.^{4b, 17} Such solvent separated ion pair (SSIP) complexes are usually accessed *via* metal alkyls and although it is noted that formation of SSIPs from amide reagents in general would be unlikely on the basis of their respective pK_a values, we have been able to accomplish this for uranium-Tren^{TMS} [Tren^{TMS} = $\{N(CH_2CH_2N(SiMe_3)_3\}^{3-}$] systems.¹⁸ Due to the combination of the larger ionic radius of Th(IV) (94 pm) *vs.* U(IV) (89 pm)¹³ and increased steric protection of Tren^{DMBS} *vs.* Tren^{TMS}, Tren^{DMBS}-thorium amides could open up a previously inaccessible pathway to thorium SSIPs that avoids metal-alkyl intermediates, with many of the latter known to undergo thermolytic decomposition at ambient temperatures and induce undesirable side-reactions.^{8c, 10-11}

Complex **1** was treated with a slight excess of LiNEt₂ in toluene to afford, after work-up and crystallization from hexamethyldisiloxane, the diethylamido derivative [Th(Tren^{DMBS})(NEt₂)] (**3**) as colorless crystals suitable for a single crystal X-ray diffraction study. The molecular structure of **3** is illustrated in Figure 2 with selected bond lengths and angles.

*Figure 2 – Molecular structure of **3** with displacement ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Th1–N1, 2.329(2); Th1–N2, 2.317(2); Th1–N3, 2.323(2); Th1–N4, 2.761(3); Th1–N5, 2.302(3); N4–Th1–N5, 175.85(9).*

The Th center in **3** is five-coordinate, adopting a distorted trigonal bipyramidal geometry with the N4 and N5 centers occupying the axial sites [$\text{N4–Th1–N5} = 175.85(9)^\circ$]. The bond lengths and angles in **3** are unremarkable, with Th–N_{amide} and Th–N_{amine} bond lengths of 2.318(2) (av.) and 2.761(3) Å, respectively, typical of Th–N_{amide} and Th–N_{amine} bond distances.¹² The uranium analogue of **3** has been structurally characterized previously and is essentially isostructural, with any significant deviation between the metal-ligand bond distances presented by the two complexes attributed to the smaller ionic radius of U(IV) (89 pm) vs. Th(IV) (94 pm).^{8d, 13}

No reaction was observed between equimolar quantities of **3** and $[\text{Et}_3\text{NH}][\text{BPh}_4]$ at room temperature in THF as determined by ^1H NMR spectroscopy, even after two weeks. Heating the mixture to reflux resulted in an intractable mixture of products, including

Tren^{DMBS}H₃ as evidenced by ¹H NMR spectroscopy, and an insoluble white solid which we presume to be products of ring-opening/oxo abstraction of THF solvent by thorium. Heating either **3** and [Et₃NH][BPh₄] or just **3** in *d*₈-toluene at temperatures above 70 °C also resulted in decomposition and the production of Tren^{DMBS}H₃.

With these results in hand, attention turned to accessing the putative benzyl complex [Th(Tren^{DMBS})(CH₂Ph)], which was envisaged to undergo thermally promoted cyclometallation to afford the alkyltriamidoamine formulated as [Th{N(CH₂CH₂NSiMe₂Bu^t)₂(CH₂CH₂NSiMeBu^tCH₂)}], like **1**.¹⁹ Accordingly the treatment of **2** with benzylpotassium (Scheme 1) in toluene afforded, after work-up and crystallization from hexanes, colorless crystals of **4** suitable for a single crystal X-ray diffraction study. The molecular structure of **4** is illustrated in Figure 3 with selected bond lengths and angles.

Figure 3 – Molecular structure of 4 with displacement ellipsoids set at 30% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond

lengths (Å) and angles (°): Th1–C1, 2.875(9); Th1–C25, 2.767(10); Th1–N1, 2.299(7); Th1–N2, 2.325(8); Th1–N3 2.325(7); Th1–N4 2.648(7); Th2–C1, 2.739(9); Th2–C25, 2.720(14); Th2–N5, 2.290(7); Th2–N6, 2.321(7); Th2–N7, 2.311(7); Th2–N8, 2.663(8); N1–Th1–C1, 63.7(3); Th1–C1–Th2, 95.6(3); C1–Th1–C25, 80.7(3); N5–Th2–C25, 66.8(3); Th1–C25–Th2, 97.3(2); C1–Th2–C25, 84.0(3).

The solid state structure of $[\text{Th}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t-\mu\text{-CH}_2)\}_2]$, **4**, is dinuclear and in this regard is superficially reminiscent of the dinuclear tuck-in-tuck-over tuck-over complex $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2)_2\}\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}]$.¹⁰ One methyl group of each of the Tren^{DMBS} ligands has been deprotonated such that the anionic CH_2^- centers C1 and C25 bridge the two Th centers in a tuck-in-tuck-over coordination mode with the four Th–C bond distances ranging from 2.720(14) to 2.875(9) Å. Of these bond distances, only the longest (Th1–C1) bond distance is statistically distinct, being remarkably long at 2.875(9) Å, actually lying outside the sum of the covalent radii of the component elements (2.50 or 2.82 Å for sp^3 -hybridization of C according to Pyykkö or Alvarez, respectively),²⁰ although this is perhaps not unexpected given the highly ionic bonding regime present for organometallic Th(IV) systems. Indeed, a search of the Cambridge Structural Database revealed that the longest Th–C single bonds that warrant a meaningful comparison with that in **4** (excluding complexes with multi-hapto Th–C interactions such as in $[\text{Li}(\text{THF})_4]_2[\text{Th}(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})_2\text{Br}_2]$ ²¹ or exhibiting extensive disorder²²) feature in the dianionic hexabenzyl complex $[\text{K}(\text{THF})]_2[\text{Th}(\text{CH}_2\text{Ph})_6]$.²³ The thorium-carbon σ -bonds in this complex lie in the range 2.59(2) to 2.69(2) Å, which is unexceptional for actinide benzyl complexes but significantly shorter than that in **4**. Even when constrained within a four-membered metallacycle thorium alkyl linkages are not known to extend beyond 2.77(2) Å, for instance within the chelating thorium *bis*(ylide)

complex $[\text{Th}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{PPh}_2\text{CH}_2)_2]$.²⁴ The remainder of the coordination environment at the thorium centers comprises the tetradentate $\text{Tren}^{\text{DMBS}}$ ligand such that each Th atom adopts a distorted octahedral geometry with Th–N_{amide} and Th–N_{amine} bond distances of 2.312(7) (av.) and 2.656(3) Å, respectively, which reside within the reported range for Th(IV)–N_{amide} and Th(IV)–N_{amine} bond distances.¹² The bite angles of 63.7(3)° and 66.8(3)° at Th1 and Th2, respectively, allude to the high degree of geometric strain within the four-membered [Th–N–Si–C] thoracyclic rings with the former value contributing to the considerably extended Th1–C1 bond distance in **4**.

