

Synthesis and reactivity of uranium(IV) amide complexes supported by a triamidotriazacyclononane ligand†

Maria Augusta Antunes, Marta Dias, Bernardo Monteiro, Ângela Domingos, Isabel C. Santos and Noémia Marques*

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Reaction of $[U\{(SiMe_2NPh)_3-tacn\}Cl]$ with $LiNEt_2$ or $LiNPh_2$ affords the corresponding amide compounds, $[U\{(SiMe_2NPh)_3-tacn\}(NR_2)]$ ($R = Et$ (**1**), $R = Ph$ (**2**)). The complexes have been fully characterized by spectroscopic methods and the solid-state structure of **1** was determined by single-crystal X-ray diffraction analysis. The six nitrogen atoms of the tris(dimethylsilylanilide)-triazacyclononane ligand are in a trigonal prismatic configuration with the nitrogen atom of the diethylamide ligand capping one of the trigonal faces of the trigonal prism. Crystallization of **2** from CH_3CN solution gave crystals of the six-membered heterocycle $[U\{(SiMe_2NPh)_3-tacn\}-\{\kappa^2-(HNC(Me))_2CC\equiv N\}]$ (**3**). The reactivity of the amides was investigated. Both compounds undergo acid–base reactions with protic substrates such as $HOC_6H_2-2,4,6-Me_3$, 3,5- Me_2pzH ($pz =$ pyrazolyl) and HSC_3H_4N to give the corresponding $[U\{(SiMe_2NPh)_3-tacn\}X]$ ($X = OC_6H_2-2,4,6-Me_3$ (**4**), 3,5- Me_2pzH (**5**), $\kappa^2-SC_3H_4N$ (**6**)) complexes. The solid-state structures of **3** and **6** were determined by single-crystal X-ray diffraction and revealed that the compounds are eight-coordinate with dodecahedral geometry.

Introduction

It seems likely that while C_5Me_5 will continue to be of predominant interest in the inorganic and organometallic chemistry of uranium, the search for other alternative ligand systems that can offer an opportunity of new and unforeseen reactivity is of current interest.

The 1,4,7-triazacyclononane-based ligands (*tacn*) are becoming increasingly popular due to the ease with which this macrocycle can be derivatized at the nitrogen atoms to give access to ligands with one or more pendant functionalities.¹ Although widely used and established as an important class for the main group and d-transition elements, the chemistry of f-elements with these type of ligands has hardly been investigated. Recent successes on this area include the synthesis of neutral and cationic complexes of yttrium and lanthanum with monoanionic triazacyclononane-amide ligands that are active in ethene polymerization and in *cis*-selective linear dimerization of phenylacetylene² and the isolation of the uranium(III) complex, $[U\{(ArO)_3-tacn\}]$ ($Ar = 3,5$ -di-*tert*-butyl-2-hydroxybenzyl), that showed a remarkable reactivity.³ Recently, we reported the synthesis of the uranium(III) complex, $[U\{(SiMe_2NPh)_3-tacn\}]$,⁴ achieved by reaction of one equivalent of $Na_3[(SiMe_2NPh)_3-tacn](THF)_2^5$ with uranium triiodide. Also we have shown that the U(IV) derivatives, $[U\{(SiMe_2NPh)_3-tacn\}X]$ ($X = Cl, I$), could be prepared *via* oxidation of $[U\{(SiMe_2NPh)_3-tacn\}]$ with benzyl chloride or I_2 .⁴

Here we wish to report that $[U\{(SiMe_2NPh)_3-tacn\}Cl]$ is a useful starting material for obtaining the amide uranium complexes, $[U\{(SiMe_2NPh)_3-tacn\}(NR_2)]$ ($R = Et, Ph$). Amine elimination reactions of these complexes with protic substrates constitutes an efficient route for the synthesis of U(IV) complexes with U–O, U–N and U–S bonds. This contribution also describes that $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ reacts with acetonitrile to yield $[U\{(SiMe_2NPh)_3-tacn\}\{(HNC(Me))_2CC\equiv N\}]$, a uranium(IV) complex in which the metal is coordinated to the anionic ligand $[\{HNC(Me)\}_2CC\equiv N]$, resulting of a trimerization of the nitrile.

