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Synthesis of a highly strained uranacycle: molecular structures of organometallic products arising from reduction, oxidation and protonolysis

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Abstract

The reaction of $[U(NN'_3)I]$ $[NN'_3 = N(CH_2CH_2NSiMe_2Bu^t)_3]$ with Group 1 and 2 metal alkyls gives, via metalation of a methylsilyl group, a highly strained metallacycle $[U(\mathit{bit}\text{-}NN'_3)]$ in high yield. The molecular structure of this compound shows that it has an unusually long U–C bond (ca. 2.75 Å) and additional C–H···M agostic interactions. On exposure of the complex in solution to $^2H_2$ the methylsilyl groups and the metallacyclic UCH_2Si group are deuterated, leaving the *tert*-butyl and methylene groups intact. The analogous thorium metallacycle is prepared from the reactions of $[Th(NN'_3)Cl]$, or by attempted reduction of $[Th(NN'_3)I]$ with potassium metal in pentane. Attempted reduction of $[U(NN'_3)I]$ in a similar manner in toluene gave a high yield of a fascinating dimeric metallacyclic anion $\{[K(\eta^6\text{-}C_6H_5Me)][U(\mathit{bit}\text{-}NN'_3)]\}_2$, which was characterised by X-ray crystallography. The authenticity of this compound as U(III) is established by near-IR spectroscopy, and also by its production from the reaction of the neutral uranacycle $[U(\mathit{bit}\text{-}NN'_3)]$ with potassium. A mechanism for the formation of the anion is postulated. Its reaction with benzyl chloride led to oxidation to the parent uranacycle. Oxidation of $[U(\mathit{bit}\text{-}NN'_3)]$ with air or oxide sources leads to formation of an oxo-bridged dimer with intermonomer metalated methylsilyl groups and pentavalent uranium centres. Reactions of $[U(\mathit{bit}\text{-}NN'_3)]$ with a range of acids HX occur rapidly, reprotonating the previously metalated methylsilyl group and forming complexes $[U(NN'_3)X]$. For example, lutidinium hydrochloride, diethylamine and *tert*-butanol gave $[(NN'_3)UCl]$, $[(NN'_3)U(NEt_2)]$ and $[(NN'_3)U(OBu^t)]$, respectively. Reactions with carbon acids were also successful. For example, β-hydropyridines gave η^2-dehydropyridyl complexes. One of these, $[U(NN'_3)(\eta^2\text{-}NC_5H_4)]$, is shown in the first X-ray crystallographic study of such an actinide complex to contain an essentially planar $U(\eta^2\text{-}NC_5H_4)$ unit. Monosubstituted alkynes react with the uranacycle in a similar manner to give η^1-alkynyls. The molecular structure of one example shows that the U–C≡C unit is bent (156°) in contrast to other structurally characterised non-bridging alkynyls of the f-elements. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: C–H activation; Metallacycle; Protonolysis

1. Introduction

Although the intramolecular C–H activation of peripheral ligands is often a troublesome side-reaction in organo f-element coordination and organometallic chemistry, and is relatively common among complexes containing bulky alkyls [1], amides (vide infra), phosphides [2] and phenoxides [3], the metallacyclic products have, by virtue of their reactive M–C bonds, been used as starting materials for a wide range of complexes. For example, Andersen's metallacycles $[\{(Me_3Si)_2N\}_2M\{N(SiMe_3)(SiMe_2CH_2)\}]$ (M = U, Th) [4] have been exploited by a number of workers [5]. Molecular models suggested to us that triamidoamine [6] $[(RNCH_2CH_2)_3N)]^{3-}$ complexes of metals with large van der Waals radii would be less prone to intramolecular metalation because of conformational restrictions (vide infra), and might instead undergo *inter*molecular reactions with C–H bonds. With this in mind we set out to synthesise species such as $[\{(RNCH_2CH_2)_3N\}MR']$ (M = U, Th; R′ = H, alkyl).

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While we have prepared a wide range of triamidoamine complexes containing bonds between the early actinides and other elements [7], the synthesis of M–C σ-bonds proved troublesome. For example, reactions of the uranium and thorium chlorides [{$(RNCH_2CH_2)_3$-N}MCl] (R = $SiMe_3$) and related compounds with a wide variety of metal alkyls led to the formation of intractable yellow mixtures. More recently, however, we have shown that the bulkier triamidoamine (where R = $SiMe_2Bu^t$, henceforth NN'_3), forms much more synthetically useful complexes with the f-elements [8,9]. Use of this ligand has allowed us to isolate extremely reactive and structurally fascinating metallacyclic actinide complexes which are excellent starting material for the synthesis of other organometallic compounds.

2. Results and discussion

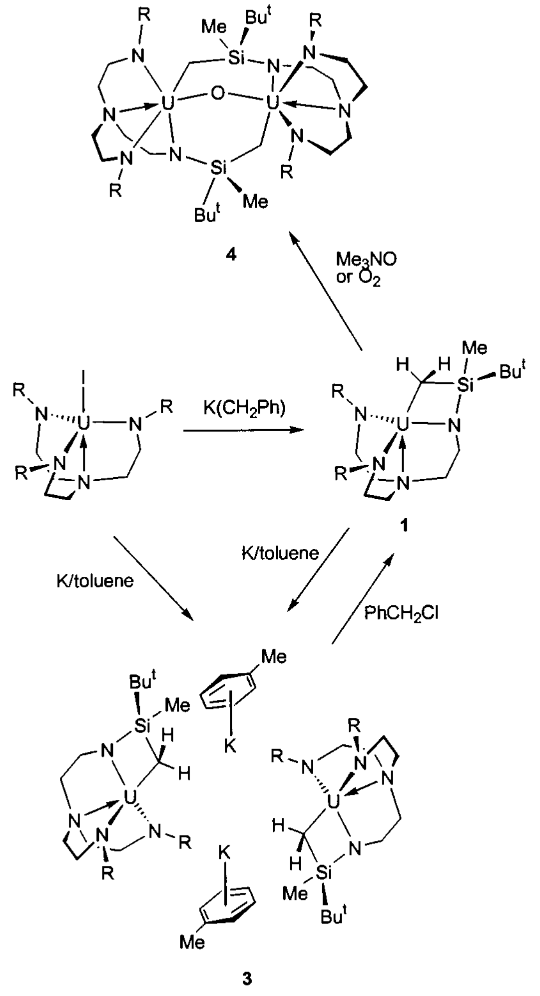
2.1. Synthesis and structure of the metallacycles [M(*bit*-NN'_3)] (M = U **1**, Th **2**)

Reactions of [U(NN'_3)Cl] [8] with a range of lithium, potassium, magnesium and zinc alkyls in pentane gave brown solutions from which extremely air-sensitive orange–brown crystals of the metallacycle [U(*bit*-NN'_3)] (**1**) could be isolated in modest yield (Scheme 1). After experimenting with many combinations of reagents, we found that optimum yields (71% isolated) could be obtained by reaction of [U(NN'_3)I] [8] with a stoichiometric amount of diethylzinc, lithium neopentyl or potassium benzyl in toluene followed by filtration and cooling the solution to −30°C. When this latter reaction was performed in an NMR tube and monitored by ^{1}H-NMR spectroscopy, smooth and quantitative conversion of [U(NN'_3)I] to **1** with co-production of toluene was observed within minutes at ambient temperature. Although we were unable to detect any intermediate species such as an alkyl **I** (Scheme 2) or a deprotonated species **II** we prefer the mechanism via **I** since the reaction proceeds reasonably well even for less basic alkylating agents such as $ZnEt_2$. In any event, the rapidity of the metalation reaction is quite surprising; by comparison, conversion of the titanium [10] and molybdenum [11] triamidoamines [{$(Me_3SiNCH_2CH_2)_3N$}$TiBu^s$] and [{$(Me_3SiNCH_2CH_2)_3N$}MoH] to their respective metallacycles occurs only slowly and at elevated temperatures. Similarly, Andersen's metallacycle [U{$N(SiMe_3)_2$}$_2${$N(SiMe_3)(CH_2SiMe_2)$}] is produced by thermolysis of [U{$N(SiMe_3)_2$}$_3$X] (X = H, Me) [4].