Significantly, the Th1–C1 bond distance in **4** is approximately 0.12 Å longer than the comparable U–C bond distance [2.752(11) Å] in the reported uranium(IV) analogue $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t\text{CH}_2)\}]$ (**I**). This distance is more than double the expected extension (*ca.* 0.05 Å) resulting from the difference in ionic radius between U(IV) (0.89 Å) and Th(IV) (0.94 Å)^{13, 19} however it should be noted that the mean value for the other three Th–C bond distances in **4** of 2.775(11) Å is statistically identical to the U–C bond distance in **I** and that **I** is mononuclear in the solid state and features one tuck-in cyclometallated alkyl unit. The presence of a second highly polarizing thorium center in **4** forming a $\mu^2\text{-CH}_2$ unit reduces the degree of localization of electron density at the CH₂ centers which could account for the extended Th1–C1 bond length; the difference in Th–C bond distances within **4** is tentatively ascribed to a combination of solid state effects whereby a geometric distortion within the Th₂C₂ ring acts to favorably redistribute electron density.

The lowering of the approximate symmetry of the $\text{Tren}^{\text{DMBS}}$ ligand from C_{3v} in **2** to C_s in **4** is reflected in the ¹H and ¹³C{¹H} NMR spectra of the latter, each of which exhibits a total of seventeen resonances in the range 0.04 to 4.02 and –6.58 to 56.72 ppm, respectively, therefore it is not clear whether the dinuclear structure of **4** is maintained in

solution at room temperature. Both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **4** show broadly close agreement with the published assignment¹⁹ and the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **4** features only a single resonance at -2.67 ppm. No intermediates were observed when the reaction of **2** with benzylpotassium was monitored by ^1H NMR spectroscopy, with the only resonances present in the final spectrum assigned to **4** and toluene.

The isolation of **4** – and not the corresponding thorium benzyl complex – is notable in that we have previously shown that $[\text{Th}(\text{Tren}^{\text{TIPS}})(\text{CH}_2\text{Ph})]$ could be prepared and required thermolysis to access the cyclometallated derivative,¹¹ whereas evidently the putative complex “ $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{CH}_2\text{Ph})]$ ” readily cyclometallates and extrudes toluene to afford **4**. This contrast in reactivities is ascribed to the increased proximity of the alkylsilyl arm of the $\text{Tren}^{\text{DMBS}}$ ligand to the thorium center relative to that for $\text{Tren}^{\text{TIPS}}$, explaining also how the formation of a more geometrically strained four-membered metallacyclic ring does not require thermal initiation whereas a less strained five-membered ring does. We suggest that the dimeric nature of **4** compared to monomeric **I** can be attributed to the larger size of thorium, compared to uranium, thus enabling dimerization in the former in the solid state.

In attempts to access a target SSIP complex, equimolar quantities of **4** and $[\text{Et}_3\text{NH}][\text{BAr}_4]$ [$\text{Ar} = \text{Ph}$; $3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$] were reacted at room temperature in THF. Despite exhaustive attempts at varying work-up procedures, the pale yellow oily solids obtained proved to be intractable and their ^1H NMR spectra consistently suggested a mixture of products. Whilst Tren-uranium SSIP complexes are known to be poorly crystalline, even the addition of one equivalent of **1** to these mixtures failed to produce sufficiently suitable crystalline material for XRD analysis.¹⁸

In order to assess whether $\text{Tren}^{\text{DMBS}}$ SSIP complexes might be accessible we examined the reaction of **1** with $[\text{Et}_3\text{NH}][\text{BPh}_4]$ in THF (Scheme 2).

Scheme 2 – Experimental synthesis of the $\text{Tren}^{\text{DMBS}}$ -uranium SSIP complex **5**.

Following work-up, the green-brown solid produced appeared to be consistent with the formation of “ $[\text{U}(\text{Tren}^{\text{DMBS}})(\text{THF})][\text{BPh}_4]$ ” by inspection of its ^1H NMR spectrum however persistent impurities precluded any further analysis and slowly cooled saturated solutions of this solid in THF afforded oily material. However, dissolution in a toluene/acetonitrile mix resulted in the formation of a yellow-brown solution which upon cooling yielded green-brown crystals suitable for a single crystal X-ray diffraction study. The molecular structure of $[\text{U}(\text{Tren}^{\text{DMBS}})(\text{NCMe})_2][\text{BPh}_4]$ (**5**) is illustrated in Figure 4 with selected bond distances and angles.

Figure 4 – Molecular structure of 5 with displacement ellipsoids set at 30% probability. Hydrogen atoms, lattice solvent and minor disorder components are omitted for clarity. Selected bond lengths (Å) and angles (°): U1–N1, 2.208(6); U1–N2, 2.231(6); U1–N3, 2.223(7); U1–N4, 2.577(6); U1–N5, 2.542(6); U1–N6, 2.647(7); N2–U1–N6, 176.3(2); N5–U1–N4, 165.6(2); N5–U1–N6, 83.21(19).

