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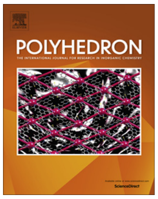

Uranium–halide and –azide derivatives of the sterically demanding triamidoamine ligand $Tren^{TPS}$ [$Tren^{TPS} = \{N(CH_2CH_2NSiPh_3)_3\}^{3-}$]

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ABSTRACT

Treatment of tri(2-aminoethyl)amine with three equivalents of Bu^nLi followed by the addition of three equivalents of Ph_3SiCl afforded the triaminoamine $Tren^{TPS}H_3$ [**1**, $Tren^{TPS}H_3 = N\{CH_2CH_2N(H)SiPh_3\}_3$]. Subsequent treatment with three equivalents of Bu^nLi afforded the tri-lithium complex [$(Tren^{TPS})(Li)_3$] (**2**), which reacts with UCl_4 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 [$U(Tren^{TPS})(N_3)$] (**5**) when treated with Me_3SiI or NaN_3, 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 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, $\{N(CH_2CH_2NR)_3\}^{3-}$ [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 $R = SiMe_3$ ($Tren^{TMS}$), $SiMe_2Bu^t$ ($Tren^{DMBS}$), and more recently $SiPr^i_3$ ($Tren^{TIPS}$) [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 proligand with N-$SiPh_3$ 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.

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2. Results and discussion

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

Treatment of tri(2-aminoethyl)amine with three equivalents of Bu^nLi at −78 °C in THF, followed by the addition of three equivalents of Ph_3SiCl afforded the triaminoamine $Tren^{TPS}H_3$ [**1**, $Tren^{TPS}H_3 = N\{CH_2CH_2N(H)SiPh_3\}_3$] as a colourless solid in good (84%) yield after work-up and isolation, Scheme 1. Treatment of **1** with three further equivalents of Bu^nLi, 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 $[(Tren^{DMBS})(Li)_3]$ 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 N*H* 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 $^{29}Si\{^1H\}$ 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 (Figs. 1 and 2).

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 $Tren^{TMS/DMBS/TIPS}$ ligand sets [3], since they are potential synthons to a wide range of novel uranium–ligand linkages, for example terminal-nitride, parent $U\text{-}EH_2$ (E = N, P, As), parent pnictidene U = EH, and uranium–arsenido linkages that have been prepared with the $Tren^{TIPS}$ variant [12].

Accordingly, **2** reacts with uranium tetrachloride in THF, and following work-up gives $[U(Tren^{TPS})(Cl)]$ (**3**) as a green powder in excellent (95%) yield, Scheme 1. The ^1H NMR spectrum of **3** in

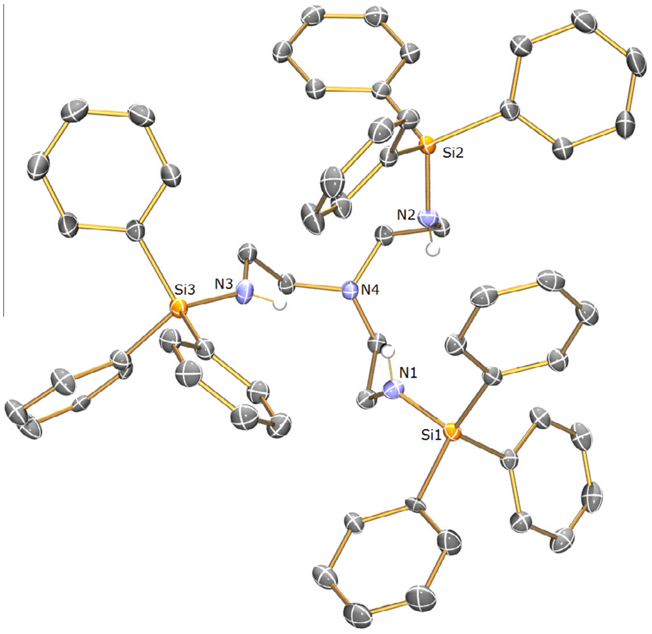


Fig. 1. Molecular structure of **1** with displacement ellipsoids set to 40% and selective labelling. Non-NH hydrogen atoms are omitted for clarity.

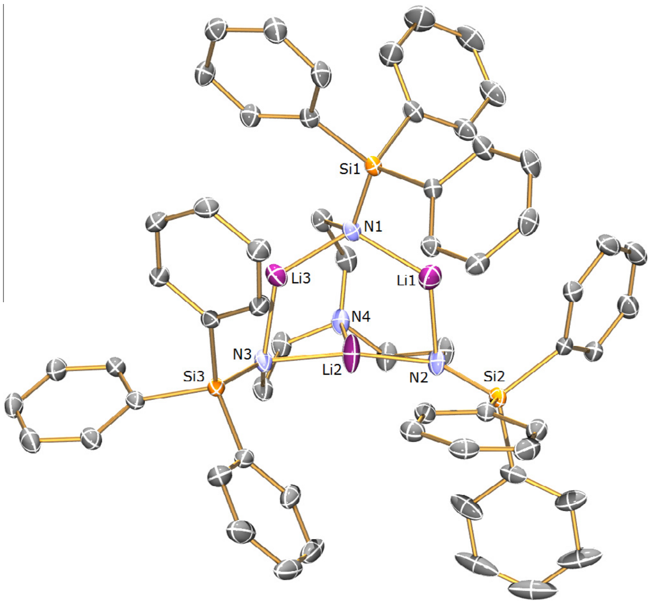
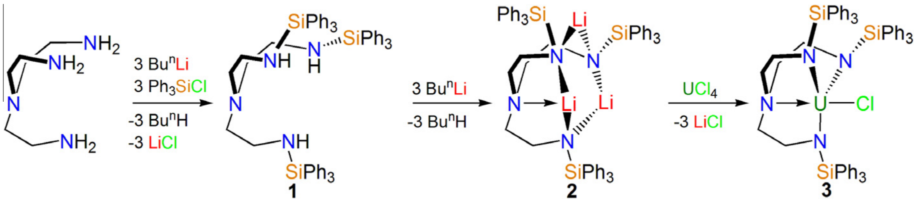


Fig. 2. Molecular structure of **2** with displacement ellipsoids set to 40% and selective labelling. Selected bond lengths (Å): Li(1)–N(1) 2.006(4), Li(1)–N(2) 1.980(4), Li(2)–N(2) 1.924(3), Li(2)–N(3) 1.954(3), Li(2)–N(4) 2.024(4), Li(3)–N(3) 1.980(3). Li(3)–N(1) 1.998(3).



Scheme 1. Synthesis of **1**–**3**.

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