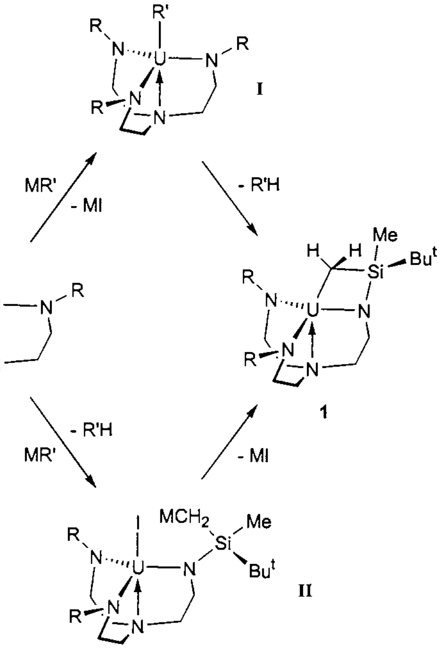
Single crystals of **1** were grown from a saturated solution of the pure compound in pentane and the molecular structure (Fig. 1) was determined by X-ray crystallography (Table 1). Two aspects of this structure are of interest: the geometry of the metallacyclic unit and the conformation of the supporting triamidoamine.

The metallacyclic U–C(108) distance of 2.752(11) Å is significantly longer than any other U–C σ-bond hitherto recorded; the usual range is ca. 2.4–2.55 Å [12], although distances of ca. 2.60 Å have been measured in complexes of chelating phosphorus ylids [13]. This is a consequence of the constraints imposed by the triamidoamine ligand (vide infra); Schrock's molybdenum metallacycle [Mo(*bit*-NN_3)] (which contains $SiMe_3$ substituents) has Mo–C = 2.249(3) Å, ca. 0.06–0.08 Å longer than the bonds in acyclic alkyls [Mo(NN_3)R] (R = CD_3, *cyclo*-C_6H_{11}). In contrast, the metallacyclic phosphide [$Cp^*_2U(CH_2SiMe_2PSiMe_3)$] [2] and amide [$Cp^*_2Th_2(CF_3SO_3)_3(NSiMe_3)(CH_2SiMe_2NSiMe_3)$] [14], which contain M–C–Si–N rings similar to that in **1**, have M–C distances of 2.415(20) and 2.43(5) Å, well within the normal An–C ranges.

Despite the presence of the metallacycle unit, **1** adopts the approximate C_3 symmetry observed in many triamidoamine complexes, and so it is appropriate to



Scheme 1. Synthesis and interconversion of complexes **1**, **3** and **4**. R = $SiMe_2Bu^t$.



Scheme 2. Mechanisms for the formation of **1**. R = SiMe$_2$Bu^t.

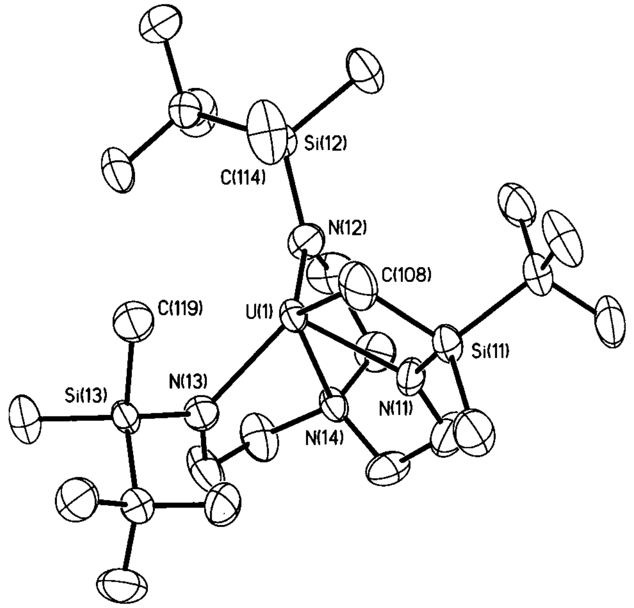


Fig. 1. Thermal ellipsoid plot of the molecular structure of **1**; hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): U(1)–N(12) 2.219(5), U(1)–N(11) 2.228(5), U(1)–N(13) 2.254(6), U(1)–N(14) 2.577(5), U(1)–C(108) 2.752(11), N(12)–U(1)–N(11) 107.2(2), N(12)–U(1)–N(13) 108.5(2), N(11)–U(1)–N(13) 107.7(2), N(12)–U(1)–N(14) 69.02(19), N(11)–U(1)–N(14) 68.79(19), N(13)–U(1)–N(14) 68.96(19), N(14)–U(1)–C(108) 134.8(2).

compare the conformation of the ligand in this compound with those in complexes [U(NN$'_3$)X]. Fig. 2 contains projections of the structures of **1** (a) and [U(NN$'_3$)Cl] [8], (b), a threefold symmetric complex. The upper views are projections along the U–N$_{ax}$ vector, while in the lower views the molecules have been rotated by 90°. All hitherto structurally characterised

Table 1
Experimental data for the X-ray diffraction studies of **1**, **3**, **4**, **5a** and **6b**