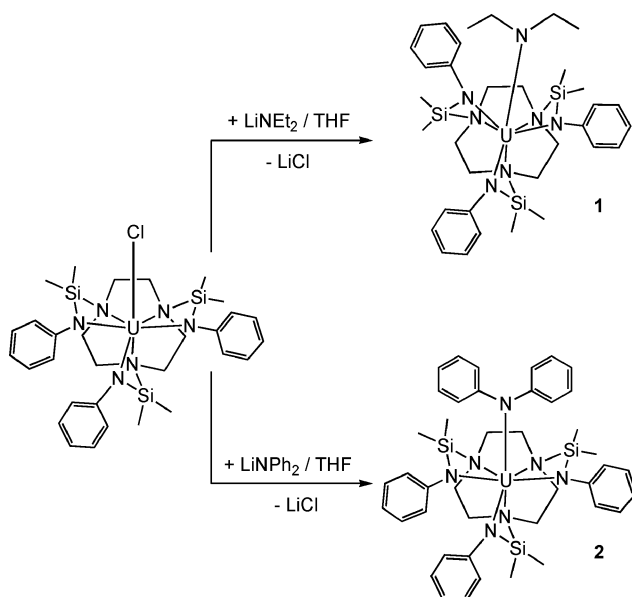
Results and discussion

Metathesis of $[U\{(SiMe_2NPh)_3-tacn\}Cl]$ with one equivalent of either $LiNEt_2$ or $LiNPh_2$ at room temperature resulted in a gradual color change from green to golden–brown. Standard workup of the reaction mixture yielded $[U\{(SiMe_2NPh)_3-tacn\}(NEt_2)]$ (**1**) and $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (**2**), respectively. The complexes were obtained as golden solids in moderate yield (Scheme 1).

Both compounds were soluble in THF and aromatic solvents and moderately soluble in aliphatic solvents. The room-temperature ¹H NMR spectra of **1** and **2** exhibited only one set of proton signals associated with the $\{(SiMe_2NPh)_3-tacn\}$ ligand, indicating that the compounds are fluxional on the NMR time scale. The spectra presented one single peak accounting for the 18 protons of the $SiMe_2$ groups, one set of resonances associated with the aniline groups and two resonances assigned to the methylenic protons of the cyclic amine. In addition the spectra showed the resonances due to the amide ligands, two for the diethylamide and three for the diphenylamide, with the expected intensities.

Departamento de Química, ITN, Estrada Nacional 10, P-2686-953, Sacavém, Portugal. E-mail: nmarques@itm.mces.pt

† Electronic supplementary information (ESI) available: ¹H NMR data, selected bond lengths and angles, crystallographic data and ORTEP diagram. See DOI: 10.1039/b603000a



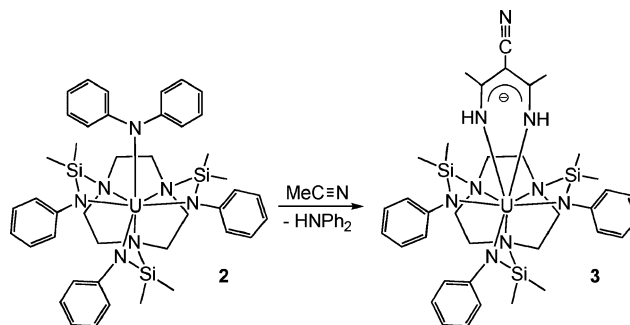
Scheme 1

Although complexes **1** and **2** are fluxional in solution and exhibited resonances strongly shifted from the diamagnetic position, the ¹H NMR spectra indicated that their coordination geometries may be different. In the spectrum of **1** the 18 protons of the SiMe₂ groups gave rise to one sharp resonance at high field, while for **2** they appeared as a broad resonance at low field. In addition the protons of the amide ligands were at low and high field for complexes **1** and **2**, respectively. These differences may be due to the anisotropy of the magnetic susceptibility, and to the position of the protons inside the dipolar cone,⁶ as they have been observed consistently in seven-coordinate complexes displaying capped trigonal prismatic or bicapped trigonal bipyramidal geometries. The ¹H NMR spectrum of **1** was similar to that observed in the seven-coordinate [U{(SiMe₂NPh)₃-tacn}(OPPh₃)] (ESI[†]), a complex that displays a capped trigonal prismatic geometry, suggesting a similar geometry for complex **1**. This was confirmed by a X-ray structural determination (*vide infra*).

In contrast, the room-temperature ¹H NMR spectrum of **2** was similar to those found for [U{(SiMe₂NPh)₃-tacn}Cl]⁴ and [U{(SiMe₂NPh)₃-tacn}(η²-N₂Ph₂)],⁷ two compounds in which the arrangement of the atoms around the uranium displays a bicapped trigonal bipyramidal geometry. Variable-temperature ¹H NMR studies confirmed this assumption. On cooling a sample of **2** in toluene-*d*₈ the resonances broadened into the baseline and by -80 °C had resolved into six broad peaks assigned to the methylenic protons of the cyclic amine and three resonances due to the methyl protons of the SiMe₃ groups. Although the slow exchange limit could not be reached before the solvent froze, this pattern is consistent with a C_s symmetric coordination sphere and has been observed in low-temperature ¹H NMR studies performed in the complexes [U{(SiMe₂NPh)₃-tacn}X] (X = I,⁴ N₂Ph₂⁷). Although without X-ray structural confirmation, the ¹H NMR spectrum of **2** points for a similar geometry for this complex.

