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Uranium halide complexes stabilised by a new sterically demanding tripodal *tris*(*N*-adamantylamidodimethylsilyl)methane ligand

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Abstract

The new *tris*(*N*-adamantylamine-dimethylsilyl)methane $\text{HC}\{\text{SiMe}_2\text{N}(\text{H})\text{Ad}\}_3$ ($\text{Ts}^{\text{Ad}}\text{H}_3$, **1**) and its trilithium salt $[\text{HC}\{\text{SiMe}_2\text{N}(\text{Li})\text{Ad}\}_3]$ ($\text{Ts}^{\text{Ad}}\text{Li}_3$, **2**) were synthesised and characterised by multinuclear NMR and IR spectroscopy, elemental microanalysis and single crystal X-ray diffraction. The utility of **2** as a ligand transfer reagent for uranium was examined by targeting Ts^{Ad} -uranium(IV) and (III) complexes *via* its reaction with UCl_4 and $\text{UI}_3(\text{THF})_4$; however the crystalline material isolated, $[\text{U}(\text{Ts}^{\text{Ad}})(\text{Cl})(\mu\text{-Cl})\{\text{Li}(\text{THF})_3\}]$ (**4**) and $[\text{U}(\text{Ts}^{\text{Ad}})\text{U}(\text{I})]$ (**5**) are products of lithium chloride inclusion and uranium disproportionation/ligand redistribution, respectively, and hints at the wide scope of reactivity accessible to Ts^{Ad} -uranium complexes. Complex **5** was also independently synthesised stepwise in good yield from **2** *via* treatment with UCl_4 and, subsequently, Me_3SiI . The uranium complexes were characterised by a combination of NMR and IR spectroscopy, elemental microanalysis, magnetometric methods and single crystal X-ray diffraction.

Keywords

uranium / organometallic / actinide / X-ray diffraction / tripodal / steric protection / complex

1. Introduction

Aside from the remediation of nuclear waste and the development and recycling of nuclear fuel materials,[1, 2] understanding the bonding, electronic structure and chemical reactivity of uranium complexes has wide-ranging chemical, industrial, and environmental significance. Fundamental questions regarding the extent to which uranium can engage in covalent bonding with its environment, the origin of the dynamic magnetic behaviour observed in many uranium complexes, and the ability of uranium to activate and transform otherwise inert small molecules – facilitated by the rich redox chemistry accessible to uranium in non-aqueous media – must be addressed if Nature's heaviest naturally occurring element is to be understood.[3-9]

Actinide chemistry in general has traditionally been considered as underdeveloped relative to the rest of the Periodic Table as exemplified by alkylidene, carbyne or terminal nitride complexes that are well-known for the d-block but which are still – or until very recently were – unknown for uranium.[10, 11][12-17] Metallocene derivatives[18] and first-row-based multiply bonded ligands dominated much of the early progress in organouranium chemistry; but a

recent resurgence has seen dramatic advances in the nature and variety of supporting ligands, highlighted by multiply bonded post-first-row ligands.[19, 20]

Multidentate, sterically-demanding tripodal ligands have proven to be effective supports for low-valent uranium, exemplified by the isolation of unstable yet significant main group fragments including multiply bonded mono- and polychalcogenides and -pnictides[20-41] and have demonstrated concerted capacity to activate important small molecules such as N₂, CO and CO₂. [5] We have previously shown that the *tris*(*N*-arylamidodimethylsilyl)methane ligand systems HC[SiMe₂N(p-Tol)₃]³⁻ [Ts^{p-Tol}, p-Tol = 4-Me-C₆H₄] and HC[SiMe₂N(Xy)₃]³⁻ [Ts^{Xy}, Xy = 3,5-Me₂-C₆H₃], developed by Gade and later ourselves, respectively,[42, 43] when coordinated to a uranium centre can impart sufficient kinetic and thermodynamic control to access a range of novel chemistry including uranium–metal bond formation, isolation of remarkable 10π-electron arene tetra-anions sandwiched between two uranium(V) centres, reductive assembly of cyclobutadienyl and diphosphacyclobutadienyl inverted sandwiches, and Zintl-cluster formation chemistry.[44-47] However, Ts^{p-Tol} and Ts^{Xy} are not particularly sterically demanding, and inspection of space filling diagrams from crystal structure data show that these ligands occupy at best a hemisphere of the coordination sphere at uranium. In order to occupy and control a greater amount of coordination space at uranium in such complexes we envisaged that increasing the steric protection afforded to the uranium centre by the Ts^R ligand could enable main group fragments, that are otherwise too reactive to be isolated,[20, 28] to be stabilised at uranium. This would enable us to extend the range of chemical reactivity accessible to metal-Ts^R systems, as well as uranium in general. To this end, a new class of these *tris*(amidodimethylsilyl)methanes was targeted utilising the *N*-adamantyl group.[48]