The solid state structure of **5** consists of a $[\text{U}(\text{Tren}^{\text{DMBS}})(\text{NCMe})_2]^+$ cation and a non-coordinated tetraphenylborate anion. The uranium center in **5** is six-coordinate, adopting a distorted octahedral geometry with two molecules of acetonitrile coordinated through nitrile centers N5 and N6 residing essentially *trans* to the amine and amide centers N4 and N1, respectively $[\text{N5–U1–N4} = 165.6(2)^\circ, \text{N2–U1–N6} = 176.3(2)^\circ]$ and approximately *cis* to each other $[\text{N5–U1–N6} = 83.21(19)^\circ]$. The bond lengths and angles in **5** are generally as expected, with $\text{U–N}_{\text{amide}}$ and $\text{U–N}_{\text{amine}}$ bond lengths of 2.220(6) (av.) and 2.577(6) Å, respectively, typical of $\text{U(IV)–N}_{\text{amide}}$ and $\text{U(IV)–N}_{\text{amine}}$ bond distances, exhibiting the expected contraction relative to many comparable neutral Tren-uranium systems as is the case for $[\text{U}(\text{Tren}^{\text{TMS}})(\text{THF})_2][\text{BPh}_4]$ (**II**).^{12, 18} The $\text{U–N}_{\text{nitrile}}$ bond distances of 2.542(6) and 2.647(7) Å are statistically distinct but lie within the reported range of $\text{U(IV)–N}_{\text{nitrile}}$ bond distances, with the comparatively lengthened U1–N6 bond distance a consequence of its location *trans* to the anionic amide center N1 and not a neutral amine, as is the case for N5. The metrical parameters of the tetraphenylborate anion in the solid state structure of **5** are unremarkable.

The ^1H NMR spectrum of **5** exhibits paramagnetically shifted resonances that span the chemical shift range +17 to –42 ppm and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** reveals one resonance at –7.12 ppm, which compares to a chemical shift range of +16 to –43 ppm and one resonance at –10.17 ppm in the ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, respectively, for **II**.¹⁸ Complex **5** exhibits a room temperature solution magnetic moment of 1.50 μ_{B} , as

obtained by Evans method, which is low for Tren-uranium(IV) complexes although it compares to a value of 2.10 for **II**. The μ_{eff} value of 1.50 μ_{B} for **5** suggests that the orbital angular contribution at uranium to the solution room temperature effective magnetic moment is partially suppressed, potentially due to the cationic nature of complex **5**.²⁵ All other analytical data are as expected.

Reactivity of Complex 4

The extended nature of the Th–C bonds in **4**, and the implicit implication for high reactivity, is borne out in the observation that when stored as a solution in ethereal solvents above 0 °C for periods of more than 24 hours, **4** decomposes into a number of unidentifiable products. On one occasion, however, a very small quantity of colorless single crystals suitable for an X-ray diffraction study were able to be isolated and the molecular structure of $[\text{Th}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)_2(\text{CH}_2\text{CH}_2\text{NSiMeBu}^t\text{CH}_2-\mu\text{-O})\}]_2$, **6**, is illustrated in Figure 5 with selected bond lengths and angles.

Figure 5 – Molecular structure of **6** with displacement ellipsoids set at 30% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond lengths (Å) and angles (°): Th1–O1, 2.425(5); Th1–O2, 2.387(4); Th1–N1, 2.366(6); Th1–N2, 2.341(5); Th1–N3, 2.343(6); Th1–N4, 2.656(5); O1–C1, 1.454(8); Th2–O1, 2.369(4); Th2–O2, 2.415(5); Th2–N5, 2.350(6); Th2–N6, 2.288(19); Th2–N7, 2.288(19); Th2–N8, 2.721(5) O2–C25, 1.444(9); N1–Th1–O1, 72.86(18); N5–Th2–O2, 74.08(19).

The solid state structure of **6** is dinuclear, featuring one Tren^{DMBS} ligand coordinated to each thorium center, which is bridged by two μ^2 -alkoxide centers. The Th centers each adopt a distorted octahedral geometry with Th–N_{amide}, Th–N_{amine} and Th–O bond lengths of 2.329(10) (av.), 2.689(5) and 2.399(4) Å, respectively, typical of Th(IV)–N_{amide}, Th(IV)–N_{amine} and Th(IV)–(μ^2 -O) bond distances.¹² The C–O bond distances of 1.454(8) and 1.444(9) Å are indistinguishable and suggestive of single bond character. The Th₂O₂ ring is slightly unsymmetrical with the Th–O bond distances suggesting that O1 exhibits a slightly closer association with Th2 and O2 with Th1 as demonstrated by a contraction

of *ca.*0.04 Å of the Th2–O1/Th1–O2 bond distances relative to the Th1–O1/Th2–O2 bond distances. The bite angles of 72.86(18)° and 74.08(19)° are expanded by approximately 8° *versus* those observed in **4** and are reflective of the 5-membered [Th–N–Si–C–O] ring in **6** relative to the smaller ring size in **4**.

The isolation of **6** is suggestive of oxo insertion into the thorium alkyl bond with the source of O presumably the ethereal solvent, which is supported by the observation that no such decomposition is seen upon storage of **4** as a solution in hydrocarbon solvents. Due to the low crystalline yield of **6** no further characterization could be carried out and unfortunately our attempts to prepare **6** by rational methods have not been successful.

Summary and Conclusions

As part of our investigations into actinide triamidoamine chemistry, we have prepared and characterized Th(IV) chloride [Th(Tren^{DMBS})(Cl)(THF)] (**1**) and iodide [Th(Tren^{DMBS})(I)] (**2**) complexes supported by the sterically encumbered Tren^{DMBS} ligand. Targeting separated ion pair compounds as useful synthetic intermediates, **1** was converted into the diethylamido derivative [Th(Tren^{DMBS})(NEt₂)] (**3**) although this did not transform into the desired ion pair complex upon reaction with [Et₃NH][BPh₄]. Attempting to access the benzyl derivative of **2** via reaction with PhCH₂K instead furnished a cyclometallated Th-Tren^{DMBS} complex [Th{N(CH₂CH₂NSiMe₂Bu^t)₂(CH₂CH₂NSiMeBu^t-μ-CH₂)}]₂ (**4**), which was shown to be dinuclear in the solid state featuring the longest yet reported Th(IV)–C_{alkyl} bond distance of 2.875(9) Å. A thorium-Tren^{DMBS} SSIP complex remained elusive, although we were able to show that the analogous uranium system could be accessed in the form of [U(Tren^{DMBS})(NCMe)₂][BPh₄] (**5**). Complex **4** decomposed upon storage in ethereal solvents and we have identified a product of oxo insertion into the thorium-σ-alkyl bond

in **4**, [$\{\text{Th}(\text{N}[\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t]_2[\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t\text{CH}_2-\mu^2\text{-O}])_2\}$] (**6**) which exhibits a dinuclear Th_2O_2 core.