All our attempts to obtain crystals of **2** suitable for X-ray diffraction analysis from THF or toluene solutions were unsuccessful. Dissolution of **2** in CH₃CN resulted in the formation of dark yellow crystals in a few hours. However, unexpectedly

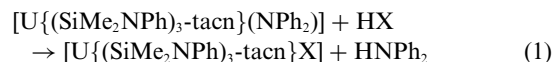
the resulting compound was shown to be [U{(SiMe₂NPh)₃-tacn}{(HNC(Me))₂CC≡N}] (**3**), a uranium complex in which the metal is coordinated to the anionic ligand [(HNC(Me))₂CC≡N]⁻, resulting of a trimerization of the nitrile (Scheme 2).



Scheme 2

Reactivity of U{(SiMe₂NPh)₃-tacn}(NR₂) (**2**)

Protonolysis of compounds [U{(SiMe₂NPh)₃-tacn}(NR₂)] with reagents containing acidic protons such as 2,4,6-trimethylphenol, 3,5-dimethylpyrazole and mercaptopyridine in THF, at room temperature, gave the corresponding [U{(SiMe₂NPh)₃-tacn}X] complexes (X = OC₆H₂-2,4,6-Me₃ (**4**), 3,5-Me₂pz (**5**) or SC₅H₄N (**6**), eqn (1)). The reactions were faster for the diphenylamide compound (NMR experiments).



Compound **6** could be prepared by an alternative route by using the reducing properties of [U{(SiMe₂NPh)₃-tacn}]. Addition of 1/2 equivalent of (C₅H₄N)SS(C₅H₄N) to one equivalent of [U{(SiMe₂NPh)₃-tacn}] in toluene yielded the yellowish-green complex **6** in high yield.

In order to get some insight in the formation of **3** the ¹H NMR spectrum of [U{(SiMe₂NPh)₃-tacn}(NPh₂)] in CD₃CN was recorded. In 2–3 h the resonances due to **2** have disappeared to give rise to several resonances strongly shifted from the diamagnetic position and diphenylamine. In addition resonances assigned to methylenic and aromatic protons in the diamagnetic position indicated that attack on the [(SiMe₂NPh)₃-tacn] ligand had occurred. In order to minimize the degradation of the ligand, acetonitrile was added to a benzene-*d*₆ solution of **2** in the stoichiometric ratio 3 : 1. The reaction proceeded very slowly and only after several days underwent completion. However, if a large excess of acetonitrile was added to a benzene-*d*₆ solution of **2** the reaction was complete after a few hours with minor decomposition of the [(SiMe₂NPh)₃-tacn] ligand.

Compound **3** was obtained in a macroscopic scale, as a dark yellow solid, by reaction of an excess of acetonitrile with **2** in THF solution. The reaction was complete after stirring overnight. The diphenylamine formed in the reaction could be removed by washing the solid with hexane, but all our attempts to separate **3** from the species resulting from decomposition of the [(SiMe₂NPh)₃-tacn] ligand were unfruitful. The IR spectrum of the solid showed a band located at 2183 cm⁻¹ assigned to the ν(N≡C) stretching vibration and one at 3278 cm⁻¹ in the region where the ν(NH) stretching vibrations are usually observed.⁸

Compounds **4–6** were soluble in aromatic and ethereal solvents and slightly soluble in hexane.

The ^1H NMR spectrum of **4** was consistent with a capped trigonal prismatic geometry, while that of **5** indicated a bicapped trigonal bipyramidal geometry^{4,7} (see Experimental section). Although complex **5** is formally eight-coordinate, the small bite of the dimethylpyrazolide ligand allows to consider that the midpoint of the N–N distance is occupying one single site of the coordination polyhedron.

The room-temperature ^1H NMR spectrum of **3** and **6** were similar but quite different of those found for complexes with capped trigonal prismatic or bicapped trigonal bipyramidal geometries. The spectra featured six resonances for the protons of the cyclic amine, three resonances of equal intensity for the protons of the SiMe_2 groups, and two sets of resonances for the aromatic protons of the aniline groups in a ratio 2 : 1. This pattern is consistent with a C_s -symmetric coordination sphere. In the solid, the eight-coordinate complexes **3** and **6** have C_1 symmetry (*vide infra*), but in solution, if inversion of the ethylenic backbone is fast in the NMR time scale, the symmetry is raised to C_s with the $\{[\text{HNC}(\text{Me})_2\text{CC}\equiv\text{N}]\}$ and $\text{SC}_2\text{H}_4\text{N}$ ligands contained in the mirror plane, as could be inferred from the presence of two resonances due to the methylic protons of the heterocycle $\{[\text{HNC}(\text{Me})_2\text{CC}\equiv\text{N}]\}$. These were assigned by comparison with the spectrum obtained by dissolution of **2** in CD_3CN , where these resonances were absent. Obviously the increased coordination number of these complexes increases the steric constraints around uranium and causes the dynamic process responsible for the fluxionality of the molecules to slow down.