2. Experimental

2.1 Materials

All manipulations were carried out using standard Schlenk techniques under nitrogen, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Hexanes, diethyl ether, tetrahydrofuran (THF) and toluene were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors (with the exception of THF and dichloromethane which were stored over activated 4Å molecular sieves). Deuterated benzene was dried over potassium, vacuum distilled, degassed by three freeze-pump-thaw cycles and stored under nitrogen. HC(SiMe₂Br)₃, UCl₄, and UI₃(THF)₄ were prepared according to published methods.[42, 49, 50] All other reagents were used as received.

2.2 Measurements

¹H, ¹³C, ²⁹Si and ⁷Li NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 400.2, 100.6, 79.5 and 155.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS or external 1 M LiCl. FTIR spectra were recorded as Nujol® mulls on a Bruker™ Tensor 27 spectrometer. Elemental microanalyses were carried out by Mr. Stephen Boyer (London Metropolitan University) and Medac Microanalysis Service, UK. Variable-temperature SQUID magnetic measurements were performed in an applied DC field of 0.1 T on a Quantum Design MPMS®-XL 5 SQUID magnetometer using doubly-recrystallised powdered samples. Samples were checked for purity before and after use and data reproducibility was carefully checked. Care was taken to ensure complete thermalisation of the sample before each data point was measured. Diamagnetic corrections (χ_D) were

applied using tabulated Pascal constants[51] and measurements were corrected for the effect of the blank sample holders (flame-sealed Wilmad NMR tube and straw).

2.3 Syntheses of 1, 2, 4 and 5

HC[SiMe₂N(H)C₁₀H₁₅]₃ Ts^{Ad}H₃ (1)

Method A: A solution of HC{Me₂SiBr}₃ (7.85 g, 18.4 mmol) in Et₂O (50 ml) was added dropwise to a cold (0 °C) stirring suspension of 1-adamantylamine (25.00 g, 165.0 mmol) in Et₂O (400 ml) over 4 h. After the addition was complete the mixture was allowed to warm to ambient temperature and stirred for a further 16 h. The mixture was filtered and the insoluble residue was washed with Et₂O (3 × 75 ml). The washings were combined with the filtrate and the volume was reduced by 70-80% *in vacuo* to yield **1** as a colourless microcrystalline solid, which was isolated by filtration. The supernatant solution was stored at –30 °C to yield a second crop of **1** as colourless crystals. Yield: 4.11 g, 35%.

Method B: ⁿBuLi (2.5 M in hexanes, 24 ml, 60.0 mmol) was added dropwise to a cold (–78 °C) stirring solution of 1-adamantylamine (8.17 g, 54.0 mmol) in hexanes. The solution was allowed to warm to room temperature over 16 h. The precipitate was collected by filtration, washed with hexanes (3 × 10 ml) and dried *in vacuo*. The colourless solid was suspended in THF, cooled to –78 °C and a solution of HC(SiMe₂Br)₃ (7.69 g, 18.00 mmol) in THF (40 ml) was added dropwise over 1 h. The resulting mixture was allowed to warm to room temperature over 16 h. The volatiles were removed *in vacuo*, and the product was extracted into toluene (~40 ml), filtered, concentrated to 10 ml and stored at –30 °C to afford colourless crystals of **1**. Yield: 6.04 g, 53%.

¹H NMR (C₆D₆, 298 K): δ –1.01 (s, 1H, HCSi₃), 0.61 (s, 18H, Me₂Si), 1.70 (m, 18H, Ad-CH₂), 2.02 (m, 18H, Ad-CH₂), 2.12 (m, 9H, Ad-CH), 2.29 (s, 3H, NH) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ 5.61 (Me₂Si), 7.83 (HCSi₃), 30.30 (CH-CH₂), 36.72 (CH₂-CH), 48.02 (C-CH₂), 50.55 (NC) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ –2.70 ppm. FTIR: ν 3296 (s), 2955 (vs), 2853 (vs), 1457 (s), 1377 (m), 1342 (m), 1308 (w), 1252 (m), 1179 (w), 1096 (m), 1008 (m), 962 (w), 940 (w), 859 (m), 823 (s) cm^{–1}. Anal. Calc'd for C₃₇H₆₇N₃Si₃: C, 69.63; H, 10.58; N, 6.58. Found: C, 69.74; H, 10.63; N, 6.53.