	1	**3**	**4**	**5a**	**6b**
Empirical formula	$C_{24}H_{56}N_4Si_3U$	$C_{31}H_{64}KN_4Si_3U$	$C_{51.75}H_{121}N_8Si_6U_2$	$C_{29}H_{61}N_5Si_3U$	$C_{33}H_{64}N_4Si_3U$
Formula weight	723.03	854.26	1516.17	802.13	839.18
Crystal dimensions (mm)	0.50 × 0.30 × 0.20	0.40 × 0.40 × 0.05	0.40 × 0.20 × 0.20	0.15 × 0.10 × 0.10	0.50 × 0.30 × 0.20
Colour	Orange–brown	Green	Black	Brown	Green
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	12.7602(5)	12.5214(10)	13.5776(10)	12.3435(2)	17.3244(10)
b (Å)	13.3286(5)	13.262	17.335(2)	13.10700(10)	12.7945(10)
c (Å)	13.3902(5)	13.3576(10)	17.7406(10)	13.1103(2)	18.6257(15)
α (°)	119.3350(10)	103.48	80.017(4)	61.1710(10)	–
β (°)	109.0980(10)	103.7160(10)	74.844(5)	87.3160(10)	97.7090(10)
γ (°)	92.8980(10)	100.6730(10)	71.628(5)	85.9680(10)	–
Cell volume (Å^3)	1813.56(12)	2026.6(2)	3806.0(6)	1853.39(4)	4091.2(5)
Z	2	2	2	2	4
D_{calc} (Mg m^{-3})	1.324	1.400	1.323	1.437	1.362
μ (mm^{-1})	4.590	4.219	4.378	4.500	4.080
Temperature (K)	180(2)	180(2)	180(2)	180(2)	180(2)
θ_{max} (°)	28.51	28.55	22.50	28.55	28.55
Total reflections	11 113	12 434	15 332	11 367	24 202
Independent reflections	8070	9020	9810	8238	9593
R_{int}	0.0296	0.0253	0.0640	0.0379	0.0922
Significant reflections, $I > 2\sigma(I)$	6567	7673	5976	6785	8001
No. parameters	293	348	651	358	386
T_{max}, T_{min}	0.4604, 0.2074	0.9280, 0.6961	0.928, 0.714	0.928, 0.712	0.4959, 0.2349
Goodness-of-fit on F^2	1.022	1.101	1.015	2.090	1.075
(Δp) max., min. (e Å^{-3}) (near U)	2.834, −4.478	2.813, −1.700	1.374, −0.967	2.057, −1.903	3.191, −2.965
R_1, wR_2 [$I > 2\sigma(I)$]	0.0459, 0.1206	0.0606, 0.1322	0.0566, 0.1296	0.0685, 0.0859	0.0559, 0.1533

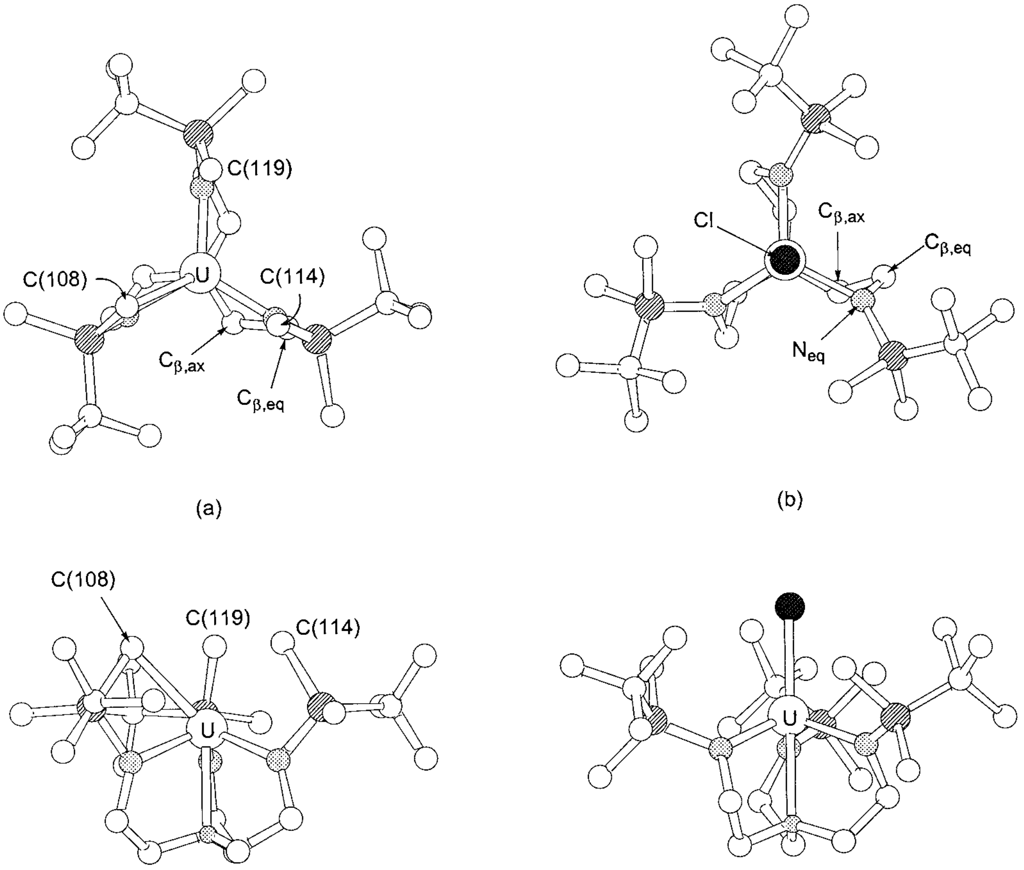


Fig. 2. Molecular structures of (a) metallacycle **1** and (b) [(NN$'_3$)UCl]. The upper views are projections along the U–N$_{ax}$ vector with the amino N$_{ax}$ behind U, while in the lower views there is the vector in the plane of the page.

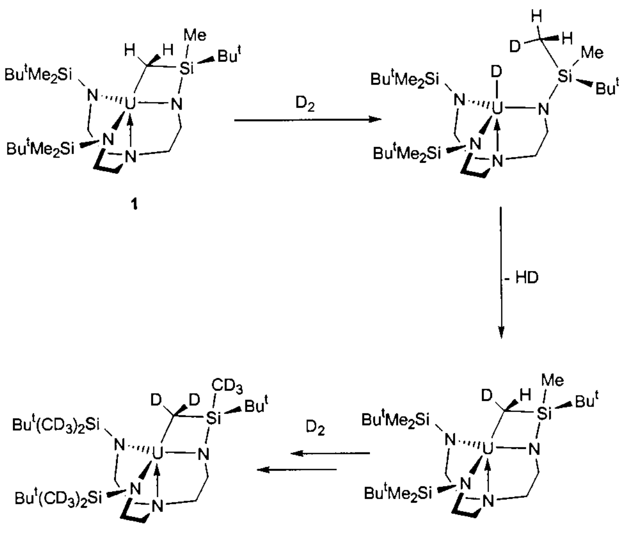
threefold symmetric triamidoamines of the lanthanides [15] and actinides [7–9] adopt the conformation shown in (b), upper, where the carbon atoms C$_{\beta,eq}$ act as the 'flap' in an envelope configuration of the UN$_2$C$_2$ rings. The dihedral angles N$_{ax}$–U–N$_{eq}$–Si are, for all known structures, in the range 125–140°; this structural parameter is essentially unaffected by the steric demand of the ligand in the fifth (axial) coordination site. The bulky *tert*-butyldimethylsilyl groups are thus directed to encircle the equatorial coordination sphere [see Fig. 2(b), lower)], i.e. the substituents are 'laid back' as compared to the 'upright' conformation observed in the molybdenum triamidoamines. These latter compounds display a much wider (and also metal-substituent-dependent) range in the above-mentioned dihedral angle (129–177°) [11]. The structure of **1** (Fig. 2(a)) shows that in this case it is C$_{\beta,ax}$ that forms the 'flap'; the three dihedral angles N$_{ax}$–U–N$_{eq}$–Si are 175–177°. The adoption of this conformation and the accompanying 'upright' substituents [Fig. 2(a), lower] is of course required in order for the methylene carbon atom C(108) to approach the U atom to which it is σ-bonded.