Experimental Section

General

All manipulations were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use except HMDSO and MeCN which were distilled from CaH_2 . All solvents were stored over potassium mirrors except ethers and MeCN which were stored over activated 4 Å and 3 Å sieves, respectively. Methylcyclohexane was distilled from potassium and stored over a potassium mirror. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. $[\text{Li}_3(\text{Tren}^{\text{DMBS}})(\text{THF})_3]$ [$\text{Tren}^{\text{DMBS}} = \text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_2\text{Bu}^t)_3$),²⁶ $[\text{KCH}_2\text{Ph}]$ ²⁷ and $[\text{Et}_3\text{NH}][\text{BPh}_4]$ ²⁸ were prepared as described previously. $[\text{LiNEt}_2]$ was isolated as a colorless solid which precipitated from the reaction between n-butyllithium and diethylamine in hexanes, dried *in vacuo* and used without further purification following filtration. $[\text{ThCl}_4(\text{THF})_{3.5}]$ was prepared from $[\text{ThCl}_4(\text{DME})_2]$ by an adapted method based on the reported procedure.¹¹ Me_3SiI was purchased from Sigma-Aldrich, filtered from activated magnesium to remove acid traces, degassed by three freeze-pump-thaw cycles and stored under nitrogen in the dark at 5 °C. All other reagents were used as received. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV400 spectrometer [operating at 400.2 (^1H), 100.6 (^{13}C) and 79.5 (^{29}Si) MHz, respectively]; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer and samples were prepared in the glovebox as Nujol® mulls between KBr discs. CHN microanalyses were

carried out by Dr Tong Liu at the University of Nottingham. Some complexes persistently present low carbon percentages which is a phenomena often observed in complexes rich in organo-silicon functionalities.²⁹

Preparation of [Th(Tren^{DMBS})(Cl)(THF)] (1)

THF (15 ml) was added to a cold (−78 °C) mixture of [ThCl₄(THF)_{3.5}] (3.13 g, 5.0 mmol) and Tren^{DMBS}Li₃(THF)₃ (3.62 g, 5.0 mmol). The resulting suspension was allowed to warm to ambient temperature whilst being stirred (1 hour) and stirred at ambient temperature for a further 16 hours to afford a pale yellow suspension. The solvent was removed *in vacuo* to afford an off-white sticky solid. Hexane (10 ml) was added and the suspension was warmed to 50 °C, allowed to settle and filtered to give a pale yellow solution. The residual white solid was washed with hexane (3 × 2 ml) and the solvent removed from the combined extracts *in vacuo* to afford an essentially pure off-white solid. Crystalline material was obtained via dissolution in pentane (5 ml) and storage at −80 °C for 24 hours to afford colorless crystals that were isolated by filtration at −80 °C, washed with cold pentane (3 × 2 ml) and dried *in vacuo* for 30 minutes. A second crop of crystals was obtained by the reduction of the supernatant solution to 1 ml and storage at −80 °C for 24 hours. Yield: solid 4.04 g (98%) or crystalline 2.35 g (57%). ¹H NMR (C₆D₆, 298 K): δ 0.51 (s, 18H, SiMe₂), 1.15 (s, 27H, ^tBu), 1.54 (s, 4H, THF), 2.47 (t, ²J_{HH} = 5.2 Hz, 6H, CH₂), 3.54 (t, ²J_{HH} = 4.8 Hz, 6H, CH₂), 3.73 (s, 4H, THF) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ −4.90 (s, SiMe₂), 20.33 (s, CMe₃), 25.43 (s, THF), 26.88 (s, CMe₃), 46.90 (s, CH₂), 63.35 (s, CH₂), 68.63 (s, THF) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ −2.18 ppm. FTIR (Nujol): ν 1304.26 (w), 1259.51 (s), 1140.76 (w), 1079.39 (s), 1061.81 (m), 1022.55 (m), 925.63 (s), 896.41 (w), 826.25 (s), 801.25 (s), 774.44 (m), 740.14 (w), 710.24 (m), 660.46 (m), 635.74 (w), 559.55 (w), 526.45 (w), 455.86 (m)

cm⁻¹. Anal. calc'd for C₂₈H₆₅ClN₄OSi₃Th: C 40.73%; H 7.94%; N 6.79%. Found: C 38.82%; H 7.61%; N 6.44%.

Preparation of [Th(Tren^{DMBS})(Cl)]

[Th(Tren^{DMBS})(Cl)(THF)] (2.35 g, 2.9 mmol) was heated carefully to 60 °C at 10⁻⁵ mbar over 1 hour and maintained at this temperature for a further 8 hours. The essentially pure white solid was recrystallised from 1.5 ml ^tBuOMe at -30 °C over 16 hours to yield colorless crystals, which were isolated by filtration at -30 °C, washed with cold hexane (3 × 2 ml) and dried *in vacuo* for 30 minutes. A second crop of crystals was obtained by the reduction of the supernatant solution to 1 ml and storage at -30 °C for 24 hours. Yield: solid 2.11 g (98%) or crystalline 0.86 g (40%). ¹H NMR (C₆D₆, 298 K): δ 0.51 (s, 18H, SiMe₂), 1.13 (s, 27H, ^tBu), 2.46 (t, ²J_{HH} = 4.8 Hz, 6H, CH₂), 3.53 (t, ²J_{HH} = 5.2 Hz, 6H, CH₂) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ -4.30 (s, SiMe₂), 20.12 (s, CMe₃), 26.76 (s, CMe₃), 46.81 (s, CH₂), 64.15 (s, CH₂) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ -2.21 ppm. FTIR (Nujol): ν 1304.79 (w), 1250.31 (s), 1141.56 (m), 1109.80 (s), 1079.89 (m), 1062.73 (w), 1024.00 (m), 1006.75 (m), 925.33 (s), 895.76 (m), 827.71 (s), 801.24 (s), 788.44 (s), 774.28 (w), 722.04 (m), 661.00 (m), 635.26 (m), 588.26 (w), 558.86 (w), 526.52 (w) cm⁻¹. Anal. calc'd for C₂₄H₅₇ClN₄Si₃Th: C 38.27 %; H 7.63 %; N 7.44 %. Found: C 38.33%; H 7.66%; N 7.40%.