HC[SiMe₂N(Li)C₁₀H₁₅]₃ TsAdLi₃ (2)

ⁿBuLi (2.5 M in hexanes, 16 ml, 40.0 mmol) was added dropwise to a cold (–78 °C) stirring solution of **1** (8.30 g, 13.00 mmol) in a mixture of Et₂O (10 ml) and hexanes (40 ml). The mixture was allowed to warm to ambient temperature and stirred for a further 16 h. The volatiles were removed *in vacuo* and the resulting off-white solid was washed with hexanes (2 × 10 ml) and dried *in vacuo* to yield a colourless solid. Colourless crystals were grown from a saturated solution of **2** in hexanes at –30 °C. Yield: 8.03 g, 94%.

¹H NMR (C₆D₆, 298 K): δ –0.93 (s, 1H, HCSi₃), 0.66 (s, 18H, Me₂Si), 1.65 (m, 18H, Ad-CH₂), 1.73 (m, 18H, Ad-CH₂), 2.08 (m, 9H, Ad-CH) ppm. ¹³C{¹H} NMR (C₆D₆, 298 K): δ 11.83 (Me₂Si), 15.12 (HCSi₃), 30.68 (CH-CH₂), 36.53 (CH₂-CH), 52.28 (C-CH₂), 52.56 (NC) ppm. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ –9.50 ppm. ⁷Li NMR (C₆D₆, 298 K): δ 3.47 ppm. FTIR: ν 2956 (vs), 2924 (vs), 2854 (vs), 1461 (s), 1404 (m), 1378 (m), 1261 (m), 1096 (m), 1018 (m), 860 (w), 802 (m) cm^{–1}. Anal. Calc'd for C₃₇H₆₄Li₃N₃Si₃: C, 67.64; H, 9.83; N, 6.41. Found: C, 67.66; H, 9.74; N, 6.34.

[U(Ts^{Ad})(Cl)(μ-Cl){Li(THF)₃}] (**4**)

THF (30 ml) was added to a **pre-cooled** (−78 °C) mixture of **2** (1.31g, 2.0 mmol) and UCl₄ (0.76 g, 2.0 mmol). The mixture was allowed to warm to ambient temperature over 16 h, before being briefly heated to 60 °C and allowed to cool back to ambient temperature. The volatiles were removed *in vacuo* and the product was extracted into 20 ml hot (70 °C) toluene. The mixture was filtered through a G4-frit and volatiles were removed *in vacuo*. The resulting brown sticky solid was washed with hexanes (2 × 20 ml) and dried *in vacuo* to yield a brown solid. Green crystals of **4** were grown from a saturated solution in THF at −30 °C. Yield: 0.23 g, 10%.

¹H NMR (C₆D₆, 298 K): δ −93.58 (s, 1H, HCSi₃), −8.55 (s, 18H, Me₂Si), 6.48 (s, 9H, Ad-CH₂), 7.24 (s, 9H, Ad-CH₂), 10.31 (s, 9H, Ad-CH), 28.88 (s, 18H, Ad-CH₂) ppm. THF signals not observed. No signal was observed in the ⁷Li NMR spectrum of **4**. FTIR: ν 2955 (vs), 2925 (vs), 2855 (vs), 1596 (s), 1541 (w), 1458 (s), 1433 (s), 1377 (m), 1332 (m), 1319 (m), 1287 (w), 1259 (w), 1247 (w), 1153 (w), 1109 (w), 1033 (m), 1002 (m), 933 (m), 837 (s), 771 (m), 731 (m), 682 (w) cm^{−1}.

[U(Ts^{Ad})(I)] (**5**)

Method 1: THF (30 ml) was added to a **pre-cooled** (−78 °C) mixture of **2** (1.31g, 2.0 mmol) and UCl₄ (0.76 g, 2.0 mmol). The mixture was allowed to warm to ambient temperature over 16 h, before being briefly heated to 60 °C and allowed to cool back to ambient temperature. The volatiles were removed *in vacuo* and the product was extracted into 20 ml hot (70 °C) toluene. The mixture was filtered through a G4-frit and volatiles were removed *in vacuo*. The resulting brown sticky solid was washed with hexanes (2 × 20 ml) and dried *in vacuo* to yield a brown solid, which was dissolved in THF (20 ml) and cooled to −78 °C. Iodotrimethylsilane (0.80 g, 4.0 mmol) was added dropwise and the solution allowed to warm to ambient temperature over 16 h before being briefly heated to 60 °C and allowed to cool back to ambient temperature. The volatiles were removed *in vacuo* and the product extracted into 20 ml hot (70 °C) toluene. The mixture was filtered through a G4-frit and volatiles were removed *in vacuo*. The resulting brown sticky solid was washed with hexanes (2 × 5 ml) and dried *in vacuo* to yield a brown solid. Brown crystals of **5** were grown from a saturated solution in hexanes at −30 °C. Yield: 1.80 g, 90%.