A further feature of the structure of **1** is the orientation of the SiMe$_2$ groups at Si(12) and Si(13) which bring one methyl groups from each, C(114) and C(119), toward the otherwise open face of the uranium centre. The non-bonded U–C distances of 3.056(14) and 3.218(10) Å, respectively are consistent with the presence of C–H → U agostic interactions [16]. The maximum deviations of any atom from the least-squares planes [U, N(12), Si(12), C(114)], [U, N(13), Si(13), C(119)] and [U, N(11), Si(11), C(108)] are 0.08, 0.05 and 0.06 Å, respectively.

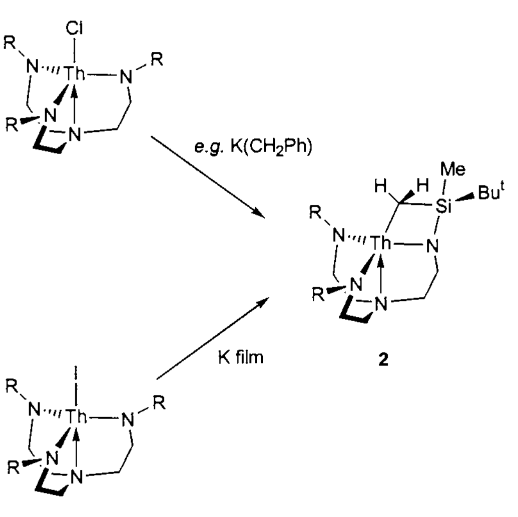
The ^{1}H-NMR spectrum of **1** recorded in toluene-*d*$_8$ contains a total of 22 peaks, indicating that the product is chiral; the metallacyclic Si atom being stereogenic. This is good evidence for the retention of the monomeric structure of **1** in solution; a dimeric structure (cf. **4**, Section 2.3) would give rise to a much more complex spectrum (up to 44 resonances in total) because of the presence of diastereomeric pairs. Of the resonances observed, 20 are readily assigned to methyl and *tert*-butyl groups or diastereotopic methylene protons in the ligand backbone. Surprisingly (given the proximity of the paramagnetic centre) we were able to observe two resonances arising from the Si–CH$_2$–U group. These appear as relatively broad peaks at −35.34 and −52.34 ppm, assigned on the basis of a selective deuteration study described below.

The SiMe$_3$ groups in Andersen's metallacycle are almost completely deuterated by exposure of a solution of the complex to $^2H_2$. The reaction is proposed to proceed via sequential σ-bond metathesis reactions [4]. Similarly, addition of dry $^2H_2$ to a sample of **1** in tolune-d_8 led at ambient temperature over a period of hours to deuteration of all $SiMe_2$ groups and also the metallacyclic CH_2. As expected, the *tert*-butyl CH_3 and the methylene CH_2 groups, which do not have α-Si atoms, are not affected by this process, which is depicted in Scheme 3.

The diamagnetic thorium metallacycle [Th(*bit*-NN$'_3$)] (**2**) is produced in an analogous manner to **1** by reaction of [Th(NN$'_3$)Cl] with alkylating agents, or by attempted reduction of [Th(NN$'_3$)I] with potassium film in pentane (Scheme 4). We propose that under these latter conditions, [Th(NN$'_3$)I] is reduced to [Th(NN$'_3$)] which rapidly undergoes intramolecular metalation to give **2**.



Scheme 3. Selective H/D exchange process for **1**.



Scheme 4. Synthesis of **2**. R = $SiMe_2Bu^t$.

2.2. Reduction of the metallacycle; synthesis, structure, absorption spectra and reactions of trivalent {[K(η^6-C_6H_5Me)][U(bit-NN$'_3$)]}$_2$ (3)

Since the uranium iodide [U(NN$'_3$)I] is reduced cleanly to [U(NN$'_3$)] by a potassium film in pentane [9], we were most surprised to find that a similar reaction using toluene as the solvent led cleanly and reproducibly to the fascinating and exceptionally air-sensitive metallacycle anion dimer {[K(η^6-C_6H_5Me)][U(*bit*-NN$'_3$)]}$_2$ (**3**) in good yield (Scheme 1).

The molecular structure of **3**, shown in Fig. 3, may be described as a centrosymmetric dimer of metallacycle anions [U(*bit*-NN$'_3$)]$^-$ with interstitial potassium cations. Each potassium ion is coordinated by an η^6-toluene ligand with K–C distances in the range 3.42–3.58 Å. A few arene complexes of potassium have been crystallographically characterised [17], and the bond lengths in **3** are not unusual. The remainder of the coordination sphere of each potassium ion is surrounded by C–H bonds, and we propose that a number of weak intra-dimer C–H···M interactions are present. The closest contact to K(1) involves the metallacyclic carbon atom C(7), 3.033(9) Å distant, and we take this as an indication of a relatively high negative charge on this atom. Longer contacts are made with C(18B) and C(23B) [3.547(9) and 3.609(9) Å, respectively]. Most interestingly, the metallacyclic U(1)–C(7) distance at 2.575(10) Å is significantly shorter than that in the neutral metallacycle **1** but it is still at the upper end of previously recorded U–C bonds distances.

Most unusually for a complex containing a uranium(III) centres, **3** is quite pale green in the solid state, but solutions are more intensely coloured. This molecule is insoluble in aliphatic hydrocarbons and reacts with THF liberating hydrogen. It is sufficiently soluble in toluene however for good quality UV–vis/near-IR spectra to be obtained in the region above 600 nm where the solvent absorptions can be subtracted successfully. The spectrum obtained, shown in Fig. 4, bears a striking resemblance to that of the brown, trigonal bipyramidal U(III) compound $[K(THF)_2]_2[U(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)_5]\cdot THF$ [18] and other authentic U(III) complexes [19]. The position and the intensity (molar absorptivities $\varepsilon = 10–80\ M^{-1}\ cm^{-1}$) of these bands are consistent with Laporte-forbidden f→f transitions of the uranium (III) centre.

In order to substantiate further the presence of trivalent uranium in **3**, we performed the following experiments (Scheme 1). Shaking an NMR tube containing a solution of pure **1** in $^2H_8$-toluene and a small potassium film led to slow (ca. 1 day) but clean conversion to **3** as evidenced by ^{1}H-NMR spectroscopy. Similarly, **3** was oxidised cleanly to **1** by treatment with benzyl chloride.

