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Uranium-Halide and -Azide Derivatives of the Sterically Demanding Triamidoamine Ligand Tren^{TPS} [Tren^{TPS} = {N(CH₂CH₂NSiPh₃)₃}³⁻]

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Abstract

Treatment of tri(2-aminoethyl)amine with three equivalents of BuⁿLi followed by the addition of three equivalents of Ph₃SiCl afforded the triaminoamine Tren^{TPS}H₃ [**1**, Tren^{TPS}H₃ = N{CH₂CH₂N(H)SiPh₃}₃]. Subsequent treatment with three equivalents of BuⁿLi afforded the tri-lithium complex [(Tren^{TPS})(Li)₃] (**2**), which reacts with UCl₄ to afford the uranium(IV) complex [U(Tren^{TPS})(Cl)] (**3**). Complex **3** is an excellent synthon for further synthetic study, as evidenced by its conversion to the iodide analogue [U(Tren^{TPS})(I)] (**4**) or the azide congener [U(Tren^{TPS})(N₃)] (**5**) when treated with Me₃SiI or NaN₃, respectively. All the compounds in this study are isolated in excellent yields (>75%) and have been variously characterised by single crystal X-ray diffraction, multi-nuclear NMR spectroscopy, FTIR and UV/Vis/NIR spectroscopies, Evans method magnetic moment, and elemental analyses. A notable feature of complexes **2-5** is that they are monomeric and solvent-free, which suggests that the Tren^{TPS} ligand is very sterically demanding and could be well-suited to stabilising novel functional groups at uranium in a [U(Tren^{TPS})] context.

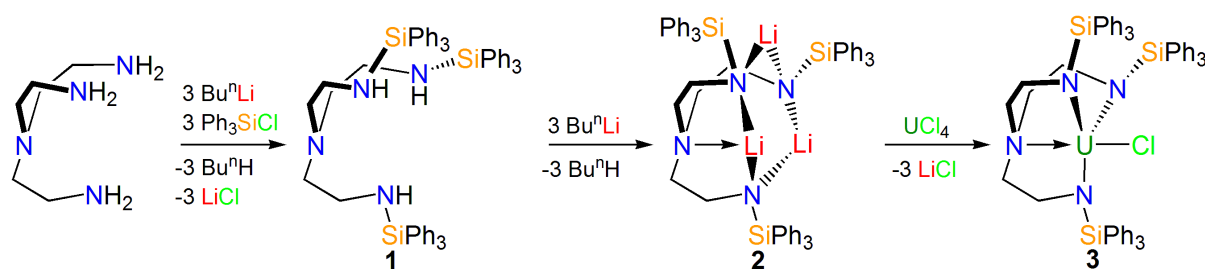
1. Introduction

As one of the largest metals in the periodic table, uranium – with a covalent single bond radius of 1.7 Å according to Pyykkö [1] – requires sterically demanding, polydentate ligands to saturate its coordination sphere and provide kinetic stabilisation to novel ligand linkages that may further our understanding of the extent and nature of covalency in uranium-ligand bonding [2]. One ligand class that has emerged as particularly effective for providing a pocket at uranium within which to stabilise reactive novel linkages, whilst closing down the remainder of the coordination sphere to avoid decomposition routes, is that of triamidoamines, $\{\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3\}^{3-}$ [3]. Indeed, in a wider context triamidoamine ligands have found many applications, for example including the stabilisation of novel ligands at metals, such as heavy NO analogues PS and AsS [4], and also metal-mediated dinitrogen reduction to ammonia [5]. Over the past two decades a range of triamidoamine-uranium complexes have been reported, and arguably the most effective of these have been where R = SiMe₃ (Tren^{TMS}), SiMe₂Bu^t (Tren^{DMBS}), and more recently SiPrⁱ₃ (Tren^{TIPS}) [3]. With these triamidoamines, whose steric bulk varies from moderate to quite demanding, a wide range of novel uranium chemistry has been reported, including the first uranium-dinitrogen complex [6], reductive homologation of carbon monoxide [7], single molecule magnetism [8], unusual photochemical- [9] and alkyl-reactivity [10], uranium-metal bonds [11], and uranium-ligand multiple bonding and novel main group fragments [12]. Indeed, recently the triamidoamine scaffold has been applied to thorium, and even neptunium and plutonium [10a,13]. Since it is well known that ligand steric demands principally impact the accessibility, stability, and thence reactivity, of uranium complexes [2], it is of interest to investigate new triamidoamine derivatives since they may provide opportunities to study complementary chemistry, or indeed provide access to new chemistry not amenable with the currently available

triamidoamines. Therefore, we have begun to investigate a new range of triamidoamines and their coordination chemistry at uranium.

Here, we report the synthesis of a new triamineamine pro-ligand with *N*-SiPh₃ substituents, and describe its conversion to the corresponding triamidoamine-tri-lithium salt. The latter is an excellent ligand transfer reagent that enables the synthesis of the corresponding triamidoamine uranium(IV)-chloride complex, which in turn can be converted to the triamidoamine-iodide or -azide derivatives. The solid state structures and spectroscopic data for these complexes are also presented.

2. Results and Discussion



Scheme 1. Synthesis of **1-3**.