Method 2: THF (30 ml) was added to a **pre-cooled** (−78 °C) mixture of **2** (3.94 g, 6.0 mmol) and UI₃(THF)₄ (7.26 g, 8.0 mmol). The mixture was allowed to warm to room temperature over 16 h. The mixture was allowed to warm to ambient temperature over 16 h, before being briefly heated to 60 °C and allowed to cool back to ambient temperature. The volatiles were removed *in vacuo* and the product was extracted into 50 ml hot (70 °C) toluene. The mixture was filtered through a G4-frit and volatiles were removed *in vacuo*. The resulting brown sticky solid was washed with hexanes (2 × 20 ml) and dried *in vacuo* to yield a brown solid. Brown crystals of **5** were grown from a saturated solution in hexanes at −30 °C. Yield: 3.38g, 56%.

¹H NMR (C₆D₆, 298 K): δ −90.27 (s, 1H, HCSi₃), −8.81 (s, 18H, Me₂Si), 6.75 (s, 9H, Ad-CH₂), 7.47 (s, 9H, Ad-CH₂), 11.12 (s, 9H, Ad-CH), 31.54 (s, 18H, Ad-CH₂) ppm. FTIR: ν 2956 (vs), 2924 (vs), 2854 (vs), 1460 (s), 1403 (m), 1377 (m), 1309 (w), 1260 (m), 1094 (s), 1020 (s), 861 (m), 800 (s) cm^{−1}.

2.4 X-ray Crystallography

Crystallographic data for **1**, **2**, **4** and **5** are summarised in Table 1. Crystals were examined either on an Oxford Diffraction SuperNova Duo diffractometer using mirror-monochromated CuK α radiation ($\lambda = 1.5418$ Å) or a Bruker SMART APEX CCD diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.7107$ Å). Intensities were integrated from a sphere of data recorded by ω rotation on narrow frames (SuperNova: 1.0°; SMART: 0.3°). Cell parameters were refined from the observed positions of all reflections in each data set. Semi-empirical absorption corrections based on symmetry-equivalent and repeat reflections were applied. The structures were solved using direct 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 the final difference syntheses were close to heavy atoms and were of no chemical significance. Programs for control and integration were CrysAlisPro[52] and Bruker AXS Smart/SAINT.[53] SHELX[54] and Olex2[55] were employed for structure solution and refinement and for molecular graphics.

Table 1 - Crystal data for 1, 2, 4 and 5

	1	2	4	5
Formula	C ₃₇ H ₆₇ N ₃ Si ₃	C ₃₇ H ₆₄ Li ₃ N ₃ Si ₃	C ₄₉ H ₈₇ Cl ₂ LiN ₃ O ₃ Si ₃ U	C ₃₇ H ₆₄ IN ₃ Si ₃ U
Formula Mass	638.21	656.00	1167.36	1000.11
Crystal size (mm)	0.38 × 0.06 × 0.04	0.55 × 0.12 × 0.04	0.24 x 0.21 x 0.14	0.09 x 0.04 x 0.03
Crystal system	Trigonal	Monoclinic	Triclinic	Orthorhombic
Space group	<i>R</i> −3	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> −1	<i>Pnma</i>
<i>a</i> (Å)	19.0168(5)	14.9431(3)	12.1230(3)	19.962(2)
<i>b</i> (Å)	19.0168(5)	20.5188(3)	12.6986(3)	15.817(2)
<i>c</i> (Å)	17.8194(5)	24.9295(5)	18.2985(5)	12.4674(15)
α (°)	90	90	76.314(2)	90
β (°)	90	105.172(2)	76.124(2)	90
γ (°)	120	90	78.019(2)	90
<i>V</i> (Å ³)	5580.8(3)	7377.3(3)	2642.37(12)	3883.0(8)
<i>Z</i>	6	8	2	4
$\rho_{\text{calc'd}}$ (g cm ^{−3})	1.139	1.181	1.467	1.711
μ (mm ^{−1})	1.376	1.390	10.543	5.097
No. of reflections measured	8144	48406	36087	23212
No. of unique reflections, <i>R</i> _{int}	2459, 0.022	14731, 0.0471	10563, 0.0467	4676, 0.0771
No. of refl'ns with $F^2 > 2\sigma(F^2)$	2112	10561	9267	3972
Transmission coeff. range	0.766 – 0.951	0.672 – 0.942	0.202 – 0.489	0.55 – 0.75
<i>R</i> ₁ , <i>R</i> _w ($F^2 > 2\sigma$)	0.0442, 0.1207	0.0605, 0.1356	0.0835, 0.2517	0.0505, 0.0983
<i>R</i> ₁ , <i>R</i> _w (all data)	0.0521, 0.1262	0.0811, 0.1446	0.0842, 0.2532	0.0696, 0.1058
<i>S</i>	1.056	1.080	1.253	1.072
Parameters	156	1090	565	264
Max., min. diff. (e Å ^{−3})	0.37, −0.52	0.80, −0.37	16.27, −3.92	2.76, −2.06