At the present stage of our investigation we are unable to rationalize definitively the formation of **3**. Trimerization of acetonitrile has been observed in f-element chemistry. Marks and co-workers⁹ reported that reaction of the heterobimetallic compound $\text{Cp}^*_2\text{Th}(\text{Cl})\text{Ru}(\text{Cp})(\text{CO})_2$ with acetonitrile gives the four-membered chelate diazathoracyclobutene $\text{Cp}^*_2(\text{Cl})\text{Th}[\text{N}(\text{H})\text{C}(\text{Me})\text{N}(\text{R})]$ where R is a cyanopropenyl fragment and recently, a neutral bis(imino)amine ligand, $[(\text{HN}=\text{CMe})_2\text{MeCNH}_2]$, has been reported to be formed in the reactions of DyI_2 and TmI_2 with an excess of acetonitrile.¹⁰ However, to the best of our knowledge, this is the first time that trimerization of acetonitrile to yield the anionic heterocycle $\{[\text{HNC}(\text{Me})_2\text{CC}\equiv\text{N}]\}$, has been observed in f-element chemistry.⁸

Molecular structures of **1**, **3** and **6**

$[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{NEt}_2)]$ crystallizes from a toluene solution as golden crystals in the triclinic space group $P\bar{1}$. The molecular structure is shown in Fig. 1 and comparative bond distances and angles are shown in Table 1.

The uranium ion is seven-coordinate by the six nitrogen atoms of the tacn ligand and the nitrogen atom of the NEt_2 group in a distorted trigonal prismatic configuration. The two trigonal planes are defined by the two sets of nitrogen donor amido (N_{123}) and amine (N_{456}) atoms and the pendant amido arms are oriented around the C_3 symmetry axis. The two planes are nearly parallel and the nitrogen atom of the NEt_2 group is capping the trigonal face defined by the three nitrogen atoms of the amido groups (the angle between the axis U–N(7) and the perpendicular to the plane defined by N1N2N3 is 3°).

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for complexes **1**, **3** and **6**

	1	3	6
U–N(1)	2.322(11)	2.296(15)	2.328(7)
U–N(2)	2.435(11)	2.254(16)	2.332(6)
U–N(3)	2.327(13)	2.340(17)	2.309(7)
U–N(4)	2.744(11)	2.719(16)	2.619(7)
U–N(5)	2.853(12)	2.724(16)	2.689(7)
U–N(6)	2.765(13)	2.767(14)	2.775(6)
U–N7	2.146(12)	2.433(15)	2.536(7)
U–N8(S)		2.47(2)	2.880(2)
N(1)–U–N(2)	115.7(4)	101.6(6)	95.4(2)
N(1)–U–N(3)	111.0(4)	158.8(6)	163.1(2)
N(2)–U–N(3)	132.2(4)	94.7(6)	92.3(2)
N(7)–U–N(1)	88.2(4)		
N(7)–U–N(2)	83.8(4)		
N(7)–U–N(3)	88.0(4)		

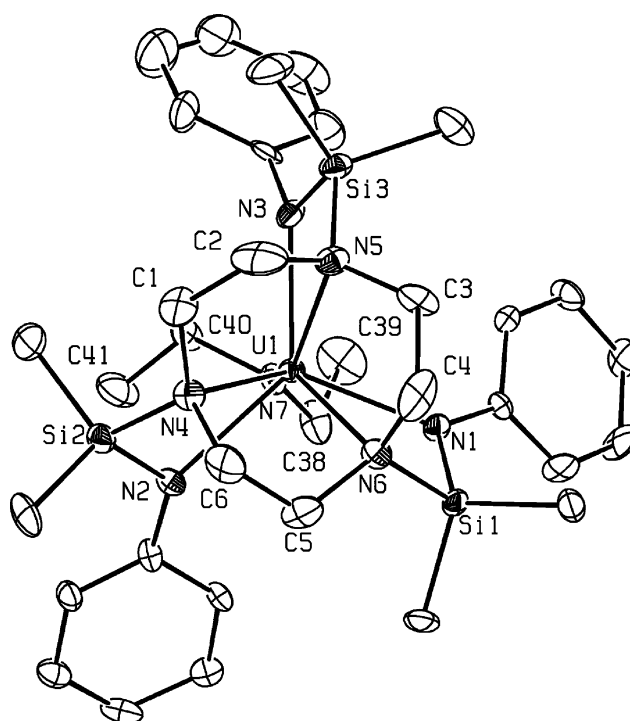


Fig. 1 ORTEP diagram of $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{NEt}_2)]$ (**1**) with 20% probability ellipsoids.