There remains, however, the intriguing question of how **3** is produced from [U(NN$'_3$)I] with K–toluene

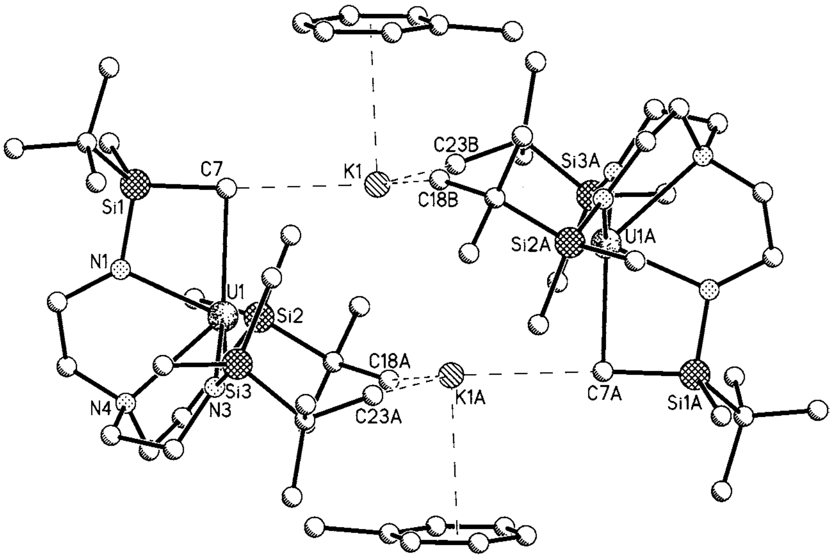


Fig. 3. Molecular structure of **3**; hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): U(1)–N(1) 2.246(8), U(1)–N(3) 2.281(8), U(1)–N(2) 2.305(8), U(1)–C(7) 2.575(10), U(1)–N(4) 2.624(7), N(1)–U(1)–N(3) 101.0(3), N(1)–U(1)–N(2) 100.4(3), N(3)–U(1)–N(2) 119.2(3), N(1)–U(1)–N(4) 66.5(3), N(3)–U(1)–N(4) 69.1(3), N(2)–U(1)–N(4) 69.0(3), C(7)–U(1)–N(4) 133.9(3), K(1)–C(7) 3.033(9).

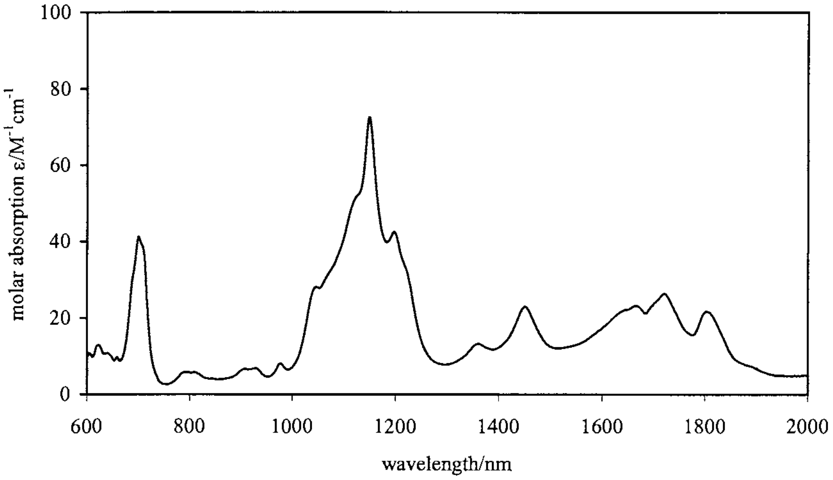


Fig. 4. Absorption spectrum of **3** measured in toluene solution (274 K, ca. 5×10^{-4} M, path length, 0.1 cm). Bands below 600 nm obscured by solvent.

when the analogous reaction with K–pentane gives pure $[U(NN'_3)]$. We noted during the toluene experiments, small pieces of potassium present in the Schlenk flask were tinged bright orange, the colour of potassium benzyl. Hence we propose the following stoichiometric mechanism. Potassium benzyl is produced in small quantities at equilibrium, perhaps in a reaction catalysed by a uranium-containing component in the reaction mixture. This reacts rapidly, as we have shown above, with $[U(NN'_3)I]$ to give metallacycle **1**. We have also shown above that **1** reacts with potassium to furnish the observed product **3**.

2.3. Oxidation of the metallacycle: structure of the pentavalent oxo-bridged dimer

During one of many attempts to grow single crystals of **1** from pentane solution, a 'streaky' ground-glass joint allowed ingress of a small quantity of air to the crystallising vessel. The dark solution thus formed deposited a few large black crystals of **4** (Scheme 1). The uranium centres in **4** are pentavalent.

An X-ray crystallographic investigation revealed **4** to be a dimer, constructed by inter-monomer metalated methylsilyl groups and bridged an oxo ligand (Fig. 5).

The metallacyclic ring strain present in **1** has been relieved by transmetalation of the alkyl group, leading to more normal U–C bond lengths U(1)–C(212) and U(2)–C(112) of 2.442(13) and 2.457(15) Å. The bridging oxo ligand has unremarkable structural parameters. The unsymmetric orientation of the triamidoamine unit is accompanied by a wider range of 'flap' dihedral angles (132–177°) in the ligand backbone.

The pentavalent oxo species **4** is produced under controlled conditions by oxidation of **1** with trimethylamine-*N*-oxide, but crystallisation of bulk samples was not achieved. ^{1}H-NMR spectra of the crude product indicated the presence of approximately equal quantities of two diastereomers (vide supra) and the compound was not characterised further.

2.4. Reactions of the metallacycle [U(bit-NN′$_3$)]: synthesis and structures of the organometallic compounds [U(NN′$_3$)(η^2-pydridyl)] (**5**) and [U(NN′$_3$)(alkynyl)] (**6**)

The synthetic utility of Andersen's metallacycle was alluded to above. In particular, Dormond has reported several organometallic derivatives formed from the reaction of the metallacycle with compounds containing acidic C–H bonds [5]. It is apparent; however, that no molecular structures of these compounds have been obtained, despite some of the formulations being quite novel and interesting. Accordingly, we set out to explore the reactions of **1** with various acids HX, and have found that it reacts rapidly and cleanly under very mild conditions to form U–X bonds with concomitant regeneration of the symmetric triamidoamine framework.

Reactions of **1** with lutidinium hydrochloride, diethylamine and ^{t}BuOH give the complexes [(NN′$_3$)UCl], [(NN′$_3$)U(NEt$_2$)] [8] and [(NN′$_3$)U(OBu^t)] [20] in essentially quantitative yields (Scheme 5). Similarly, reactions with α-hydropyridines proceed rapidly at room temperature to give η^2-pyridyl complexes **5a–c**. Reactions of **1** with phenylacetylene and *p*-methylphenylacetylene gave the alkynyl compounds [U(NN′$_3$)-(η^1-C = CC$_6$H$_4$R)] (**6a**) (R = H) and (**6b**) (R = Me), respectively.

The molecular structure of **5a** is shown in Fig. 6. Although two η^2-pyridyl complexes of zirconium [21] and one of scandium [22] have been structurally characterised, to our knowledge this is the first such structure for an f-element. Despite the imposition of an unsymmetric ligand in the axial coordination site, the triamidoamine(uranium) unit is essentially unperturbed from the familiar threefold symmetric structure, with 'laid back' *tert*-butyldimethylsilyl groups and accompanying dihedral angles N$_{ax}$–U–N$_{eq}$–Si in the range 136–137°. The U(η^2-pyridyl) unit is quite close to planarity with a dihedral angle U(1)–C(25)–N(5)–C(29) = 176.4°, although there is a fold in the pyridyl ligand of ca. 5° hinged along the C(29)–C(26) vector. The pyridyl N–C distance appears to be exceptionally short [1.235(8) Å] compared to those previously recorded (1.31–1.33 Å), but this parameter must be treated with suspicion given the strong possibility of exchange disorder of these two atoms. Attempts were made to obtain molecular structures of the analogous 4-methylpyridyl and 4-phenyl-