2.1. Synthesis of **1** and **2**

Treatment of tri(2-aminoethyl)amine with three equivalents of BuⁿLi at -78 °C in THF, followed by the addition of three equivalents of Ph₃SiCl afforded the triaminoamine Tren^{TPS}H₃ [**1**, Tren^{TPS}H₃ = N{CH₂CH₂N(H)SiPh₃}₃] as a colourless solid in good (84%) yield after work-up and isolation, Scheme 1. Treatment of **1** with three further equivalents of BuⁿLi, following work-up, afforded the tri-lithium ligand transfer reagent [(Tren^{TPS})(Li)₃] (**2**) as a colourless powder, again in good yield (76%), Scheme 1. The synthesis of **2** is straightforward like that of the related [(Tren^{TIPS})(Li)₃] complex [12h], but contrasts to

$[(\text{Tren}^{\text{DMBS}})(\text{Li})_3]$ which can only be isolated as a THF-adduct [14]. NMR spectroscopy, elemental analysis and IR spectroscopy are consistent with the proposed formulations of **1** and **2**, with the ^1H NMR spectrum of only **1** exhibiting a characteristic *NH* resonance at 1.72 ppm and with an *NH* absorption band observed in the IR spectrum at 3400 cm^{-1} . Compounds **1** and **2** exhibit singlets in their $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra at 16.19 ppm and -15.46 ppm , respectively, suggesting complete conversion to the tri-substituted and tri-lithiated compounds with only one silicon environment. Complex **2** exhibits only one resonance in its ^7Li NMR spectrum (-2.39 ppm), which suggests a symmetrical species in solution on the NMR-timescale. To confirm the formulations of **1** and **2**, crystals were grown from saturated solutions in toluene, and their molecular structures were determined by single crystal X-ray diffraction (Figures 1 and 2).

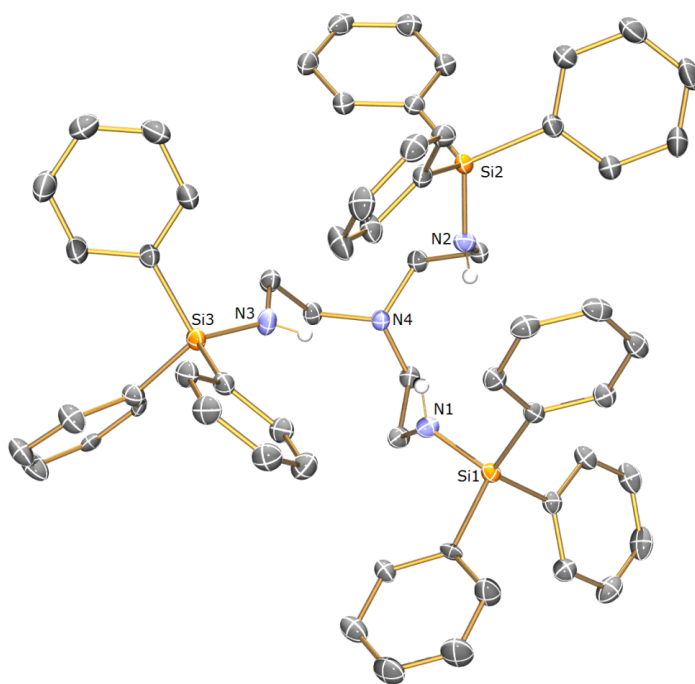


Figure 1. Molecular structure of **1** with displacement ellipsoids set to 40% and selective labelling. Non-NH hydrogen atoms are omitted for clarity.

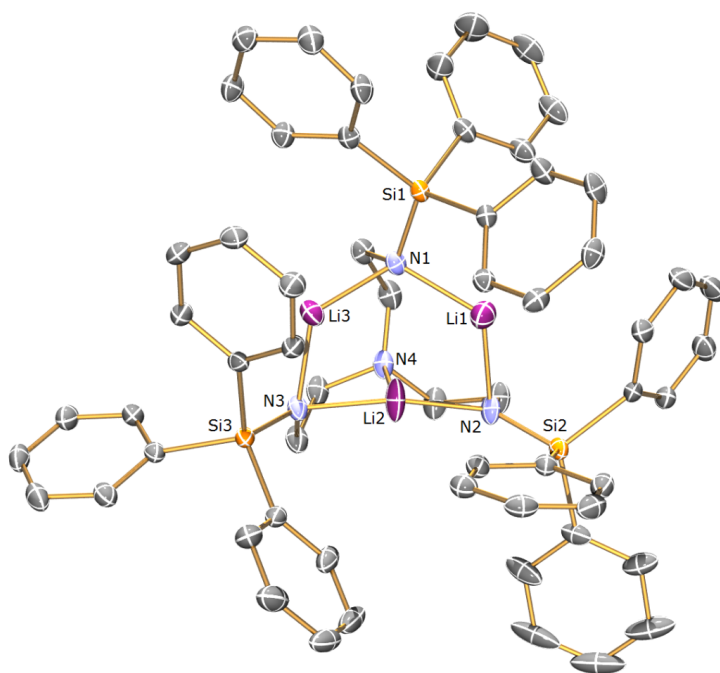


Figure 2. Molecular structure of **2** with displacement ellipsoids set to 40% and selective labelling. Selected bond lengths (Å): Li(1)-N(1) 2.006(4), Li(1)-N(2) 1.980(4), Li(2)-N(2) 1.924(3), Li(2)-N(3) 1.954(3), Li(2)-N(4) 2.024(4), Li(3)-N(3) 1.980(3), Li(3)-N(1) 1.998(3).