3. Results and Discussion

Figure 1 – Synthesis of 1-5.

Reagents/conditions: A) $n = 9$, $\text{HC}(\text{SiMe}_2\text{Br})_3$, Et_2O , 20 °C, 4h; B) $n = 3$, (1) 3 $n\text{BuLi}$, hexanes, 20 °C, 16 h, (2) $\text{HC}(\text{SiMe}_2\text{Br})_3$, THF , 20 °C, 16 h. **Although 3 has not been isolated, ^1H NMR spectra of crude reaction mixtures suggest that it may be formed but always in the presence of 4 which of the two is the only species to be structurally authenticated.**

The reaction of $\text{HC}(\text{SiMe}_2\text{Br})_3$ with nine equivalents of 1-adamantylamine (route 'A', Figure 1) in diethyl ether yielded, following work-up, a colourless microcrystalline precipitate. The room temperature ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of this material in benzene- d_6 exhibits resonances consistent with the proposed formulation, featuring resonances closely comparable with reported *tris*(aminodimethylsilyl)methanes. Alternatively, $\text{HC}(\text{SiMe}_2\text{Br})_3$ could be treated with lithium adamantylamide (obtained from the lithiation of AdNH_2) in THF (route 'B', Figure 1) to afford, after work up, a colourless microcrystalline precipitate that exhibited identical spectroscopic data to that obtained from route 'A'. Recrystallisation of either product from diethyl ether or toluene afforded colourless crystals suitable for a single crystal X-ray diffraction (XRD) study. The molecular structure obtained confirmed the anticipated formulation of 1 as $\text{HC}[\text{SiMe}_2\text{N}(\text{H})\text{C}_{10}\text{H}_{15}]_3$, $\text{Ts}^{\text{Ad}}\text{H}_3$, and is illustrated in Figure 2 with selected bond lengths and angles.

Figure 2 – Molecular structure of 1.

Ellipsoids set at 40% probability. H atoms (except NH) and minor disorder components are omitted for clarity. Selected bond distances (Å) and angles (°): C1-Si1 1.8865(8), Si1-N1 1.7412(15), N1-C4 1.470(2), Si1-C1-Si1A 113.61(6), Si1-N1-C4 130.75(12). Symmetry operations: $y-x, 1-x, z$; $1-y, 1+x-y, z$.

Ts^{Ad}H₃ **1** crystallises in the trigonal space group $R\bar{3}$ reflecting the threefold symmetry of the molecule in the solid-state. The asymmetric unit consists of one third of the Ts^{Ad}H₃ unit [C-SiMe₂-N(H)Ad], with the other two arms occupying symmetry equivalent positions and in total two Ts^{Ad}H₃ units are present in the unit cell related *via* an inversion centre. **1** is arranged in a concave conformation with the three adamantylamine arms projected away from the methane C-H bond along which a C₃ rotation axis is located. In contrast to Ts^{Xy}H₃, the N-bound hydrogens point into the ‘cavity’ formed by the three amine substituents whereas for the former they are found in ‘exo’ positions, which is ascribed to the larger steric demands of adamantyl *vs.* xylyl. All the bond distances and angles are unexceptional and compare well with previously reported examples of Ts^RH₃. [43, 56]

It is notable that for the reported syntheses of aryl-substituted Ts^{Ar}H₃ (e.g. Ar = 4-Me-C₆H₄, 3,5-Me₂-C₆H₃) *tris*(*N*-arylamino-dimethylsilyl)methanes three equivalents of arylamine and an auxiliary base (namely triethylamine) is required for a clean reaction. In the case of **1** increasing the number of equivalents of alkylamine to nine appears to affect a clean transformation without the requirement for an external auxiliary base, though of course here the adamantyl amine is acting as reagent and auxiliary base, and this is ascribed to the increased basicity of adamantylamine *cf.* arylamines.

