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The uranium–nitrogen bond in U(IV) complexes supported by the hydrotris(3,5-dimethylpyrazolyl)borate ligand

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Insertion of benzonitrile and acetonitrile into the U–C bond of $[U(Tp^{Me2})Cl_2(CH_2SiMe_3)]$ $(Tp^{Me2} = HB(3,5-Me_2pz)_3)$ gives the ketimide complexes $[U(Tp^{Me2})Cl_2\{NC(R)(CH_2SiMe_3)\}]$ (R = Ph (1); Me (2)). The identity of complex 1 was ascertained by a single-crystal X-ray diffraction study. In the solid state 1 exhibits octahedral geometry with a short U–N bond length to the ketimide ligand. We also report herein the synthesis and the X-ray crystal structures of the uranium amide complexes $[U(Tp^{Me2})Cl_2(NR_2)]$ (R = Et (3); Ph (4)). A detailed comparison of the U–N bond lengths in these compounds with other known U–N (and Th–N) distances in amide and ketimide actinide(IV) complexes is performed, confirming the short character of the U–N bond length in 1.

Introduction

During the last years a large amount of organometallic compounds of uranium and thorium with unprecedented reactivity patterns has been reported.1 Organouranium complexes with amino, alkyl or hydrogen ligands have proven to have a remarkable reaction chemistry. Most of this chemistry deals with bis(pentamethylcyclopentadienyl) compounds $[An(C_5Me_5)_2R(Cl)]$ and $[An(C_5Me_5)_2R_2]^2$ (An = actinide) or with compounds with two cyclopentadienyl ligands bridged by a SiMe₂,³ in which the approaching of the two rings leads to an increase of the coordination space around the metal and consequently to enhanced reactivity. The pronounced effect that steric coordination seems to have on the reactivity of the compounds led to the identification of new ancillary ligand systems capable of stabilizing monomeric uranium and thorium species while provoking novel reactivity patterns. Our group has a long standing interest in hydrotris(3,5-dimethylpyrazolyl)borate uranium and thorium complexes, because of the potential offered by these ligands for steric and electronic tunability. The use of Tp^{Me2} (hydrotris(3,5-dimethylpyrazolyl)borate) allowed the synthesis of the complexes [An(TpMe2)Cl₃(THF)],⁴ that showed to be good precursors for the preparation of a wide range of compounds containing An-O, An-N, An-S and An–C (σ and π) bonds.⁵ The reactivity of the U–C bond of $[U(Tp^{Me2})Cl_2\{CH(SiMe_3)_2\}]$ and $[U(Tp^{Me2})Cl_2(CH_2SiMe_3)]$ towards ketones and aldehydes has been reported.6 Herein we wish to report that nitriles undergo migratory insertion into the U-C bond of [U(TpMe2)Cl2(CH2SiMe3)] to yield the ketimide compounds $[U(Tp^{Me2})Cl_2{NC(R)(CH_2SiMe_3)}]$ (R = Ph (1), Me (2)). This synthetic route has been used previously in the preparation of the mono(ketimide) uranium complexes, $[U{(Me_3Si)_2N}_3(NC(Me)(R)] (R = CH_3, C_3H_7)^{7,8}$ and recently in the synthesis of a series of bis(ketimide) thorium and uranium complexes, $[An(C_5Me_5)_2 \{NC(Ph)(R)\}_2]^9$ (R = CH₂Ph, Ph). The structure of 1 has been ascertained by means of a singlecrystal X-ray determination. The short U-N bond distance to the ketimide ligand (2.04 Å) in comparison with other ketimide uranium complexes,9-11 prompted us to synthesize and structurally characterize two uranium amide complexes, $[U(Tp^{Me2})Cl_2(NR_2)]$ (R = Et (3); Ph (4)), in order to understand if the short U-N bond found in 1 was a result of steric and/or electronic effects.

Results and discussion

Addition of 1 equiv. of benzonitrile or acetonitrile to a toluene solution of $[U(Tp^{Me2})Cl_2(CH_2SiMe_3)]$ gives the ketimide complexes $[U(Tp^{Me2})Cl_2\{NC(R)(CH_2SiMe_3)\}]$ (R = Ph (1), Me (2)) (eqn (1))

$$\begin{split} & [U(Tp^{Me2})Cl_2(CH_2SiMe_3)] + RC \equiv N \\ & \rightarrow [U(Tp^{Me2})Cl_2\{NC(R)(CH_2SiMe_3)\}]; R = Ph~(1),~Me~(2)~(1) \end{split}$$

Synthetic procedures reported in the literature for the preparation of actinide ketimide complexes include reductive cleavage of benzophenone azine by $[U(C_5Me_3)_2Cl_2]$ in the presence of sodium amalgam¹⁰ or metathesis of UI₃(DME)₂ with K{NC(Bu^t)(C₆H₂-2,4,6-Me₃)} in DME that led to isolation of $[UI{NC(Bu^t)(C_6H_2-2,4,6-Me_3)}_3(DME)]$.¹¹ However, migratory insertion of nitriles into U=C,¹² U–CH₂^{7,8} or An–R^{8,9} bonds has been more extensively used in the synthesis of actinide ketimide complexes.