2.2. Structural characterisation of **1** and **2**

The molecular structure of **1** is unexceptional but confirms its formulation. The structure of **2** is more interesting in that one of the three lithium ions is coordinated to two amide centres and the amine atom, whereas the other two lithium centres are coordinated only to two amides in each case. This is not consistent with the solution data where only one lithium environment is observed, but clearly the lithium ions are in dynamic and rapid equilibrium in solution. Nevertheless, the structure of **2** confirms that all the amine centres have been deprotonated, and thus **2** is suitable for use as a ligand transfer reagent.

2.3. Synthesis of **3**

To test the synthetic utility of **2** we sought to prepare uranium halide and azide complexes, analogously to related $\text{Tren}^{\text{TMS/DMBS/TIPS}}$ ligand sets [3], since they are potential synthons to a wide range of novel uranium-ligand linkages, for example terminal-nitride, parent U-EH_2 ($\text{E} = \text{N, P, As}$), parent pnictidene U=EH , and uranium-arsenido linkages that have been prepared with the $\text{Tren}^{\text{TIPS}}$ variant [12].

Accordingly, **2** reacts with uranium tetrachloride in THF, and following work-up gives $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{Cl})]$ (**3**) as a green powder in excellent (95%) yield, Scheme 1. The ^1H NMR spectrum of **3** in C_6D_6 contains five resonances, suggesting effective C_{3v} point-symmetry of this complex in solution (confirmed by the solid state structure, see below). The ^1H NMR chemical shifts range from +15 to -20 ppm, which is typical for a symmetric Tren -uranium(IV) complex [3], and the ^{29}Si resonance for **3** (-110 ppm) is considerably shifted from those of **1** (~ +16 ppm) and **2** (~ -15 ppm) and is certainly consistent with the uranium(IV) formulation [15]. The magnetic moment of **3** was found to be $2.30 \mu_{\text{B}}$ in benzene solution at 298 K, and although this is lower than the theoretical free ion value of $3.58 \mu_{\text{B}}$ expected for the formal $^3\text{H}_4$ ground state of $5f^2$ uranium(IV), the value falls within the reported range for uranium (IV) complexes [16]. The optical absorption spectrum of **3** reveals multiple weak f - f transitions across the range 500-2000 nm ($\epsilon = 5\text{-}30 \text{ M}^{-1} \text{ cm}^{-1}$) that are characteristic of Laporte forbidden f - f transitions, further supporting the formulation of $5f^2$ uranium (IV) [17].

2.4. Structural characterisation of **3**

To confirm the formulation of **3** single crystals suitable for an X-ray diffraction study were grown from a saturated solution in toluene and the solid state structure is illustrated in figure 3 with selected bond angles and bond lengths.

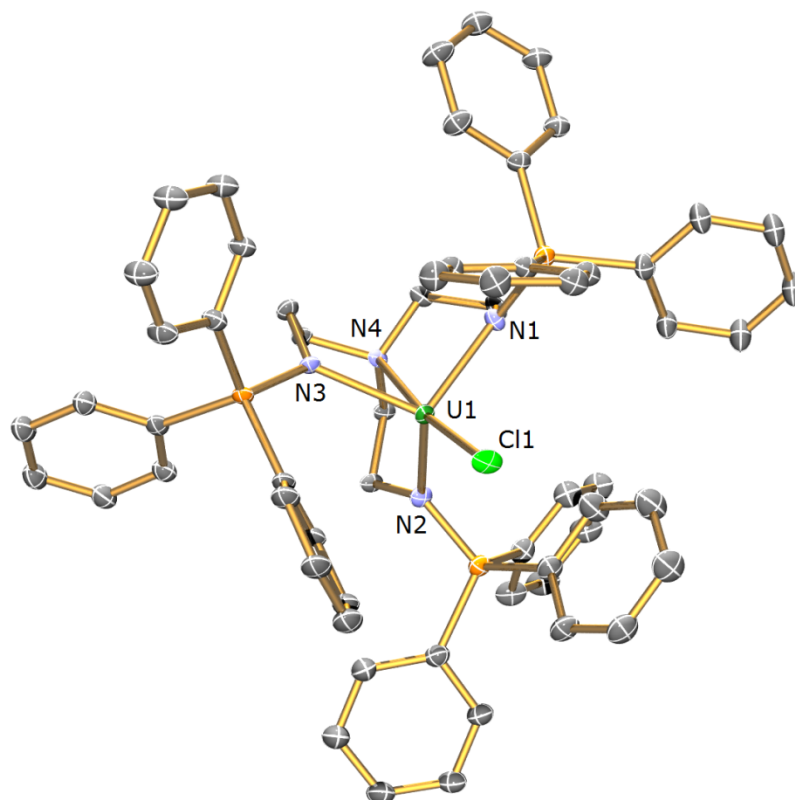
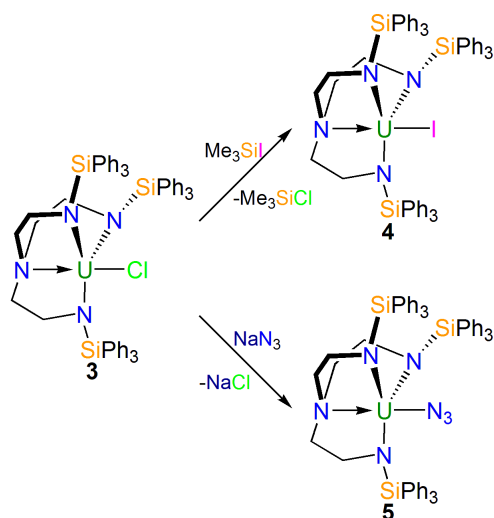


Figure 3. Molecular structure of **3** with displacement ellipsoids set to 40% and selective labelling. Selected bond lengths (Å) and angles (°): U(1)-Cl(1) 2.621(3), U(1)-N(1) 2.248(13), U(1)-N(2) 2.251(13), U(1)-N(3) 2.279(12), U(1)-N(4) 2.703(12), N(4)-U(1)-Cl(1) 170.8(3).