Preparation of [Th(Tren^{DMBS})(I)] (2)

Me₃SiI (0.4 ml, 2.7 mmol) was added *via* syringe to a cold (0 °C) stirring solution of [Th(Tren^{DMBS})(Cl)(THF)] (2.00 g, 2.4 mmol) in hexane (10 ml). The solution was allowed to warm to room temperature over 1 hour before being heated to 55 °C and maintained at this temperature for 16 hours to afford a white suspension. Volatiles were removed *in vacuo* and the white solid obtained was suspended in 10 ml hexane, filtered,

washed with hexane (2×3 ml) and dried *in vacuo* for 30 minutes to afford essentially pure material as a white solid. Crystalline material was obtained by dissolution in warm (60 °C) toluene (2.5 ml) and storage at -30 °C for 24 hours to afford colorless crystals that were isolated by filtration, washed with hexane (3×2 ml) and dried *in vacuo* for 30 minutes. Yield: solid 1.26 g (62%) or crystalline 0.87 g (43%). ^1H NMR (C_6D_6 , 298 K): δ 0.54 (s, 18H, SiMe_2), 1.14 (s, 27H, ^tBu), 2.40 (t, $^2J_{\text{HH}} = 4.8$ Hz, 6H, CH_2), 3.50 (t, $^2J_{\text{HH}} = 4.8$ Hz, 6H, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ -5.32 (s, SiMe_2), 20.13 (s, CMe_3), 27.01 (s, CMe_3), 46.97 (s, CH_2), 64.51 (s, CH_2) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ -1.76 ppm. FTIR (Nujol): ν 1335.94 (w), 1256.47 (s), 1141.00 (m), 1070.95 (s), 1062.34 (s), 1022.09 (m), 923.88 (s), 895.65 (m), 825.96 (s), 815.87 (s), 800.93 (s), 773.79 (s), 752.00 (s), 738.87 (m), 722.56 (m), 705.07 (m), 659.35 (m), 565.89 (w), 459.04 (w) cm^{-1} . Anal. calc'd for $\text{C}_{24}\text{H}_{57}\text{IN}_4\text{Si}_3\text{Th}$: C 34.12%; H 6.80%; N 6.63%. Found: C 34.61%; H 6.80%; N 6.63%.

Preparation of $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{NEt}_2)]$ (3)

Toluene (15 ml) was added to a cold (-78 °C) mixture of $[\text{Th}(\text{Tren}^{\text{DMBS}})(\text{Cl})(\text{THF})]$ (0.79 g, 1.0 mmol) and $[\text{LiNEt}_2]$ (79 mg, 1.0 mmol). The resulting solution was allowed to warm to ambient temperature whilst being stirred (1 hour) and stirred at ambient temperature for a further 16 hours to afford a turbid pale yellow solution. Volatiles were removed *in vacuo* to afford a yellow sticky solid which was extracted into warm (50 °C) hexane (10 ml) and filtered to give a pale yellow solution. The solvent was removed *in vacuo* to afford a pale pink oily solid to which hexamethyldisiloxane (HMDSO, 1 ml) was added the resulting solution was stored at 5 °C overnight to afford colorless crystals that were isolated by filtration, washed with cold (-30 °C) HMDSO (2×0.5 ml) and dried *in vacuo* for 30 minutes. Yield: 0.26 g (33%). ^1H NMR (C_6D_6 , 298 K): δ 0.41 (s, 18H, SiMe_2), 1.17 (s, 27H, ^tBu), 1.35 (t, $^2J_{\text{HH}} = 7.0$ Hz, 6H, CH_2CH_3), 2.54 (t, $^2J_{\text{HH}} = 4.7$

Hz, 6H, CH₂), 3.50 (q, ²J_{HH} = 7.0 Hz, 6H, CH₂CH₃), 3.54 (t, ²J_{HH} = 4.7 Hz, 6H, CH₂) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ -4.60 (s, SiMe₂), 14.51 (s, CH₂CH₃), 20.45 (s, CMe₃), 27.45 (s, CMe₃), 40.94 (s, CH₂CH₃), 45.61 (s, CH₂), 64.96 (s, CH₂) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ -1.43 ppm. FTIR (Nujol): ν 1302.88 (w), 1257.67 (m), 1173.87 (w), 1145.46 (w), 1074.22 (s), 1026.26 (m), 928.69 (s), 892.53 (w), 824.30 (s), 803.48 (s), 787.60 (m), 771.45 (m), 739.41 (w), 720.51 (m), 657.72 (w), 626.11 (w) cm⁻¹. Anal. calc'd for C₂₈H₆₇N₅Si₃Th: C 42.56%; H 8.55%; N 8.87%. Found: C 42.03%; H 8.58%; N 8.32%.

Preparation of [Th{N(CH₂CH₂NSiMe₂Bu^t)₂(CH₂CH₂NSiMeBu^t-μ-CH₂)}]₂ (4)

Toluene (15 ml) was added to a cold (-78 °C) mixture of [Th(Tren^{DMBS})(I)] (1.69 g, 2.0 mmol) and benzylpotassium (0.26 g, 2.0 mmol). The resulting mixture was allowed to warm to ambient temperature whilst being stirred (1 hour) and stirred at ambient temperature for a further 16 hours to afford an off-white suspension, which was filtered. The solvent was removed *in vacuo* to afford an off-white solid. Crystalline material was obtained *via* extraction into warm (40 °C) hexane (5 ml), filtration and reduction in volume to 2 ml. Storage at 5 °C for 18 hours afforded colorless crystals that were isolated by filtration at -10 °C, washed with pentane (2 × 2 ml) and dried *in vacuo* for 30 minutes. *Caution*: heating (>70 °C) of this compound as a solid or in solution leads to instantaneous decomposition to multiple products and if left in solution at room temperature for > 12 hours in the presence of ether solvents oxo abstraction products are formed. Yield: solid 1.32 g (92%) or crystalline 0.59 g (41%). ¹H NMR (C₆D₆, 298 K): δ 0.04 (s, br, 2H, 2 × ThCH), 0.12 (s, br, 2H, 2 × ThCH), 0.29 (s, 6H, 2 × MeSi), 0.40 (s, 6H, 2 × MeSi), 0.54 (s, 6H, 2 × MeSi), 0.59 (s, 6H, 2 × MeSi), 0.76 (s, 6H, 2 × MeSi), 1.03 (s, 18H, 2 × ^tBu), 1.08 (s, 18H, 2 × ^tBu), 1.36 (s, 18H, 2 × ^tBu), 2.32 (m, 4H, 4 × CH), 2.41 (m, 2H, 2 × CH), 2.93 (m, 6H, 6 × CH), 3.44 (m, 2H, 2 × CH), 3.68 (m, 2H, 2