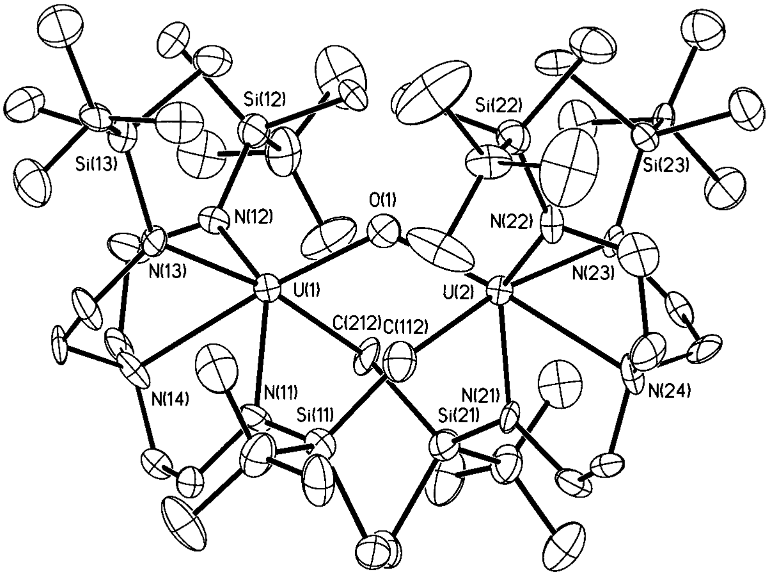
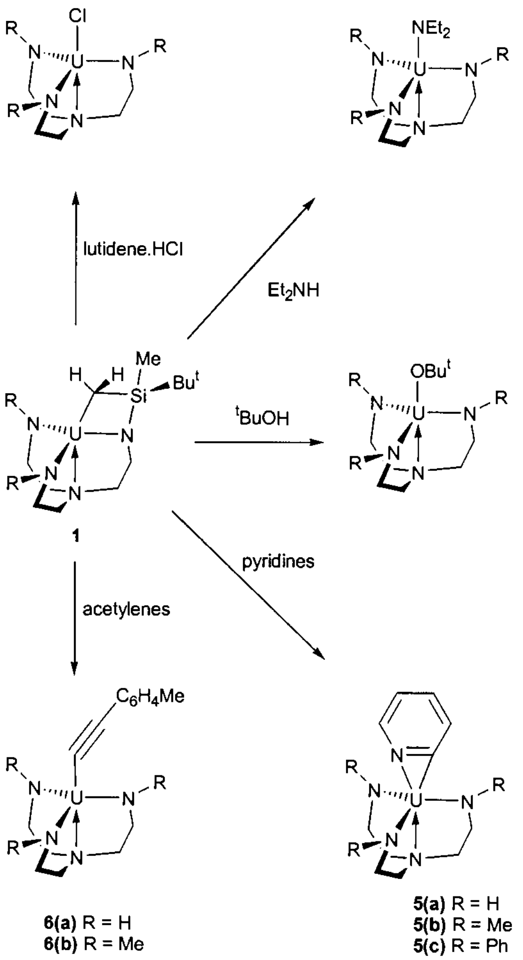


Fig. 5. Thermal ellipsoid plot of the molecular structure of **4**; hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): U(1)–O(1) 2.108(10), U(1)–N(13) 2.263(10), U(1)–N(11) 2.284(12), U(1)–N(12) 2.302(12), U(1)–C(212) 2.442(13), U(1)–N(14) 2.581(12), U(1)–U(2) 3.7835(9), U(2)–O(1) 2.087(9), U(2)–N(23) 2.248(10), U(2)–N(21) 2.256(12), U(2)–N(22) 2.308(12), U(2)–C(112) 2.457(15), U(2)–N(24) 2.567(12), U(2)–O(1)–U(1) 128.8(5), N(13)–U(1)–N(11) 88.1(4), N(13)–U(1)–N(12) 90.8(4), N(11)–U(1)–N(12) 139.1(4), N(12)–U(1)–N(14) 71.0(4), N(23)–U(2)–N(22) 90.3(4), N(21)–U(2)–N(22) 139.7(4), N(23)–U(2)–N(24) 73.2(4), N(21)–U(2)–N(24) 70.1(4), N(22)–U(2)–N(24) 71.2(4).



Scheme 5. Reactions of **1** with acids. R = $SiMe_2Bu^t$.

pridyl complexes **5b** and **5c** since the position of the pyridyl N atoms in these compounds would not be in dispute. Unfortunately, although ^1H-NMR experiments indicated that these compounds were produced cleanly, crystalline samples could not be obtained.

The molecular structure of **6b** is shown in Fig. 7. Here again, the [U(NN$'_3$)] fragment is essentially threefold symmetric and the dihedral angles N_{ax}–U–N_{eq}–Si lie in the range 136–139°. In the alkynyl unit the angle U–C(101)–C(102) of 156.4(6)° is significantly lower than the range found for the few structurally characterised non-bridging alkynyls of the f-elements (170–176°) [23]. It is unlikely that this has occurred for steric reasons, and so given that the metal centre is only five-coordinate we suggest that the alkynyl uranium fragment bends in order to allow for increased U–C π-overlap.

3. Conclusions

Despite the conformational constraints of the triamidoamine ligand, intramolecular metalation of the somewhat acidic methylsilyl groups in [U(NN$'_3$)] complexes occurs quite readily to give the metallacycle **1**. This compound may be converted readily by reduction, oxidation and protonolysis reactions to a range of highly crystalline organometallic complexes of uranium.

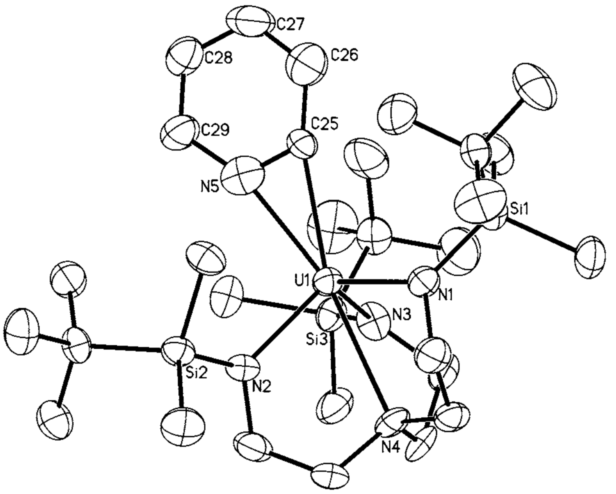


Fig. 6. Thermal ellipsoid plot of the molecular structure of **5a**; hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): U(1)–N(2) 2.242(8), U(1)–N(3) 2.250(8), U(1)–N(1) 2.266(8), U(1)–N(5) 2.469(9), U(1)–C(25) 2.469(9), U(1)–N(4) 2.726(7), N(5)–C(25) 1.248(13), C(25)–C(26) 1.394(16), C(26)–C(27) 1.346(17), C(27)–C(28) 1.363(16), C(28)–C(29) 1.336(15), N(2)–U(1)–N(3) 107.9(3), N(2)–U(1)–N(1) 106.0(3), N(3)–U(1)–N(1) 108.7(3), N(2)–U(1)–N(4) 68.3(3), N(3)–U(1)–N(4) 69.3(3), N(1)–U(1)–N(4) 68.2(3), N(5)–C(25)–C(26) 117.8(10), N(5)–C(25)–U(1) 75.4(6), C(27)–C(26)–C(25) 122.2(13), C(26)–C(27)–C(28) 118.6(11), C(29)–C(28)–C(27) 117.9(10), C(28)–C(29)–N(5) 121.3(11).