Similarly to previously reported Tren-uranium(IV)-chloride complexes [U(Tren^{TIPS})Cl] [12h] and [U(Tren^{DMBS})Cl] [18], the molecular structure of **3** reveals a monomeric complex containing a five-coordinate uranium centre that adopts a distorted trigonal-bipyramidal geometry with the amine and chloride ligand occupying the axial positions; two unique molecules crystallise in the crystallographic asymmetric unit, but since they are similar for brevity we discuss only one of them. The sterically demanding Tren^{TIPS} ligand formally occupies the three equatorial and one axial sites, leaving a single coordination site in the apical pocket for the chloride ligand. Complex **3** exhibits approximate C_{3v} symmetry and the N(4)-U(1)-Cl(1) bond angle of 170.8(3)° deviates only modestly from a linear arrangement.

The U-N_{amide} distances of 2.248(13), 2.251(13) and 2.279(12) Å and the U-N_{amine} bond length of 2.703(12) Å are typical of Tren-uranium(IV) complexes [3]. The U(1)-Cl(1) bond distance of 2.621(3) Å is within the sum of the covalent radii of 2.69 Å [1] and consistent with previously reported uranium(IV)-chloride distances supported by triamidoamine ligands [3,19].



Scheme 2. Synthesis of **4** and **5**.

2.5. Synthesis of **4**

Having established that Tren^{TPS} is sterically demanding enough to support an unsolvated monomeric uranium(IV) chloride complex like the related Tren^{TIPS} ligand system we targeted the iodide congener as there may be occasions where a softer iodide leaving group may be synthetically more desirable than a hard chloride that may inhibit further reactivity at the uranium centre.

By way of halide metathesis, straightforward treatment of **3** with trimethylsilyl iodide in toluene at 0 °C, followed by work-up, yielded the iodide substituted complex [U(Tren^{TPS})(I)] (**4**), as a pale green powder in excellent (95%) yield, Scheme 2. The ¹H NMR spectrum of **4** spans the range +18 to –35 ppm, which is slightly greater than the range observed in **3**, and

although the ^{29}Si NMR spectrum of **4** exhibits a resonance considerably shifted compared to **1** and **2** at -51 ppm; this is nearly 60 ppm shifted from **3**. The magnetic moment of **4** in benzene solution at 298K was found to be $2.72 \mu_{\text{B}}$, and although this is higher than **3** it still falls well within the range of reported magnetic moments for uranium(IV) complexes [16]. The weak $f-f$ transitions observed in optical absorption spectrum of **4** are consistent with the proposed +4 oxidation state for the uranium centre [17].

2.6. Structural characterisation of **4**

To confirm the formulation of **4** single crystals suitable for an X-ray diffraction study were grown from a saturated solution in toluene stored at -30 °C and the solid structure of **4** illustrated in figure 4 with selected bond lengths and angles.

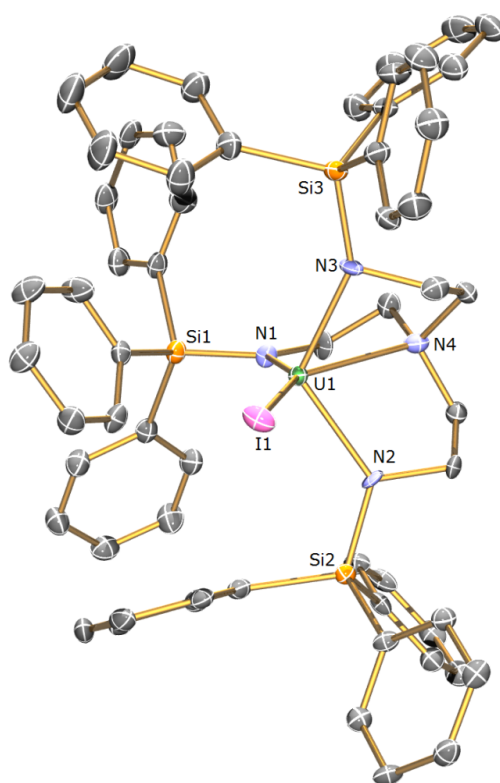


Figure 4. Molecular structure of **4** with displacement ellipsoids set to 40% and selective labelling. Selected bond lengths (Å) and angles (°): U(1)-I (1) 3.0815(4), U(1)-N(1) 2.242(4), U(1)-N(2) 2.255(4), U(1)-N(3) 2.217(4), U(1)-N(4) 2.600(6), N(4)-U(1)-I(1) 137.24(11).

The solid state molecular structure of **4** reveals a monomeric five-coordinate uranium centre in a geometry best described as distorted square base pyramidal. The N(4)-U(1)-I(1) bond angle of $137.24(11)^\circ$ is much more acute than the corresponding N(4)-U(1)-Cl(1) angle for **3** and is likely due to crystal packing effects. The U(1)-I(1) iodide distance of $3.0815(4)$ Å is moderately longer than the sum of the covalent radii of 3.03 Å [1] and is consistent with previously reported uranium(IV)-iodide complexes when supported by triamidoamines [3]. The U-N_{amide} and U-N_{amine} bond lengths compare well to those for **3**.