The average U–N amido and U–N amine distances are 2.361(12) and 2.787(13) Å, respectively, and are in the range found for other $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}\text{X}]$ complexes.^{4,7} The U–N(7) distance of 2.146(12) Å is similar to the corresponding distance in $[\text{U}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{NEt}_2)]$ (2.148(10) Å)¹¹ and $[\text{U}(\text{OC}_6\text{H}_3\text{-2,6-}^i\text{Bu}_2)_3(\text{NEt}_2)]$ (2.162(5) Å),¹² but significantly shorter than those usually found in other structurally characterized uranium(IV) amide complexes. In the triamidoamine complex $[\text{U}\{(\text{Me}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}\}(\text{NEt}_2)]$ the U–N distance to the nitrogen of the NEt_2 group is 2.220(5) Å,¹³ and in $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_6)(^i\text{BuN})\text{U}(\text{NMe}_2)_2]$ the corresponding distances to the NMe_2 groups average 2.210(4) Å.¹⁴

The molecular structure of **1** also features one short contact to the α -carbon (C40) of the NEt_2 ligand ($\text{U}\cdots\text{C}$

3.025(15) Å). This distance may be compared with those of contacts to the methyl groups within the bis(trimethylsilylamide) ligands in $[\text{U}(\text{S}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)\{\text{N}(\text{SiMe}_3)_2\}_3]$ ¹⁵ (3.158 Å) and $\text{Th}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{NMePh})_2]$ ¹⁶ (3.073(10) and 3.064(10) Å, respectively). The interaction present in the structure of **1** is responsible for the distortion observed in the trigonal prismatic environment of the uranium centre: the N(2)–U–N(3) angle increases to 132.2(4)° vs. 111.0(4)° for N(1)–U–N(3) and 115.7(4)° for N(1)–U–N(2). Although the interaction makes the angle U–N(7)–C(40) decrease to 109(1)°, the sum of the angles about the nitrogen atom N(7) is 360° (U–N(7)–C(38) 139(1)° and C(40)–N(7)–C(38) 112(1)°) indicating the planarity of the substituents.

This interaction is weak and a static structure could not be observed in solution *via* low-temperature NMR techniques.

Dark yellow crystals of **3** were grown from a solution of **2** in acetonitrile. Green crystals of **6** were obtained by slow diffusion of pentane in a saturated solution of the complex in toluene. The molecular structures are shown in Fig. 2 and 3, respectively. Selected bond distances and angles are given in Table 1.

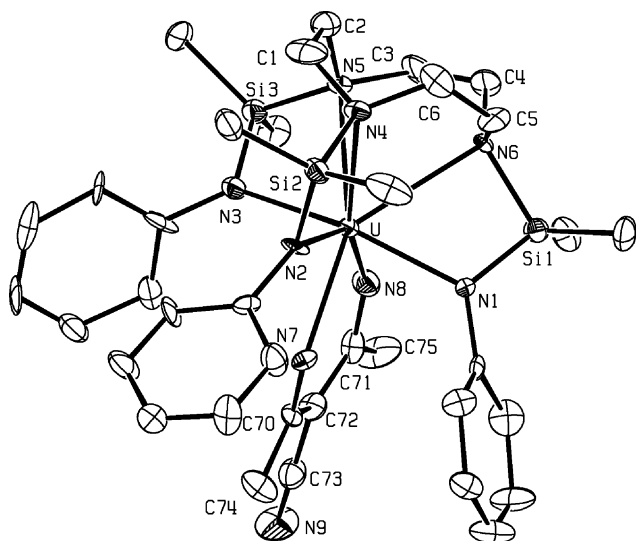


Fig. 2 ORTEP diagram of $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}\{(\text{HNC}(\text{Me})_2\text{CC}\equiv\text{N})\}]$ (**3**) with 20% probability ellipsoids.

Both structures consist of isolated molecules with no significant intermolecular contacts. In both molecules the metal centre is eight-coordinate with the uranium atom bound to the six nitrogen atoms of the $\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}$ ligand, and to the bidentate ligand (two nitrogen atoms in **3** and sulfur and nitrogen atoms in **6**). The coordination geometry around the uranium atom can be described as being dodecahedral, the trapezoids being defined by the atoms N(1)N(3)N(5)N(6) and N(2)N(4)N(7) (X = N(8) for **3** and S for **6**) (Fig. 4).¹⁷ Distortions from the DD geometries are defined by the dihedral angle of the intersecting trapezoids (90.0° for **3** and 89.7° for **6**). The trapezoids are slightly distorted with normalized ϕ angles of 7.4 and 6.5°, for **3** and 5.2 and 9.1° for **6**.

The U–N amido and the U–N amine bond distances average 2.297(17) and 2.737(16) Å in **3** and 2.323(7) and 2.694(7) Å in **6**. These are reasonable values compared to data found in the seven-coordinate complexes $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}\text{Cl}]^4$ (2.300(13) and 2.636(13) Å) and $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{NEt}_2)]$ (2.361(12) and