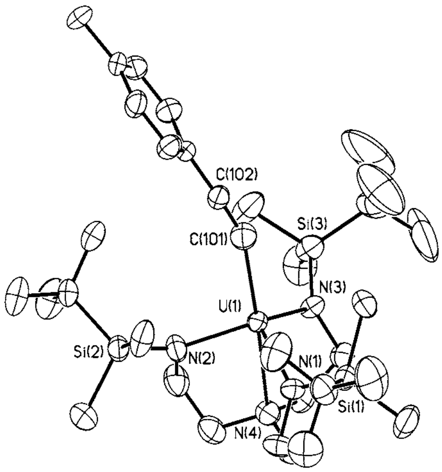


Fig. 7. Thermal ellipsoid plot of the molecular structure of **6b**; hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): U1–N2 2.216(5), U1–N1 2.226(6), U1–N3 2.235(6), U1–C101 2.468(7), U1–N4 2.676(5), C101–C102 1.196(10), N2–U1–N1 108.5(2), N2–U1–N3 108.5(2), N1–U1–N3 108.47(19), N2–U1–N4 70.0(2), N1–U1–N4 69.3(2), N3–U1–N4 69.42(19), C101–U1–N4 177.3(2).

4. Experimental

4.1. General methods

All manipulations were carried out under an inert atmosphere of argon using either standard Schlenk techniques, or in an MBraun drybox. NMR samples were made up in the drybox and the sample tubes were sealed in vacuo or using Young's type concentric stopcocks. Hydrocarbon solvents were predried over sodium wire and then distilled over potassium sodium (toluene) or sodium–potassium alloy (pentane) under an atmosphere of dinitrogen. Hexamethyldisiloxane was fractionally distilled, refluxed over CaH_2 for 5 days, then redistilled. Deuterated solvents were dried by refluxing over molten potassium in vacuo and then distilled trap-to-trap, also in vacuo. NMR spectra were recorded at ca. 295 K on Bruker AC-250, AC-400 or DMX-300 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). IR spectra were obtained as Nujol mulls in an airtight holder using a Perkin–Elmer FTIR spectrometer. UV–vis/near-IR spectra were obtained as pentane or toluene solutions in an airtight quartz cell of path length 0.1 cm using a Jasco V-540 spectrophotometer. Elemental analyses were performed by Warwick Analytical Services.

4.2. Synthesis of [U(bit-NN$'_3$)] (**1**)

4.2.1. Method A

Pentane (10 cm^3) was added at −80°C to a mixture of [U(NN$'_3$)Cl] (0.50 g, 0.65 mmol) and lithium phenyl (0.055 g, 0.65 mmol). The mixture was stirred for 1 h at ambient temperature to give a brown solution, which was filtered and cooled to −30°C to give orange–brown crystals (0.310 g, 66%).

4.2.2. Method B

Toluene (20 ml) was added at −80°C to a mixture of [U(NN$'_3$)I] (1.27 g, 1.50 mmol) and K[PhCH_2] (0.195 g, 1.50 mmol). The mixture was stirred for 2 h at ambient temperature to give a brown solution. After filtration and evaporation of volatiles a volume of pentane was added to the onset of crystallisation, which was carried out at −30°C. This afforded an orange–brown crystalline solid, which was collected by cannula filtration and dried in vacuo. (0.768 g, 71%). Anal. Found (Calc. for $C_{24}H_{56}N_4Si_3U$): C, 39.87 (39.66); H, 7.81 (7.75); N, 7.75 (7.69)%. ^{1}H-NMR (293 K, toluene-d_8) δ 53.70 (s, 1H, CH), 53.38 (s, 1H, CH), 37.14 (s, 1H, CH), 29.43 (s, 3H, MeSi), 19.62 (s, 1H, CH), 15.68 (s, 9H, ^{t}Bu), 14.09 (s, 1H, CH), 9.86 (s, 9H, ^{t}Bu), −0.60 (s, 3H, MeSi), −2.30 (s, 9H, ^{t}Bu), −10.36 (s, 1H, CH), −12.45 (s, 1H, CH), −18.50 (s, 1H, CH), −18.86 (s, 3H, MeSi), −25.89 (s, 3H, MeSi), −27.54 (s, 1H, CH), −35.34 (s, 1H, U–CH), −38.78 (s, 3H, MeSi), −40.07 (s, 1H, CH), −41.28 (s, 1H, CH), −44.45 (s, 1H, CH), −52.34 (s, 1H, U–CH). MS (EI) m/z 722 (92% M^+), 665 (36% $M^+ -{}^t$Bu). IR (Nujol) cm^{-1} 1149(m), 1132(m), 1101(m), 1074(m), 1035(w), 1016(w), 1005(w), 946(s), 929(s), 917(s), 907(s), 826(s), 773(s), 722(s), 659(m).

4.3. Synthesis of [Th(bit-NN$'_3$)] (**2**)

4.3.1. Method A

This compound was prepared in a similar manner to **1** (73%).

4.3.2. Method B

A slurry of [U(NN$'_3$)I] (0.50 g, 0.66 mmol) in pentane (20 cm^3) was added to a Schlenk vessel containing a potassium mirror (excess) and was stirred vigorously for 24 h. After filtration, the colourless solution was concentrated and cooled to −30°C to give a white crystalline solid (0.10 g, 22%). Anal. Found (Calc. for $C_{24}H_{56}N_4Si_3Th$): C, 40.12 (40.20); H, 7.98 (7.87); N, 7.69 (7.81)%. ^{1}H-NMR (293 K benzene-d_6) δ 3.9 (m, 1H, CH), 3.58 (m, 2H, 2 × CH), 3.44 (m, 2H, 2 × CH), 3.3 (m, 1H, CH), 2.8 (m, 3H, 3 × CH), 2.34 (m, 3H, 3 × CH), 1.23 (s, 9H, Bu^t), 0.96 (s, 9H, Bu^t), 0.92 (s, 9H, Bu^t), 0.54 (s, 3H, MeSi), 0.46 (s, 3H, MeSi), 0.41 (s, 3H, MeSi), 0.28 (s, 3H, MeSi), 0.28 (s, 3H, MeSi), 0.01 (br s, 2H, ThCh_2Si). $^{13}C\{^1H\}$-NMR (293 K, benzene-d_6) δ 57.27 (br s, CH_2), 56.16 (br s, CH_2), 49.45 (s, CH_2), 48.35 (br s, CH_2), 47.64 (br s, CH_2), 28.65 (s, *Me*$_3$C), 27.84 (s, *Me*$_3$C), 27.25 (s, *Me*$_3$C), 21.04 (s, Me$_3$*C*), 19.99 (s, Me$_3$*C*), 1.37 (s, MeSi), −2.09 (s, MeSi), −5.21 (br s, MeSi), −5.61 (s, MeSi). MS (EI) m/z 7.16 (27%, M^+), 659 (100%, $M^+ -$ Bu^t). IR (Nujol) 1252(m), 1147(w), 1139(w), 1121(m), 1074(m), 1062(m), 1031(w), 999(w), 949(w), 938(m), 907(m), 894(w), 825(s), 805(s), 788(m), 770(s), 721(s).