2.7. Synthesis of **5**

With the uranium(IV)-halide complexes **3** and **4** in hand, we investigated their utility as precursors for further functionalisation. As a test reaction, mixing **3** with two equivalents of sodium azide in THF afforded, following work up, the azide substituted complex [U(Tren^{TIPS})(N₃)] (**5**) as a pale brown powder in good (82%) yield after work-up, Scheme 2. Similarly to **3** and **4** the ¹H NMR spectrum of **5** exhibits resonances in the range +20 to -10 ppm. The ²⁹Si NMR spectrum of **5** exhibits a resonance at -108 ppm that is very similar to **3** but different to **4**, suggesting that the azide is electronically acting as a pseudo-halide more like chloride than iodide. Consistent with the pseudo-chloride electronic behaviour of the azide in **5**, the magnetic moment of **5** in benzene solution at 298K is $2.15 \mu_B$ which is consistent to previously reported uranium(IV) species and is closer to the value for **3** ($2.30 \mu_B$) than **4** ($2.72 \mu_B$) [16]. The optical absorption spectrum of **5** is typical of a $5f^2$ uranium (IV), with low intensity peaks in the range 500-2000 nm ($\epsilon = 20\text{-}50 \text{ M}^{-1} \text{ cm}^{-1}$) [17]. Complex **5** exhibits a strong absorption at 2086 cm^{-1} in its FTIR spectrum, which is in agreement with previously reported uranium-azide complexes [20]. Crystals of **5** suitable for an X-ray diffraction study were grown from toluene at room temperature and the solid state structure is illustrated in figure 5 with selected bond angles and bond lengths.

2.8. Structural characterisation of **5**

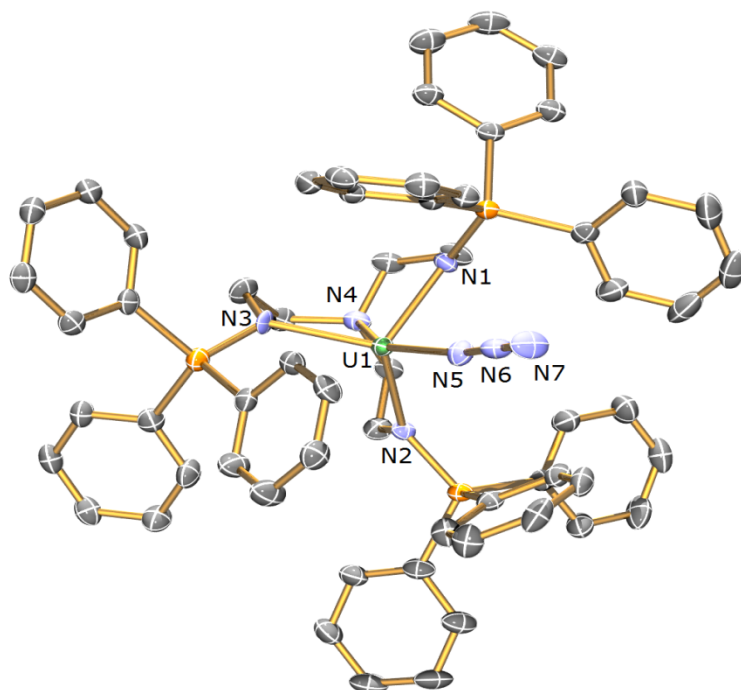


Figure 5. Molecular structure of **5** with displacement ellipsoids set to 40% and selective labelling. Selected bond lengths (Å) and angles (°): U(1)-N(1) 2.259(6), U(1)-N(2) 2.277(5), U(1)-N(3) 2.272(5), U(1)-N(4) 2.639(7), U(1)-N(5) 2.260(7), N(5)-N(6) 1.246(10), N(6)-N(7) 1.132(9), N(4)-U(1)-N(5) 151.5(2), U(1)-N(5)-N(6) 168.1(5), N(5)-N(6)-N(7) 178.5(9).

In the solid state complex **5** adopts a monomeric species with a trigonal bipyramidal uranium centre. The solid state structure exhibits typical U-N_{amide} and U-N_{amine} distances of 2.269 (av) and 2.639(7) Å, respectively, but the N(4)-U(1)-N(5) bond angle is 151.5(2)° and so in gross structural terms the N-U-X linkage is between that of the bent N-U-I and almost linear N-U-Cl angles in **4** and **3**, respectively. The azide group itself is essentially linearly bound to uranium [U-N_α-N_β = 178.5(9)°] with a U(1)-N(5) bond length of 2.260(7) Å that is within the range of reported terminal uranium azide bond lengths [2.219(6)-2.562(13) Å] [20], but it is notably shorter than the uranium-azide distance of 2.305(3) Å observed in the solid state structure of [U(Tren^{TIPS})(N₃)] [12g].