With **1** in hand we prepared the tri-lithium salt as a ligand transfer reagent. Thus, treatment of **1** with three equivalents of *n*-butyllithium in a hexane/diethyl ether mixture afforded the corresponding trilithium *tris*(*N*-adamantylamidodimethylsilyl)methane [HC{SiMe₂N(Li)Ad}₃], Ts^{Ad}Li₃ (**2**) as an off-white solid following work-up (Figure 1). The room temperature ¹H, ¹³C, ²⁹Si and ⁷Li NMR spectra of this material in benzene-*d*₆ exhibits resonances consistent with the proposed formulation and recrystallisation from hexanes afforded colourless crystals suitable for a single crystal (XRD) study. The molecular structure obtained confirmed the anticipated formulation of **2** as Ts^{Ad}Li₃, and is illustrated in with selected bond lengths and angles.

Figure 3 – Molecular structure of 2.

Ellipsoids set at 40% probability. H atoms and minor disorder components are omitted for clarity. Selected bond distances (Å) and angles (°): Li1-N1 1.950(6), Li1-N2 1.978(6), Li2-N2 1.934(6), Li2-N3 1.990(6), Li3-N1 2.001(5), Li3-N3 1.945(5), N1-Si1 1.706(2), N2-Si2 1.708(2), N3-Si3 1.721(2), N1-Li1-N2 128.1(3), N2-Li2-N3 125.0(3), N3-Li3-N1 124.8(3).

Ts^{Ad}Li₃ **2** crystallises in the monoclinic space group $P2_1/n$ and the molecular structure confirms lithiation of the amide centres forming a six-membered [Li₃N₃] ring adopting a chair conformation with each lithium centre bridging two

amide nitrogens. The six Li–N bond distances range from 1.934(6) to 2.001(5) Å but do not appear to follow any rational trends with respect to coordination number or environment and instead appear to result from steric constraints. The $\text{CSi}_3\text{N}_3\text{Li}_3$ core adopts a distorted adamantane-type structure. Although in the solid state an unsymmetrical structure of C_1 symmetry is formed the ^1H and ^{13}C NMR spectra are consistent with a C_3 -symmetric species in solution, reflecting the fluxionality of many lithium amides in solution on the NMR-timescale.

We examined the applicability of **2** as a ligand transfer reagent with uranium(IV) tetrachloride and uranium(III) triiodide. Addition of THF to a cold equimolar mixture of UCl_4 and **2** afforded a dark green solution. Following work-up, the room temperature ^1H NMR spectrum in benzene- d_6 of the brown solid obtained is strongly suggestive of the presence of two new paramagnetic compounds in a ratio of approximately 9:1. The ^7Li NMR spectrum of the brown solid also revealed a low intensity very broad single resonance. Repeated recrystallisations from numerous solvents and mixtures of solvents were unable to improve the purity of the product, anticipated to be “[$\text{U}(\text{Ts}^{\text{Ad}})(\text{Cl})$]” (**3**) on the basis of previous work,[43, 46] as judged by NMR spectroscopy; however on one occasion a batch of green crystals of sufficient quality for a single crystal XRD study were obtained from a saturated THF solution. The molecular structure obtained revealed the new compound [$\text{U}(\text{Ts}^{\text{Ad}})(\text{Cl})(\mu\text{-Cl})\{\text{Li}(\text{THF})_3\}$] (**4**) and is illustrated in Figure 4 with selected bond lengths and angles.

Figure 4 – Molecular structure of 4.

Ellipsoids set at 40% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): U1–Cl1 2.710(2), U1–Cl2 2.852(2), U1–N1 2.255(8), U1–N2 2.234(7), U1–N3 2.242(7), Cl2–Li1 2.333(18), Cl1–U1–Cl2 83.06(7), N1–U1–Cl2 173.88(18), N2–U1–Cl2 84.9(2), U1–Cl2–Li1 139.2(4).