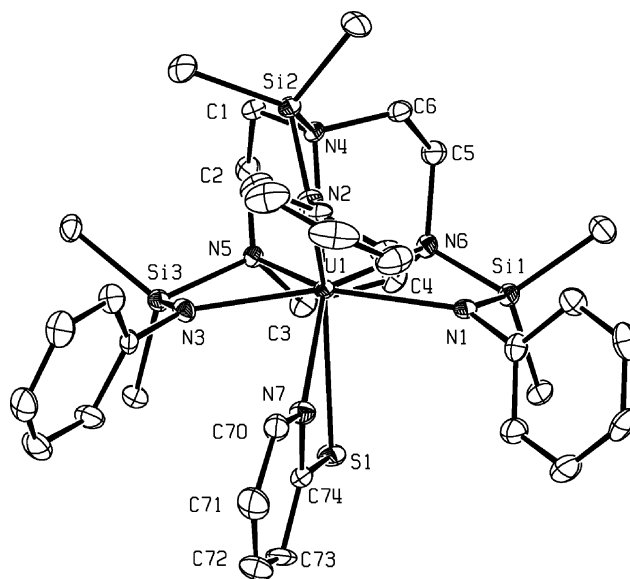


Fig. 3 ORTEP diagram of $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{SC}_3\text{H}_4\text{N})]$ (**6**) with 20% probability ellipsoids.

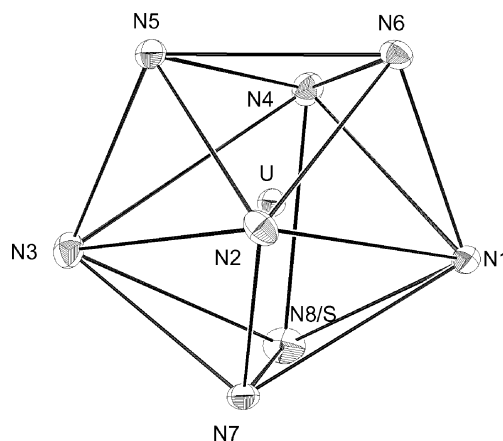


Fig. 4 View of the dodecahedral coordination polyhedron of **3**.

2.787(13) Å). The U–S and U–N(7) bond distances in **6** (2.880(2) and 2.536(7) Å) and the average U–N bond distance of 2.45(2) Å to the bidentate ligand in **3** compare with the corresponding distances in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\kappa^2\text{-SC}_5\text{H}_4\text{N})]^{18}$ (Sm–S 2.862(4) and Sm–N 2.523(9) Å) and in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\kappa^2\text{-3,5-Me}_2\text{pz})]^{19}$ (2.374(5) Å) after adjustment for the difference in ionic radii of U(III) and Sm(III).²⁰ The N(7)–C(70) (1.28(2) Å), N(8)–C(71) (1.28(3) Å), C(70)–C(72) (1.43(3) Å), C(71)–C(72) (1.39(3) Å) bond distances compare with the corresponding distances in $[\text{Me}_2\text{Ga}\{(\text{HNC}(\text{Me})_2\text{CC}\equiv\text{N})\}]^8$.

Conclusions

It is clear that the pocket afforded by the “[U{(SiMe₂NPh)₃-tacn}]” fragment is effective for the binding of anionic ligands allowing an entry into uranium(IV) chemistry. Metathesis of $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}\text{Cl}]$ yields the amide complexes $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{NR}_2)]$ (R = Et, Ph). Amine elimination reactions of these compounds with protic substrates provides a

synthetic route for uranium(IV) compounds containing U–O, U–N and U–S bonds. Therefore, $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ reacts with acetonitrile to yield a U(IV) heterocycle complex in which the anionic ligand $[\{HNC(Me)_2CC\equiv N\}]$ is η^2 -bonded to the metallic centre. Some of the complexes were characterized by means of X-ray diffraction analysis, but solution studies show that the tacn ligand provides a convenient NMR handle, as the 1H NMR spectra of the complexes are diagnostic of their coordination geometries.

Experimental

General procedures

All preparations and subsequent manipulations were carried out using standard Schlenk-line and dry-box techniques in an atmosphere of dinitrogen. THF, toluene, acetonitrile and *n*-hexane were dried by standard methods and degassed prior to use. Toluene- d_8 and benzene- d_6 were dried over Na and distilled. $HOC_6H_2-2,4,6-Me_3$, 3,5- Me_2pzH , $S_2(C_5H_4N)_2$ and $HNPh_2$ were sublimed prior to use. $HNEt_2$ was dried over BaO and distilled. Mercaptopyrindine, HSC_5H_4N , was purchased from Aldrich and used without further purification. $LiNPh_2$ and $LiNEt_2$ were synthesized by addition of *n*-BuLi to solutions of the amines in *n*-hexane, at 0 °C. $Na_3[(SiMe_2NPh)_3-tacn](THF)_2$,⁵ $[U\{(SiMe_2NPh)_3-tacn\}]^4$ and $[U\{(SiMe_2NPh)_3-tacn\}Cl]^4$ were prepared by published procedures. 1H NMR spectra were recorded on a Varian INOVA-300 spectrometer at 300 MHz. Spectra were referenced internally using the residual proton resonances relative to tetramethylsilane (benzene- d_6 , 7.15 ppm; toluene- d_8 , 2.09 ppm). Carbon, hydrogen and nitrogen analyses were performed in-house using a EA110 CE Instruments automatic analyser.