× CH), 3.73 (m, 6H, 6 × CH), 4.02 (m, 2H, 2 × CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ -6.58 (s, MeSi), -6.41 (s, MeSi), -6.06 (s, MeSi), -5.65 (s, MeSi), -2.42 (s, MeSiCH₂Th), 19.70 (s, Me₃C), 19.92 (s, Me₃C), 20.74 (s, Me₃C), 26.96 (s, Me₃C), 27.61 (s, Me₃C), 28.46 (s, Me₃C), 47.75 (s, CH₂), 48.32 (s, CH₂), 49.24 (s, CH₂), 56.17 (s, CH₂), 56.84 (s, br, CH₂), ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ -2.67 ppm. FTIR (Nujol): ν 1259.64 (s), 1141.98 (m), 1074.92 (s), 1022.98 (s), 929.61 (s), 900.75 (m), 824.37 (s), 806.04 (s), 771.72 (m), 721.88 (m), 658.07 (w), 587.80 (w), 533.83 (w) cm^{-1} . Anal. calc'd for $\text{C}_{48}\text{H}_{112}\text{N}_8\text{Si}_6\text{Th}_2$: C 40.20 %; H 7.88%; N 7.82 %. Found: C 39.48%; H 7.79%; N 7.53%.

Preparation of $[\text{U}(\text{Tren}^{\text{DMBS}})(\text{NCMe})_2][\text{BPh}_4]$ (5)

THF (20 ml) was added to a cold ($-78\text{ }^\circ\text{C}$) mixture of $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t)(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}^t\text{CH}_2)\}]$ (0.72 g, 1.0 mmol) and $[\text{Et}_3\text{NH}][\text{BPh}_4]$ (0.42 g, 1.0 mmol). The resulting green mixture was allowed to warm to ambient temperature whilst being stirred (1 hour) and stirred at ambient temperature for a further 16 hours to afford a green solution. The solvent was removed *in vacuo* to afford a green solid, which was suspended in toluene/MeCN (2:1 ml) and warmed to $70\text{ }^\circ\text{C}$ until the solid dissolved. The yellow-brown solution was allowed to cool to room temperature and stored at $-30\text{ }^\circ\text{C}$ for 18 hours to afford green crystals, which were isolated by filtration at $-10\text{ }^\circ\text{C}$ washed with toluene ($3 \times 2\text{ ml}$) and dried *in vacuo* for 30 minutes. Yield: 0.34 g (30%). ^1H NMR ($\text{C}_6\text{D}_6 + 10\text{ vol\% MeCN}$, presaturation suppression at $\delta = 1.45\text{ ppm}$, 298 K): δ -41.51 (s, 6H, CH₂), 1.62 (s, 6H, NCMe), 6.42 (m, 4H, *p*-ArH), 6.48 (m, 8H, *m*-ArH), 6.80 (m, 8H, *o*-ArH), 10.27 (s, 27H, Bu^t), 10.95 (s, 18H, SiMe₂) 17.43 (s, 6H, CH₂) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6 + 10\text{ vol\% MeCN}$, 298 K): δ -7.12 ppm. μ_{eff} (Evans method, $\text{C}_6\text{D}_6 + 10\text{ vol\% MeCN}$, 298 K): $1.50\text{ }\mu_{\text{B}}$. FTIR (Nujol): ν 2360.37 (s), 2341.44 (s), 2261.38 (s), 1308.14 (m), 1258.66 (m), 1179.95 (m), 1141.99 (w), 921.47

(m), 898.93 (m), 827.40 (w), 803.85 (m), 776.86 (w), 759.46 (m), 729.71 (m), 703.80 (m), 668.38 (w), 625.35 (w), 614.40 (w), 605.12 (m), 587.91 (w) cm^{-1} . Anal. calc'd for $\text{C}_{52}\text{H}_{83}\text{BN}_6\text{Si}_3\text{U}\cdot 0.25(\text{C}_7\text{H}_8)$: C 56.22%; H 7.46%; N 7.32%. Found: C 56.06%; H 7.74%; N 7.52%.

X-ray Crystallography

Crystal data for compounds **1-6** can be found in cif format in the Supporting Information. Selected bond lengths and angles are listed in the figure captions. Crystals were examined variously on a Bruker APEX CCD area detector diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), or on an Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Intensities were integrated from data recorded on 0.3° (APEX) or 1° (SuperNova) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption correction based on symmetry-equivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption correction with a beam profile correction (Supernova) were applied. The structures were solved variously by direct and heavy atom methods and were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{\text{iso}}(\text{H})$ was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Highly disordered solvent molecules of crystallization in **1**· C_6H_{14} , **5**· C_7H_8 could not be modelled and were treated with the Platon SQUEEZE procedure.³⁰ Programs were Bruker AXS SMART³¹ and CrysAlisPro³² (control), Bruker

AXS SAINT³¹ and CrysAlisPro³² (integration), and SHELX³³ and OLEX2³⁴ were employed for structure solution and refinement and for molecular graphics.