Complex **4** crystallises in the triclinic space group $P\bar{1}$ and the molecular structure reveals a [$\text{U}(\text{Ts}^{\text{Ad}})(\text{Cl})_2$] $^-$ unit coordinated through a bridging chloride centre (Cl2) to a [$\text{Li}(\text{THF})_3$] $^+$ moiety so that overall the structure carries zero net charge. The uranium centre in **4** is coordinated by the three amide centres of the Ts^{Ad} ligand, one terminal chloride atom and a second chloride which bridges to a lithium ion that is coordinated by three THF molecules. The uranium centre adopts a distorted trigonal bipyramidal geometry such that the N1 and Cl2 atoms occupy the axial sites. Whilst the U–N bond distances are typical of uranium(IV)– N_{amide} bonds [2.244(7) Å (av.)],[57] the U1–Cl2 bond distance of 2.852(2) Å is lengthened by ~0.14 Å relative to the U1–Cl1 bond length of 2.710(2) Å. This is a consequence of the bridging coordination mode of the Cl2 centre and the associated polarisation of electron density away from the

U1–Cl2 bond by the lithium centre, with the terminal Cl1 atom remaining unaffected. Whilst chlorides are well known to bridge between uranium and lithium in the solid state, no structural examples are known that feature lithium coordinated by three Lewis basic solvent molecules, although $[\text{U}(\text{L})_n(\mu\text{-Cl})_2\{\text{Li}(\text{THF})_2\}]$ is a common structural motif in non-aqueous uranium coordination chemistry[56] and highlights the significant steric demands of the Ts^{Ad} ligand system. The remainder of the metrical parameters lie within reported ranges.

The room temperature ^1H NMR spectrum of **4** in benzene- d_6 features a total of six paramagnetically shifted resonances ranging from -93.58 to 28.88 ppm for the Ts^{Ad} ligand consistent with a C_3 -symmetric conformation in solution on the NMR timescale. Neither the signals for the coordinated THF molecules in the ^1H NMR spectrum nor any resonance in the ^7Li NMR spectrum of **4** are observed, which is assigned to a mixture of line broadening arising from dynamic processes, fast relaxation from the presence of coordinated uranium centres and potential decoordination of solvated lithium chloride to form insoluble $[\text{Li}(\text{THF})_x(\text{Cl})]_n$ oligomers and **3**. [58]

The room temperature (Evans method) effective magnetic moment of **4** in benzene of $3.37 \mu_{\text{B}}$ (μ_{B} = Bohr magneton) 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), [59] although uranium(IV) compounds usually fall in the range $2.5\text{--}3.1 \mu_{\text{B}}$. [60] We attempted to verify the uranium oxidation state assignment of +4 for **4** by variable-temperature superconducting quantum interference device (SQUID) measurements but reliable results could not be obtained due to batches persistently being mixtures of **3** and **4** in crystalline samples.

In order to ascertain a pure Ts^{Ad} -uranium(IV) halide complex and to target more weakly coordinated groups such as iodides or tetra-aryl borates – that may sometimes be synthetically preferred from the viewpoint of preparing derivatives by salt elimination – the conversion of the anticipated chloride complex “[$\text{U}(\text{Ts}^{\text{Ad}})(\text{Cl})$]” (**3**) and **4** to the corresponding iodide complex via halide metathesis was investigated. Accordingly, the brown solid obtained after work-up from the initial reaction of **2** with UCl_4 , was treated with a two-fold excess of trimethylsilyl iodide (to ensure complete conversion). Following work-up, a saturated solution in hexanes yielded brown crystals suitable for a single crystal XRD study. The molecular structure obtained revealed the new compound $[\text{U}(\text{Ts}^{\text{Ad}})(\text{I})]$ (**5**) and is illustrated in Figure 5 with selected bond lengths and angles.

Figure 5 – Molecular structure of 5.

Ellipsoids set at 40% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): U1–I1 3.0942(7), U1–N1 2.190(5), U1–N1A 2.190(5), U1–N2 2.210(8), N1–U1–I1 116.05(13), N1A–U1–I1 116.05(13), N2–U1–I1 117.0(2) C1–U1–I1 179.66(19). Symmetry operation: $x, \frac{1}{2}-y, z$.

Complex **5** crystallises in the orthorhombic space group *Pnma*. The uranium centre in **5** is coordinated by the three amide centres of the Ts^{Ad} ligand and one terminal iodide atom and adopts a distorted tetrahedral geometry, with the overall structure possessing *C*₃ point group symmetry. The U–I and mean U–N bond distances of 3.0942(7) and 2.197(6) Å, respectively, in **5** are unexceptional for uranium(IV)–iodide and –N_{amide} bonds[56] but each are shorter by ~0.05 Å than for the respective bond lengths in the reported complex [U(Ts^{Xy})(I)(THF)] (**6**), in which the U–I and mean U–N bond distances are 3.1561(3) and U–N 2.243(3) Å, respectively. This is attributed to the lower steric demands of the Ts^{Xy} ligand in **6** vs. Ts^{Ad}; in **5** the steric demands of the Ts^{Ad} ligand are sufficient to prevent coordination of a THF molecule which renders the uranium centre in **5** more electron deficient relative to **6** resulting in shorter U–I and U–N bond lengths in **5** than in **6**.