Synthetic procedures

$[U\{(SiMe_2NPh)_3-tacn\}(NEt_2)]$ (1). Addition of a solution of $LiNEt_2$ (16 mg, 0.20 mmol) in THF to a solution of $[U\{(SiMe_2NPh)_3-tacn\}Cl]$ (171 mg, 0.20 mmol) in the same solvent resulted in a gradual colour change of the solution from green to golden over 3 h. Removal of the solvent followed by extraction with toluene and separation of the LiCl gave a golden solid, that was washed with hexane and dried under vacuum. Washing with hexane results in a lower yield due to the solubility of the compound in hexane. Yield: 55% (95 mg, 0.11 mmol) (Found: C, 45.92; H, 6.10; N, 10.54. $USi_3C_{34}H_{55}N_7$ requires C, 46.19; H, 6.27; N, 11.09%). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 20 °C) 46.59 (4H, $CH_2(NEt_2)$); 23.41 (6H, CH_2); 18.79 (6H, $CH_3(NEt_2)$); 11.66 (6H, CH_2); 6.02 (6H, t, *H-m*); 5.67 (3H, t, *H-p*); –9.37 (6H, d, *H-o*); –13.91 (18H, $SiMe_2$).

$[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (2). The compound was obtained as described above by reaction of a solution of $LiNPh_2$ (125 mg, 0.71 mmol) in THF with a solution of $[U\{(SiMe_2NPh)_3-tacn\}Cl]$ (604 mg, 0.71 mmol) in the same solvent. The golden solid was obtained with a yield of 69% (481 mg, 0.49 mmol) (Found C, 51.43; H, 5.45; N 9.79. $USi_3C_{42}H_{53}N_7$ requires C, 51.46; H, 5.66; N, 10.0%). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 60 °C) 30.9 (6H, br, *H-o*), 13.45 (6H, *H-m*), 9.79 (18H, $SiMe_2$), 8.81 (3H, *H-p*), –5.89 (2H, *H-p* (NPh_2)), –9.21 (4H, *H-m* (NPh_2)), –12.3 (4H, br, *H-o* (NPh_2)), –33.94 (6H, CH_2), –46.70 (6H, CH_2).

$[U\{(SiMe_2NPh)_3-tacn\}(\{HNC(Me)_2CC\equiv N\})]$ (3). An excess of acetonitrile (60 mmol) was added to a solution of $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (112 mg, 0.11 mmol) in THF. After stirring overnight, the solvent was removed under vacuum. The oily product obtained was stirred with hexane resulting in formation of a light-brown solid. $\nu_{max}(\text{film})/cm^{-1}$ 2183 ($C\equiv N$); 3278 (NH). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 20 °C) 63.4 (br, 4H, *H-o*), 52.82 (6H, $SiMe_2$), 27.78 (4H, *H-m*), 18.61 (2H, *H-o*), 16.41 (2H, *H-m*), 12.41 (6H, $SiMe_2$), 3.19 (2H, CH_2), –6.23 (2H, *H-p*), –8.34 (1H, *H-p*), –9.36 (2H, CH_2), –20.49 (6H, $SiMe_2$), –36.48 (3H, CH_3), –38.22 (3H, CH_3), –42.60 (2H, CH_2), –53.08 (2H, CH_2), –53.74 (2H, CH_2), –77.97 (2H, CH_2).

$[U\{(SiMe_2NPh)_3-tacn\}(OC_6H_2-2,4,6-Me_3)]$ (4). To a solution of $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (133 mg, 0.14 mmol) in THF was added dropwise a solution of $HOC_6H_2-2,4,6-Me_3$ (19 mg, 0.14 mmol) in the same solvent. Stirring overnight resulted in a dark brown solution. Removal of the solvent yielded a brown oil, that after being stirred with hexane, resulted in formation of a golden solid. The modest isolated yield (25%, 0.035 mmol) was a result of the high solubility of the compound in hexane (Found: C, 49.31; H, 5.85; N, 8.55. $USi_3C_{39}H_{56}N_6O$ requires C, 49.45; H, 5.96; N, 8.87%). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 20 °C) 25.07 (6H, CH_3-o), 18.85 (2H, *H-m*); 10.86 (3H, CH_3-p), 8.79 (6H, CH_2), 7.95 (6H, *t*; *H-m*), 6.59 (3H, *t*, *H-p*) –4.27 (6H, *d*, *H-o*), –5.85 (6H, CH_2), –12.47 (18H, $SiMe_2$).

$[U\{(SiMe_2NPh)_3-tacn\}(3,5-Me_2pz)]$ (5). The compound was obtained as described for 4 by using 151 mg of $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (0.15 mmol) and 15 mg (0.15 mmol) of 3,5- Me_2pzH . The light-green compound was obtained with a yield of 40% (55 mg, 0.06 mmol) (Found: C, 46.45; H, 5.53; N, 11.99. $USi_3C_{35}H_{52}N_8$ requires C, 46.34; H, 5.78; N, 12.35%). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 40 °C) 13.96 (6H, br, *H-o*), 12.21 (18H, $SiMe_2$), 11.14 (6H, *H-m*); 5.83 (3H, *H-p*), –7.23 (1H, *H-4* (3,5- Me_2pz)), –11.7 (6H, CH_2), –31.81 (6H, CH_3 (3,5- Me_2pz)), –40.80 (6H, CH_2).