4.4. Synthesis of [{U(bit-NN$'_3$)-μ-K(η^6-C_6H_5Me)}$_2$] (**3**)

A slurry of [U(NN$'_3$)I] (3.00 g, 3.50 mmol) in toluene (40 cm^3) was added to a vessel containing an excess of potassium mirror. The mixture was stirred vigorously for 24 h. After filtration, the dark green solution was concentrated and cooled to −30°C to give extremely air-sensitive green crystals (2.00 g, 67%). Anal. Found (Calc. for $C_{31}H_{64}N_4Si_3KU$): C, 42.35 (43.59); H, 7.44 (7.55); N, 6.54 (6.56)%. ^{1}H-NMR (298 K benzene-d_6, not assigned) δ 35.81 (1H), 29.78 (2H), 26.15 (4H), 24.40 (18H), 20.12 (2H), 4.36 (v br, ca. 9H), −5.62 (v br, 18H), −22.91 (4H), −27.63 (v br, 4H), −37.99 (2H), −43.25 (2H), −45.20 (2H).

4.5. Synthesis of [U(NN$'_3$)(η^2-NC_5H_4)] (**5a**) and related compounds

Dry pyridine (43 μl, 0.50 mmol) was added to a solution of metallacycle (0.361 g, 0.50 mmol) in pentane at −80°C. The mixture was stirred for 4 h at ambient temperature to give a brown solution. After filtration and evaporation of volatiles, to the residue was extracted with 1–2 cm^{-3} of hexamethyldisiloxane and was cooled to −30°C to give a brown crystalline solid (0.32 g, 80%). Anal. Found (Calc. for $C_{29}H_{61}N_5Si_3U$): C, 43.44 (43.28); H, 7.61 (7.58); N, 8.74 (8.30)%. ^{1}H-NMR (298 K, benzene-d_6) δ 30.34 (d, 1H, Py), 25.14 (m, 1H, Py), 22.52 (s, 2H, CH_2), 21.06 (m, 1H, Py), 16.65 (d, 1H, Py), 9.57 (s, 4H, CH_2), 5.06 (s, 27H, ^{t}Bu), −4.17 (s, 2H, CH_2), −5.08 (s, 4H, CH_2), −20.98 (s, 18H, Me_2Si). MS (EI) m/z 827 (12%), 801 (15% M^+), 635 (33%). IR (Nujol) cm^{-1} 1573(m), 1534(w), 1468(s), 1408(m), 1378(m), 1330(m), 1246(s), 1143(w), 1060(s), 1026(m), 926(s), 894(m), 714(s), 660(s), 556(m).

*4.5.1. H-NMR spectra of [U(NN′$_3$)(η^2-NC$_5$H$_3$Me)] (**5b**) and [U(NN′$_3$)(η^2-NC$_5$H$_3$Ph)] (**5c**)*

5b: ^{1}H-NMR (298 K benzene-d_6) δ 31.46 (1H, s, Py), 24.98 (s, 1H, Py), 22.51 (s, 4H, CH_2), 11.76 (s, 1H, Py), 9.58 (s, 4H, CH_2), 4.98 (s, 27H, Bu^t), 3.30 (s, 3H, CH_3), −9.98 (s, 2H, CH_2), −21.15 (s, 18H, $SiMe_2$).

5c: ^{1}H-NMR (298 K benzene-d_6) δ 30.14 (s, 1H, Py), 25.47 (s, 1H, Py), 22.84 (s, 2H, CH_2), 18.44 (s, 1H, Py), 10.53 (d, 2H, phenyl), 9.84 (s, 4H, CH_2), 9.73 (s, 2H, phenyl), 8.08 (m, 1H, phenyl), 5.37 (s, 27H, Bu^t), −4.18 (s, 2H, CH_2), −5.38 (s, 4H, CH_2), −21.02 (s, 18H, $SiMe_2$).

*4.6. Synthesis of [U(NN′$_3$)(C$\equiv$CC$_6$H$_4$Me)] (**6b**) and related compounds*

p-Methylphenylacetylene (1.66 ml, 0.303 M solution in pentane, 0.50 mmol) was added dropwise at −80°C to a solution of **1** (0.364 g, 0.50 mmol) in pentane (6 cm^3). The mixture was stirred for 3 h at ambient temperature. After filtration, the solution was concentrated under reduced pressure and then cooled to −30°C to give a yellow–green crystalline product which was collected and dried in vacuo (0.336 g, 80%). Anal. Found (Calc. for $C_{33}H_{64}N_4Si_3U$): C, 47.25 (47.21); H, 7.64 (7.62); N, 6.68 (6.84)%. ^{1}H-NMR (293 K, benzene-d_6) δ 8.1 (s, 6H, CH_2), 5.14 (s, 27H, ^{t}Bu), 3.8 (s, 18H, Me_2Si), 3.5 (d, 2H, aryl), 1.82 (d, 2H, aryl), −1.26 (s, 3H, CH_3), −15.59 (s, 6H, CH_2). MS (EI) m/z 838 (20%, M^+), 781 (12%, $M^+-{}^t$Bu), 723 (17%, $M^+-MeC_6H_4C_2$). IR (Nujol) cm^{-1} 2050(w), 1593(w), 1482(w), 1461(s), 1376(m), 1333(w), 1258(m), 1196(w), 1141(w), 1071(m), 1023(w), 925(s), 894(w), 827(m), 799(m), 774(m), 754(m), 660(w), 512(w), 457(w).

The related complex **6a** was prepared in similar manner as a yellow–green crystalline solid (87%). Anal. Found (Calc. for $C_{33}H_{62}N_4Si_3U$): C, 46.40 (46.45); H, 7.52 (7.45); N, 6.80 (6.71)%. ^{1}H-NMR (293 K, benzene-d_6) δ: 8.09 (s, 6H, CH_2), 5.25 (s, 27H, ^{t}Bu), 4.07 (s, 18H, Me_2Si), 3.33 (s, 2H, C_6H_5), 2.83 (s, 1H, C_6H_5), 1.49 (s, 2H, C_6H_5). IR (Nujol) cm^{-1} 2052(m), 1593(m), 1461(s), 1377(s), 1258(s), 1196(s), 1141(m), 1071(s), 924(s), 800(s).

*4.7. Molecular structures of **1**, **3**, **4**, **5a** and **6b***

Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Siemens SMART three-circle with CCD area detector). Absorption correction was performed by multiscan (SADAB). The structures were solved by direct methods using SHELXS [24] with additional light atoms found by Fourier methods. [For **3** both the *tert*-butyl groups and the toluene showed positional disorder and were modelled using two positions each (50% occupancy) with isotropic displacement parameters. Only one set is shown in the figure for clarity.] Hydrogen atoms were added at calculated positions and refined (where appropriate) using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl groups. The structures were refined using SHELXL-96 [25]. The structures showed relatively large peaks in the final difference Fourier syntheses, but in all cases these were located close to the uranium atoms; they are attributed to series termination effects.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 127471 (**1**), 127472 (**3**), 127473 (**4**), 127474 (**5a**) and 127475 (**6b**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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