The room temperature ¹H NMR spectrum of **5** in benzene-*d*₆ features a total of six paramagnetically shifted resonances ranging from –90.27 to 31.54 ppm for the Ts^{Ad} ligand consistent with a *C*₃-symmetric conformation in solution. The room temperature (Evans method) effective magnetic moment of **5** could not be reliably obtained due to the poor solubility of **5** in benzene; however we were able to investigate the magnetism of **5** by variable-temperature SQUID measurements. At low temperature, uranium(IV) systems normally have a singlet magnetic ground state, typically resulting in a magnetic moment of approximately 0.5 μ_B at 1.8 K from temperature independent paramagnetism with the magnetisation trace tending to zero. For **5**, the value of μ_{eff} at 300 K is 2.62 μ_B, which declines smoothly as the temperature is lowered to around 50 K, where it begins to decrease more sharply and at 1.8 K the magnetic moment is 0.40 μ_B (Figure 6). The SQUID magnetisation trace indeed tends to zero at this temperature, consistent with a 5f² electronic configuration and a +4 oxidation state assignment for uranium.

Figure 6 – SQUID trace for **5.**

Applied DC field: 0.1 T. Diamagnetic correction: 5.6852×10^{-4} emu mol⁻¹.

During the course of investigations into a Ts^{Ad}-uranium(III) derivative, **2** reacted with dark blue uranium(III) triiodide THF solvate, [UI₃(THF)₄] to produce dark purple reaction mixtures, which after work-up and crystallisation from hexanes yielded brown crystals that were identified as **5** via crystallographic unit cell checks and NMR spectroscopy. Therefore it is proposed that **5** is the product of disproportionation and ligand redistribution reactions of the putative

uranium(III)-Ts^{Ad} compound “[U(Ts^{Ad})(THF)]”, which is supported by the observation that a dark grey solid was isolated from the reaction mixture which is highly likely to be elemental uranium. The reason for disproportionation to produce **5** and 0.25 equivalents of uranium(0) is unclear, however it is not uncommon within the context of organouranium chemistry[61-64] and most likely is a consequence of coordinative unsaturation of the U(III) ion in “[U(Ts^{Ad})(THF)]”.

4. Summary, Conclusions & Future Work

The new *tris*(*N*-adamantylamine-dimethylsilyl)methane HC{SiMe₂N(H)Ad}₃ (Ts^{Ad}H₃, **1**) was prepared and converted to the corresponding trilithium derivative [HC{SiMe₂N(Li)Ad}₃] (Ts^{Ad}Li₃, **2**) with three equivalents of *n*-butyllithium. The salt elimination reaction between **2** and UCl₄ afforded a brown solid from which, rather than the anticipated chloride complex “[U(Ts^{Ad})(Cl)]” (**3**), crystalline [U(Ts^{Ad})(Cl)(μ-Cl){Li(THF)₃}] (**4**) was isolated, although the poor crystallinity of **3** precluded XRD analysis and it is highly likely that it is the major product from this reaction. The halide exchange reaction between this mixture and Me₃SiI produced [U(Ts^{Ad})(I)] (**5**) in good yield, supporting the hypothesis that **3** is the major product of the reaction between **2** and UCl₄. The independent synthesis of **5** was achieved *via* the reaction of **2** with UI₃(THF)₄, in which the presumed initial uranium(III) product “[U(Ts^{Ad})(THF)]” undergoes disproportionation to produce **5** (max. yield 75%) and elemental uranium. This disproportionation most likely arises from the lack of coordinative saturation at the uranium centre and points to insufficient steric protection conveyed by the Ts ligand to stabilise the uranium(III) species. Investigations are ongoing into further derivatising **5** and isolating a stable Ts^{Ad}-uranium(III) complex employing Lewis base stabilisers.

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Disclosure Statement

No potential conflict of interest is declared by the authors.

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ToC Figure

ToC Text

The synthesis of a new bulky *tris*(*N*-adamantylaminedimethylsilyl)methane proliligand and its use in preparing uranium derivatives is described.