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Supporting Information

Crystallographic data for **1-6** in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

1. (a) Hayes, C. E.; Leznoff, D. B. *Coord. Chem. Rev.* **2014**, 266-267, 155-170; (b) Mulvey, R. E.; Robertson, S. D., *Angew. Chem., Int. Ed.* **2013**, 52, 11470-11487; (c) Baker, R. J. *Coord. Chem. Rev.* **2012**, 256, 2843-2871; (d) Liu, P.; Zhang, Y.; Yao, Y.; Shen, Q., *Organometallics* **2012**, 31, 1017-1024; (e) Wu, Y.; Wang, S.; Zhu, X.; Yang, G.; Wei, Y.; Zhang, L.; Song, H.-b., *Inorg. Chem.* **2008**, 47, 5503-5511; (f) Yao, Y.; Zhang, Z.; Peng, H.; Zhang, Y.; Shen, Q.; Lin, J., *Inorg. Chem.* **2006**, 45, 2175-2183; (g) Sessler, J. L.; Melfi, P. J.; Pantos, G. D. *Coord. Chem. Rev.* **2006**, 250, 816-843; (h) Grotjahn, D. B.; Sheridan, P. M.; Jihad, I. A.; Ziurys, L. M., *J. Am. Chem. Soc.* **2001**, 123, 5489-5494; (i) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G., *J. Am. Chem. Soc.* **2000**, 122, 8799-8800; (j) Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B., *Angew. Chem., Int. Ed.* **1998**, 37, 3180-3183; (k) Beberich, H.; Roesky, P. W., *Angew. Chem., Int. Ed.* **1998**, 37, 1569-1571; (l) Berthet, J. -C.; Ephritikhine, M. *Coord. Chem. Rev.* **1998**, 178-180, 83-116; (m) Paver, M. A.; Russell, C. A.; Wright, D. S., *Angew. Chem., Int. Ed. Engl.* **1995**,

- 34, 1545-1554; (n) Plass, W.; Verkade, J. G., *J. Am. Chem. Soc.* **1992**, *114*, 2275-2276;
- (o) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M., *Angew. Chem., Int. Ed.* **1992**, *104*, 1489-1492.
2. Selected examples: (a) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F., *Inorg. Chem.* **2009**, *48*, 11444-11450; (b) Lappert, M.; Protchenko, A.; Power, P.; Seeber, A., *Metal Amide Chemistry*. John Wiley & Sons, Inc.: 2008; (c) Hitchcock, P. B.; Hulkes, A. G.; Lappert, M. F., *Inorg. Chem.* **2004**, *43*, 1031-1038; (d) Hitchcock, P. B.; Huang, Q.-G.; Lappert, M. F.; Wei, X.-H., *J. Mater. Chem.* **2004**, *14*, 3266-3273; (e) Bourget-Merle, L.; Hitchcock, P. B.; Lappert, M. F., *J. Organomet. Chem.* **2004**, *689*, 4357-4365; (f) Antolini, F.; Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F., *Eur. J. Inorg. Chem.* **2003**, 3391-3400; (g) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Hulkes, A. G.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V., *J. Organomet. Chem.* **2002**, *647*, 71-83; (h) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R., *Chem. Rev.* **2002**, *102*, 3031-3066; (i) Hitchcock, P. B.; Lappert, M. F.; Merle, P. G., *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *168-169*, 363-366; (j) Daniele, S.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G., *J. Chem. Soc., Dalton Trans.* **2001**, 13-19; (k) Bourget-Merle, L.; Hitchcock, P. B.; Lappert, M. F., *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *168-169*, 609-612; (l) Antolini, F.; Hitchcock, P. B.; Lappert, M. F.; Merle, P., *Chem. Comm.* **2000**, 1301-1302; (m) Hitchcock, P. B.; Jang, E.; Lappert, M. F., *J. Chem. Soc., Dalton Trans.* **1995**, 3179-3187.
3. (a) Smiles, D. E.; Wu, G.; Hayton, T. W., *Inorg. Chem.* **2014**, *53*, 10240-10247; (b) Goodwin, C. A. P.; Tuna, F.; McInnes, E. J. L.; Liddle, S. T.; McMaster, J.; Vitorica-Yrezabal, I. J.; Mills, D. P., *Chem.-Eur. J.* **2014**, *20*, 14579-14583; (c) Franke, S. M.; Heinemann, F. W.; Meyer, K., *Chem. Sci.* **2014**, *5*, 942-950; (d) Lewis, A. J.; Mullane, K. C.; Nakamaru-Ogiso, E.; Carroll, P. J.; Schelter, E. J., *Inorg. Chem.* **2014**, *53*, 6944-

- 6953; (e) Mullane, K. C.; Lewis, A. J.; Yin, H.; Carroll, P. J.; Schelter, E. J., *Inorg. Chem.* **2014**, *53*, 9129-9139; (f) Anderson, N. H.; Odoh, S. O.; Yao, Y.; Williams, U. J.; Schaefer, B. A.; Kiernicki, J. J.; Lewis, A. J.; Goshert, M. D.; Fanwick, P. E.; Schelter, E. J.; Walensky, J. R.; Gagliardi, L.; Bart, S. C., *Nat. Chem.* **2014**, *6*, 919-926; (g) Hayton, T. W., *Chem. Comm.* **2013**, *49*, 2956-2973; (h) Lewis, A. J.; Williams, U. J.; Carroll, P. J.; Schelter, E. J., *Inorg. Chem.* **2013**, *52*, 7326-7328; (i) La Pierre, H. S.; Meyer, K., *Inorg. Chem.* **2013**, *52*, 529-539; (j) Lewis, A. J.; Carroll, P. J.; Schelter, E. J., *J. Am. Chem. Soc.* **2013**, *135*, 511-518; (k) Fortier, S.; Brown, J. L.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W., *Inorg. Chem.* **2012**, *51*, 1625-1633; (l) Brown, J. L.; Fortier, S.; Lewis, R. A.; Wu, G.; Hayton, T. W., *J. Am. Chem. Soc.* **2012**, *134*, 15468-15475; (m) Lam, O. P.; Franke, S. M.; Nakai, H.; Heinemann, F. W.; Hieringer, W.; Meyer, K., *Inorg. Chem.* **2012**, *51*, 6190-6199; (n) Lewis, A. J.; Nakamaru-Ogiso, E.; Kikkawa, J. M.; Carroll, P. J.; Schelter, E. J., *Chem. Comm.* **2012**, *48*, 4977-4979; (o) Arnold, P. L.; Mansell, S. M.; Maron, L.; McKay, D., *Nat. Chem.* **2012**, *4*, 668-674; (p) Lam, O. P.; Heinemann, F. W.; Meyer, K., *Chem. Sci.* **2011**, *2*, 1538-1547; (q) Lam, O. P.; Meyer, K., *Angew. Chem., Int. Ed.* **2011**, *50*, 9542-9544; (r) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L., *J. Am. Chem. Soc.* **2011**, *133*, 9036-9051; (s) Arnold, P. L., *Chem. Comm.* **2011**, *47*, 9005-9010; (t) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K., *Science* **2004**, *305*, 1757-1760.
4. (a) King, D. M.; Liddle, S. T. *Coord. Chem. Rev.* **2014**, *266-267*, 2-15; (b) King, D. M.; McMaster, J.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T., *J. Am. Chem. Soc.* **2014**, *136*, 5619-5622; (c) Gardner, B. M.; Balazs, G.; Scheer, M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Angew. Chem., Int. Ed.* **2014**, *53*, 4484-4488; (d) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Nat. Chem.* **2013**, *5*, 482-488; (e) King, D. M.;

- Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Science* **2012**, 337, 717-720.
5. (a) King, D. M.; Tuna, F.; McMaster, J.; Lewis, W.; Blake, A. J.; McInnes, E. J. L.; Liddle, S. T., *Angew. Chem., Int. Ed.* **2013**, 52, 4921-4924; (b) Gardner, B. M.; Patel, D.; Cornish, A. D.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Chem.-Eur. J.* **2011**, 17, 11266-11273; (c) Patel, D.; King, D. M.; Gardner, B. M.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Chem. Comm.* **2011**, 47, 295-297; (d) Gardner, B. M.; McMaster, J.; Moro, F.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Chem.-Eur. J.* **2011**, 17, 6909-6912; (e) Gardner, B. M.; McMaster, J.; Lewis, W.; Liddle, S. T. *Chem. Commun.* **2009**, 2851-2853
6. Gardner, B. M.; Patel, D.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Angew. Chem., Int. Ed.* **2011**, 50, 10440-10443.
7. (a) Cleaves, P. A.; King, D. M.; Kefalidis, C. E.; Maron, L.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem. Int. Ed.* **2014**, 53, 10412-10415; (b) Gardner, B. M.; Stewart, J. C.; Davis, A. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 9265-9270.
8. (a) Roussel, P.; Boaretto, R.; Kingsley, A. J.; Alcock, N. W.; Scott, P., *J. Chem. Soc., Dalton Trans.* **2002**, 1423-1428; (b) Roussel, P.; Errington, W.; Kaltsoyannis, N.; Scott, P., *J. Organomet. Chem.* **2001**, 635, 69-74; (c) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P., *Chem. Comm.* **1999**, 1701-1702; (d) Roussel, P.; Alcock, N. W.; Boaretto, R.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P., *Inorg. Chem.* **1999**, 38, 3651-3656; (e) Roussel, P.; Scott, P.; D, T. N., *J. Alloys Compd.* **1998**, 271-273, 150-153; (f) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, 120, 1070-1071; (g) Roussel, P.; Hitchcock, P. B.; Tinker, N. D.; Scott, P., *Inorg.*

- Chem.* **1997**, *36*, 5716-5721; (h) Scott, P.; Hitchcock, P. B., *J. Chem. Soc., Dalton Trans.* **1995**, 603-609; (i) Scott, P.; Hitchcock, P. B., *Polyhedron* **1994**, *13*, 1651-1653.
9. (a) Johnson, K. R. D.; Hayes, P. G., *Chem. Soc. Rev.* **2013**, *42*, 1947-1960; (b) Montalvo, E.; Miller, K. A.; Ziller, J. W.; Evans, W. J., *Organometallics* **2010**, *29*, 4159-4170.
 10. Gardner, B. M.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T., *J. Am. Chem. Soc.* **2009**, *131*, 10388-10389.
 11. Gardner, B. M.; Cleaves, P. A.; Kefalidis, C. E.; Fang, J.; Maron, L.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Chem. Sci.* **2014**, *5*, 2489-2497.
 12. Allen, F. H., *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380-388.
 13. Shannon, R., *Acta Cryst., Sect. A* **1976**, *32*, 751-767.
 14. Maynadie, J.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M., *Organometallics* **2006**, *25*, 5603-5611.
 15. (a) Liddle, S. T.; McMaster, J.; Mills, D. P.; Blake, A. J.; Jones, C.; Woodul, W. D., *Angew. Chem., Int. Ed.* **2009**, *48*, 1077-1080.
 16. (a) Patel, D.; Moro, F.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem. Int. Ed.* **2011**, *50*, 10388-10392; (b) Patel, D.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Dalton Trans.* **2010**, *39*, 6638-6647.
 17. Evans, W. J.; Miller, K. A.; Hillman, W. R.; Ziller, J. W., *J. Organomet. Chem.* **2007**, *692*, 3649-3654.
 18. Gardner, B. M.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Inorg. Chem.* **2011**, *50*, 9631-9641.

19. Boaretto, R.; Roussel, P.; Alcock, N. W.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P., *J. Organomet. Chem.* **1999**, *591*, 174-184.
20. (a) Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, *15*, 186-197; (b) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S., *Dalton Trans.* **2008**, 2832-2838.
21. Rabinovich, D.; Chamberlin, R. M.; Scott, B. L.; Nielsen, J. B.; Abney, K. D., *Inorg. Chem.* **1997**, *36*, 4216-4217.
22. Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S., *Organometallics* **2001**, *20*, 5017-5035.
23. Seaman, L. A.; Walensky, J. R.; Wu, G.; Hayton, T. W., *Inorg. Chem.* **2013**, *52*, 3556-3564.
24. Cramer, R. E.; Hitt, J.; Chung, T.; Gilje, J. W., *New J. Chem.* **1995**, *19*, 509-514.
25. Cotton, S., Electronic and Magnetic Properties of the Actinides. In *Lanthanide and Actinide Chemistry*, John Wiley & Sons, Ltd: 2006; 201-208.
26. Roussel, P.; Alcock, N. W.; Scott, P., *Inorg. Chem.* **1998**, *37*, 3435-3436.
27. Schlosser, M.; Hartmann, J., *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508-509.
28. Barker, B. J.; Sears, P. G., *J. Chem. Phys.* **1974**, *78*, 2687-2688.
29. Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. *Angew. Chem. Int. Ed.* **2008**, *47*, 1488-1491.
30. Spek, A. L. *Platon* University of Utrecht, Utrecht, The Netherlands, **2000**.
31. *SMART* and *SAINT* Bruker AXS Inc., Madison, WI, USA, **2001**.

32. *CrysAlis PRO*, Agilent Technologies, Yarnton, England **2010**.
33. Sheldrick, G. M. *SHELXTL Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.
34. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2 J. Appl. Cryst.* **2009**, *42*, 339-341.

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