3. Conclusions

Seeking to expand the range of sterically demanding Tren-ligand environments for uranium that may be used in future endeavours to stabilise novel uranium-ligand multiple bond linkages, we have prepared the new Tren^{TIPS}-ligand (**1**) with *N*-SiPh₃ substituents. The synthesis of **1** is straightforward and can be carried out on multi-gram scales and the corresponding tri-lithium salt **2** is straightforwardly prepared. Compound **2** is an effective ligand transfer reagent, enabling the synthesis of the uranium(IV)-chloride complex **3** in high yield. Complex **3** can be straightforwardly converted to the corresponding iodide (**4**) and/or azide (**5**) complexes that have much potential for subsequent chemistry. Although there appears to be more flexibility of the N_{amine}-U-X angle compared to analogous Tren^{TIPS} derivatives all the complexes reported here are monomeric and solvent-free. This suggests that a complementary range of uranium-ligand multiple bonds may be accessible with the Tren^{TIPS} compared to Tren^{TIPS} ligand that may exhibit different reactivities or binding modes. Furthermore, the Tren^{TIPS} ligand is less soluble than Tren^{TIPS} giving higher yields generally, which may prove beneficial where Tren^{TIPS} does not present the optimum solubility level. We are currently investigating further derivatives of uranium-Tren^{TIPS} utilising **3-5** and will report on these in due course.

4. Experimental

4.1. 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. All solvents were stored over potassium

mirrors except for ethers which were stored over activated 4 Å sieves. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. Commercially available reagents were supplied by Sigma-Aldrich: BuⁿLi (2.5 M solution in hexanes) and trimethylsilyl iodide were used as received, ClSiPh₃, NaN₃ were dried under vacuum for 6 hours, and tri(2-aminoethyl)amine was distilled prior to use. Depleted-UO₃ was supplied by the National Nuclear Laboratory and UCl₄ was prepared as described previously [21].

¹H, ⁷Li, ¹³C{¹H}, and ²⁹Si NMR spectra were recorded on a Bruker AV400 or AV(III)400 spectrometer operating at 400.2, 155.5, 100.6, and 79.5 MHz, respectively. Chemical shifts (δ) are quoted in ppm and are relative to external TMS (¹H, ¹³C, ²⁹Si) or 1M aqueous LiCl (⁷Li). Single crystal data were collected on an Oxford Diffraction Ltd SuperNova Atlas CCD diffractometer. FTIR spectra were recorded on a Bruker Alpha spectrometer with Platinum-ATR module. UV/Vis/NIR spectra were recorded on a Perkin Elmer Lambda 750 spectrometer. Data were collected in 1mm path length cuvettes loaded in an MBraun UniLab glovebox and were run versus the appropriate THF reference solvent. Elemental microanalyses were carried out by Tong Liu at The University of Nottingham School of Chemistry Microanalysis service.

4.2. Preparation of Tren^{TPS}H₃ (1)

BuⁿLi (2.5 M, 34.0 ml, 84.78 mmol) was added dropwise to a pre-cooled (−78 °C) solution of N(CH₂CH₂NH₂)₃ (4.13 g, 28.26 mmol) in THF (100 ml). The colourless slurry was allowed to warm to room temperature and was stirred for a further 16 hours. The solution was cooled to −78 °C and ClSiPh₃ (25 g, 84.78 mmol) was added. The solution was allowed to warm to room temperature and was stirred for 4 hours. Volatiles were removed *in vacuo* and the product was extracted into toluene. The solvent was removed *in vacuo* and the colourless solid washed with hexanes (2 x 20 ml) to yield **1**. Yield: 22.02 g, 84%. Crystalline material

was obtained by dissolution of a small portion in toluene (5 ml) and storage at $-30\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{60}\text{H}_{60}\text{N}_4\text{Si}_3$: C, 78.21; H, 6.56; N, 6.08%. Found: C, 78.69; H, 6.91; N, 6.07%. ^1H NMR (C_6D_6 , 298 K): δ 1.72 (t, 3H, NH), 2.34 (t, 6H, (CH_2)), 3.00 (q, 6H, CH_2), 7.30 (m, 27H, Si(Ar-*H*)), 7.83 (d, 18H, Si(*p*-Ar-*H*)) ppm. $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 298 K): δ 40.35 (CH_2), 58.11 (CH_2), 127.39 (Si(*m*-Ar-CH)), 129.59 (Si(*p*-ArH)), 135.69 (Si(*o*-Ar-CH)), 136.20 (Si(*i*-Ar-C)) ppm. ^{29}Si NMR (C_6D_6 , 298 K): δ 16.19 ppm. FTIR v/cm^{-1} (Nujol): 3400 (w), 2956 (s), 1427 (m), 1144 (s), 769 (w), 519 (m).

4.3. Preparation of [(Tren^{TPS})(Li)₃] (2)

Bu^nLi (2.5 M, 34.0 mL, 84.78 mmol) was added dropwise to a pre-cooled ($-78\text{ }^{\circ}\text{C}$) solution of **1** (22.02 g, 23.90 mmol) in toluene (100 ml). The colourless slurry was allowed to warm to room temperature and was stirred for a further 16 hours. Volatiles were removed *in vacuo* and the solid was washed with hexanes (2 x 20 ml) to yield **2** as a colourless powder. Yield: 20.29 g, 76%. Crystalline material was obtained by dissolution of a small portion in toluene (6 ml) and storage at $-30\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{60}\text{H}_{57}\text{N}_4\text{Si}_3\text{Li}_3$: C, 76.73; H, 6.12; N, 5.97%. Found: C, 77.32; H, 6.55; N, 5.96%. ^1H NMR (C_6D_6 , 298 K): δ 2.40 (t, 6H, (CH_2)), 3.40 (t, 6H, (CH_2)), 7.25 (m, 27H, Si(Ar-*H*)), 7.60 (m, 18H, Si(*o*-Ar-*H*)) ppm. $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 298 K): δ 44.97 (CH_2), 58.62 (CH_2), 128.06 (Si(*m*-Ar-CH)), 128.98 (Si(*p*-ArCH)), 135.09 (Si(*o*-Ar-CH)), 139.72 (Si(*i*-Ar-C)) ppm. ^{29}Si NMR (C_6D_6 , 298 K): δ -15.46 ppm. ^7Li NMR (C_6D_6 , 298 K): δ -2.39 ppm. FTIR v/cm^{-1} (Nujol): 2966 (s), 1427 (m), 1260 (m), 1069 (m), 1025 (m), 799 (m), 519 (m).