$[U\{(SiMe_2NPh)_3-tacn\}(SC_5H_4N)]$ (6). (a) The compound was obtained as described for 4 by using 115 mg of $[U\{(SiMe_2NPh)_3-tacn\}(NPh_2)]$ (0.12 mmol) and 14 mg (0.13 mmol) of HSC_5H_4N . The yellowish-green compound was obtained with a yield of 72% (79 mg, 0.09 mmol).

(b) To a solution of $[U\{(SiMe_2NPh)_3-tacn\}]$ (123 mg, 0.15 mmol) in toluene was slowly added a solution of $S_2(C_5H_4N)_2$ (17 mg, 0.077 mmol) in the same solvent. The brown solution turns almost immediately to green. Stirring was continued for an additional 1–2 h. The solution was centrifuged. Removal of the solvent gave a yellowish-green solid that was further washed with hexane. Yield 90% (124 mg, 0.13 mmol) (Found: C, 45.79; H, 5.69; N, 10.74. $USi_3C_{35}H_{49}N_7S$ requires C, 45.59; H, 5.36; N, 10.63%). δ_H (300 MHz; C_6D_6 ; Me_4Si ; 20 °C) 56.30 (4H, *H-o*), 53.08 (6H, $SiMe_2$), 23.54 (4H, *H-m*), 20.79 (2H, *d*, *H-o*), 15.75 (6H, $SiMe_2$), 15.02 (2H, *t*, *H-m*), 3.52 (2H, CH_2), –6.74 (2H, *H-p*), –6.96 (1H, *H-p*), –12.70 (2H, CH_2), –12.96 (1H, *t*, SC_5H_4N), –15.72 (6H, $SiMe_2$), –17.84 (1H, *t*, SC_5H_4N), –23.40 (1H, *d*, SC_5H_4N), –44.67 (2H, CH_2), –51.68 (2H, CH_2), –58.03 (2H, CH_2), –78.26 (2H, CH_2), –78.44 (1H, *t*, SC_5H_4N).

Table 2 Crystallographic data

	1	3	6
Formula	C ₃₄ H ₅₅ N ₇ Si ₃ U	C ₃₆ H ₅₃ N ₉ Si ₃ U	C ₃₅ H ₄₉ N ₇ SSi ₃ U
<i>M</i> _r	884.15	934.17	922.17
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	12.8662(17)	11.1504(15)	14.213(3)
<i>b</i> /Å	10.7009(10)	11.274(3)	17.6693(17)
<i>c</i> /Å	16.9568(19)	19.834(4)	15.321(3)
<i>a</i> /°	100.262(9)	77.114(19)	
<i>β</i> /°	98.029(10)	83.551(13)	94.273(15)
<i>γ</i> /°	119.404(9)	62.636(15)	
<i>V</i> /Å ³	1929.8(4)	2158.5(7)	3837.1(11)
<i>Z</i>	2	2	4
<i>D</i> _c /g cm ⁻³	1.522	1.437	1.596
Crystal size/mm	0.34 × 0.22 × 0.10	0.35 × 0.10 × 0.08	0.45 × 0.25 × 0.15
<i>μ</i> (Mo-Kα)/mm ⁻¹	4.331	3.878	4.413
<i>θ</i> Range/°	1.88–24.99	2.07–24.99	1.84–24.98
Measured reflections	7011	7742	6975
Independent reflections (<i>R</i> _{int})	6758 (0.0716)	7509 (0.1231)	6689 (0.0453)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	4017	3381	4637
<i>R</i> ₁	0.0865	0.1035	0.0509
<i>wR</i> ₂	0.1140	0.1809	0.0995

X-Ray crystallographic analysis

Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled glove-box. Data were collected at r.t. on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) in the ω - 2θ scan mode. Data were corrected²¹ for Lorentz and polarization effects, and for absorption by empirical corrections based on Ψ scans.

The structure of **1** was solved using Patterson methods²² and successive difference Fourier techniques and refined by full-matrix least-squares refinements on *F*² using SHELXL-97.²³ The structures of **3** and **6** were solved by direct methods using SIR97²⁴ and refined by full-matrix least-squares refinements on *F*² using SHELXL-97²³ and the WinGX software package.²⁵ All non-hydrogen atoms were refined with anisotropic thermal motion parameters, and the hydrogen atoms were assigned idealized positions based on the geometries of their attached carbon atoms. The drawings were made with ORTEP3.²⁶ The poor quality of data/refinement for **3** was due to the low quality of the crystal. A summary of the crystallographic data is given in Table 2.

CCDC reference numbers 269724 (**1**), 269726 (**3**), 269725 (**6**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603000a

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