4.4. Preparation of [U(Tren^{TPS})(Cl)] (3)

THF (30 ml) was added to a pre-cooled ($-78\text{ }^{\circ}\text{C}$) stirring mixture of **2** (8.42 g, 8.96 mmol) and UCl_4 (3.41 g, 8.96 mmol). The resulting mixture was allowed to warm to room temperature and stirred for 16 hours. The mixture was heated to reflux for 5 minutes, allowed to cool to room temperature, and volatiles removed *in vacuo*. Extraction of the product in

warm toluene, followed by removal of volatiles yielded a dark green oil. The product was washed with hexanes (2 x 20 ml) to yield **3** as a pale green powder. Yield: 10.3 g, 96%. Crystalline material was obtained by dissolution in toluene (3 ml) and storage at room temperature. Anal. Calcd for $C_{134}H_{130}Cl_2N_8Si_6U_2$: C, 60.46; H, 5.10; N, 4.36%. Found: C, 60.56; H, 4.92; N, 4.36%. 1H NMR (C_6D_6 , 295 K): δ 12.96 (6H, br, NCH_2CH_2), 10.36 (18H, d, *o*-Ar-*H*), 6.48 (18H, t, *m*-Ar-*H*), 6.14 (9H, t, *p*-Ar-*H*), -17.83 (6H, br, NCH_2CH_2) ppm. ^{29}Si NMR (C_6D_6 , 295 K): δ -110 (Si(*i*-ArH)) ppm. FTIR ν/cm^{-1} (ATR): 2951 (m), 2853 (m), 1427 (w), 1247 (s), 1109 (s), 1054 (s), 924 (m), 824 (m), 606 (m), 504 (w). Magnetic moment (Evan's Method, C_6D_6 , 298 K): $\mu_{eff} = 2.30 \mu_B$. UV-vis (THF) λ_{max} (nm), ϵ ($M^{-1} cm^{-1}$): 1257 (15.0), 1069, (27.2), 642 (16.2), 609 (16.3), 521 (21.8).

4.5. Preparation of $[U(Tren^{TPS})(I)]$ (**4**)

Trimethylsilyl iodide (1.25 ml, 8.8 mmol) was added dropwise over 3 minutes to a pre-cooled (0 °C) stirring solution of **3** (9.54 g, 8.0 mmol) in toluene (30 ml) to afford a yellow-green slurry. The reaction mixture was stirred at 0 °C for 20 minutes, then warmed to room temperature and stirred for 16 hours. Volatile materials were removed *in vacuo* to afford a sticky brown solid. Pentane (10 ml) was added to the sticky solid and the mixture was stirred for 30 minutes to afford a brown powder. The volatiles were removed *in vacuo* leaving **4** as a pale brown powder. Yield: 9.7 g, 95%. Crystalline material was obtained by dissolution of small portion in toluene (4 ml) and storage at -30 °C. Anal. Calcd for $C_{60}H_{57}IN_4Si_3U$: C, 56.16; H, 4.48; N, 4.37%. Found: C, 55.42; H, 4.78; N, 3.98%. 1H NMR (C_6D_6 , 295 K): δ 17.47 (18H, d, *o*-Ar-*H*), 10.78 (6H, b, NCH_2CH_2), 7.01 (18H, t, *m*-ArH), 6.21 (9H, t, *p*-Ar-*H*), -35.38 (6H, b, NCH_2CH_2) ppm. ^{29}Si NMR (C_6D_6 , 298 K): -50.54 (Si(*i*-ArH)) ppm. FTIR ν/cm^{-1} (ATR): 3044 (w), 2838 (w), 1426 (m), 1249 (w), 1105 (m), 938 (m), 923 (m), 769 (m), 736 (m), 697 (s), 533 (s), 494 (s), Magnetic moment (Evan's Method, C_6D_6 , 298 K): $\mu_{eff} =$

2.72. UV-vis (THF) λ_{\max} (nm), ϵ ($M^{-1} \text{ cm}^{-1}$): 1122, (37.7), 1066 (40.7), 685 (14.7), 646 (12.9), 618 (11.5), 520 (22.0).

4.6. Preparation of [U(Tren^{TPS})(N₃)] (5)

THF (30 ml) was added to a pre-cooled (-78 °C) stirring mixture of **3** (10.71 g, 8.99 mmol) and NaN₃ (1.17 g, 18.0 mmol). The resulting mixture was allowed to warm to room temperature and stirred overnight. The mixture was heated to reflux for 5 minutes, allowed to cool to room temperature, and volatiles removed *in vacuo*. Extraction of the product in hot toluene, followed by removal of volatiles yielded a brown-green oil. The product was washed with hexanes (3 x 20 ml) to yield **5** as a pale green powder. Yield: 8.87 g, 82% Crystalline material was obtained by dissolution of a small portion in toluene (4 ml) and storage at -30 °C. Anal. Calcd for C₆₀H₅₇Cl₂N₈Si₆U: C, 60.13; H, 4.79; N, 8.18%. Found: C, 59.92; H, 4.89; N, 8.23%. ¹H NMR (C₆D₆, 295 K): δ 15.49 (6H, b, NCH₂CH₂), 6.48 (9H, t, *p*-Ar-*H*), 6.38 (18H, t, *m*-Ar-*H*), 5.66 (18H, d, *o*-Ar-*H*), -2.34 (6H, b, NCH₂CH₂) ppm. ²⁹Si NMR (C₆D₆, 295 K): δ -108.00 ppm. FTIR ν/cm^{-1} (ATR): 3065 (w), 2876 (w), 2152 (m), 2086 (s), 1426 (m), 1370 (m), 1102 (m), 926 (m), 759 (s), 731 (s), 695 (s), 535 (s), 491 (m). Magnetic moment (Evan's Method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.15 \mu_{\text{B}}$. UV-vis (THF) λ_{\max} (nm), ϵ ($M^{-1} \text{ cm}^{-1}$): 1336 (30.5), 1132 (46.9), 1073 (49.7), 686 (46.4), 656 (51.6).

4.7. X-ray crystallography

Crystal data for compounds **1-5** are given in Table 1, and further details of the structure determinations are in the Supplementary information. Crystals were examined variously on a Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated CuK α radiation ($\lambda = 1.5418$ Å) or a Agilent SuperNova diffractometer using high intensity CuK α radiation ($\lambda = 1.5418$ Å) mounted using Fomblin® oil onto micromounts. Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical

absorption corrections were applied based on Gaussian grid face-indexed absorption correction with a beam profile correction. The structures were solved by direct or 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. Programs were CrysAlisPro [22] (control and integration), and SHELXTL, [23] Platon, [24] Olex2, [25] and Ortep-3 [26] were employed for structure solution and refinement and for molecular graphics.

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Appendix A. Supplementary information

CCDC 1482232-1482236 contains the supplementary crystallographic data for **1-5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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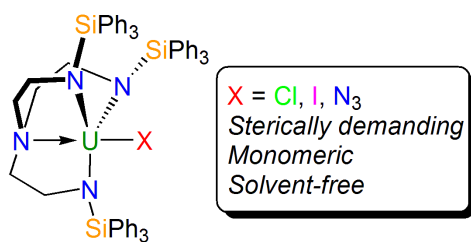
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Table 1. Crystallographic data for 1-5.

	1	2	3	4	5
Formula	C ₆₀ H ₆₀ N ₄ Si ₃	C ₆₀ H ₅₇ Li ₃ N ₄ Si ₃	C ₆₇ H ₆₅ ClN ₄ Si ₃ U	C _{63.5} H ₆₁ IN ₄ Si ₃ U	C ₆₇ H ₆₅ N ₇ Si ₃ U
Fw	921.39	939.18	1283.98	1329.36	1290.56
Cryst size, mm ³	0.1907 × 0.1172 × 0.0541	0.0862 × 0.0835 × 0.0687	0.1477 × 0.1065 × 0.082	0.1541 × 0.0617 × 0.0337	0.2549 × 0.1760 × 0.1405
Cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /n	P-1	P2 ₁ /n
a, Å	9.7948(4)	12.62321(17)	9.40445(16)	9.6728(3)	14.0571(9)
b, Å	11.3865(3)	19.6176(3)	60.1025(12)	13.8023(4)	14.5238(15)
c, Å	23.0872(8)	20.9468(3)	20.6897(3)	21.3078(6)	29.315(3)
α, °	86.252(3)	90	90	86.913(2)	90
β, °	89.697(3)	92.8659(13)	94.9720(16)	86.266(2)	99.730(7)
γ, °	86.776(3)	90	90	82.898(2)	90
V, Å ³	2565.31(16)	5180.70(12)	11650.5(4)	2813.90(14)	5899.0(9)
Z	2	4	8	2	4
ρ _{calc} g cm ⁻³	1.193	1.204	1.464	1.569	1.453
μ, mm ⁻¹	1.172	1.162	9.195	13.366	8.692
no. of reflections measd	19043	34239	38551	21143	25641
no. of unique reflns, R _{int}	10139, 0.0385	10249, 0.0351	21343, 0.0563	11048, 0.0641	11694, 0.0585
no. of reflns with F ² > 2s(F ²)	8660	8264	18190	9954	10268
transmn coeff range	0.971 - 0.915	0.942 - 0.925	0.590 - 0.391	0.701 - 0.272	0.264 - 0.078
R, R _w ^a (F ² > 2s(F ²))	0.0464, 0.1166	0.0386, 0.0934	0.0896, 0.2239	0.0459, 0.1182	0.0552, 0.1289
R, R _w ^a (all data)	0.0547, 0.1255	0.0536, 0.1018	0.1011, 0.2277	0.0515, 0.1229	0.0646, 0.1333
S ^a	1.058	1.03	1.203	1.029	1.409
Parameters	708	631	1341	686	687
max.,min. diff map, e Å ⁻³	0.497, -0.293	0.313, -0.244	1.907, -3.799	2.010, -2.396	1.791, -1.766

For all data: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(F_o2 - F_c2)^2 / \sum w(F_o2)^2]^{1/2}$; $S = [\sum w(F_o2 - F_c2)^2 / (\text{no. data} - \text{no. params})]^{1/2}$

ToC Figure



ToC Text

The synthesis and characterisation of uranium-halide and -azide derivatives supported by a bulky *N*-SiPh₃-substituted triamidoamine ligand are described.