The air-sensitive compounds 1 and 2 were obtained in good yields, as dark reddish and dark yellow solids, respectively. Both compounds were soluble in ethereal and aromatic solvents and poorly soluble in aliphatic solvents.

The IR spectra of **1** and **2** show the typical ν (B–H) stretching vibration at 2540 cm⁻¹, characteristic of a κ^3 -coordination mode of the Tp^{Me2} ligand,¹³ and one strong band at 1605 cm⁻¹ assigned to the ν (N=C) stretching vibration. This band is located at the low end of the region where ν (NC) is found in the spectra of lanthanide and actinide ketimide complexes,^{7,8} and probably reflects a decrease in the C=N bond order due to donation of electron density from the nitrogen lone pair to the uranium ion. This is in agreement with the slight increase in the C–N distance observed in the X-ray structure of the compound (see below).

The ¹H NMR spectra of both complexes at room temperature exhibit four Tp^{Me2} methyl and two H-4 singlets in the ratio 2 : 1, indicating that two pyrazolyl rings are equivalent but the third is distinct. In addition, the spectra displayed resonances associated with the ketimide ligand: one single resonance for the methyl protons and one for the methylenic protons of the CH₂SiMe₃ group, and one and three resonances, respectively, for the methyl and phenyl protons of the inserted nitriles. Hence, the spectra are consistent with C_s-symmetric structures for both compounds, with the ketimide ligand contained in the mirror plane, in accordance with the solid-state structure of **1** (see below).

The ORTEP diagram of **1** is shown in Fig. 1. A listing of relevant bond lengths and angles is available in Table 1; selected crystal and refinement data are given in Table 2. The molecular



Fig. 1 ORTEP diagram of $[U(Tp^{Me2})Cl_2\{NC(Ph)(CH_2SiMe_3)\}]$ (1) using 20% probability ellipsoids.

	1	3	4
U–Cl(1)	2.600(6)	2.629(4)	2.608(4)
U-Cl(2)	2.620(7)	2.627(4)	2.603(4)
U–N(11)	2.501(19)	2.518(10)	2.474(11)
U-N(21)	2.48(2)	2.487(10)	2.493(12)
U-N(31)	2.536(19)	2.483(10)	2.465(11)
U–N(4)	2.04(2)	2.148(10)	2.225(10)
U - C(40)		2.942(13)	2.949(13)
N(4) - C(4)	1.33(3)		
Cl(1)-U-Cl(2)	99.9(2)	97.08(14)	99.37(13)
Cl(1)-U-N(4)	98.2(6)	103.6(3)	103.2(3)
Cl(2)-U-N(4)	99.7(6)	103.4(3)	105.3(3)
N(11) - U - N(21)	75.5(6)	76.3(3)	75.0(4)
N(11) - U - N(31)	75.0(7)	77.7(4)	76.7(4)
N(21)–U–N(31)	75.5(7)	73.3(3)	74.8(4)
U-N(4)-C(4)	174.4(18)		
U-N(4)-C(40)		107.1(8)	105.5(8)
U-N(4)-C(42)		134.6(9)	
U-N(4)-C(46)			140.2(8)
C(40)-N(4)-C(42)		118.0(11)	
C(40)-N(4)-C(46)			114.2(11)

Table 2Crystallographic data for 1, 3 and 4

The marked difference between the U–N distances in bispentamethyl bis(ketimide) complexes and triscyclopentadienyl or hydrotrispyrazolylborate ketimide complexes raises the question if it is reliable to compare uranium–nitrogen distances in systems with different sets of ancillary ligands. As no U– N bond distances are known for amido complexes based on the "U(Tp^{Me2})Cl₂" core, we decided to synthesize and to characterize by single-crystal X-ray diffraction analysis two uranium(IV) amide complexes, [U(Tp^{Me2})Cl₂(NEt₂)] (**3**) and [U(Tp^{Me2})Cl₂(NPh₂)] (**4**).

Metathesis of $[U(Tp^{Me2})Cl_3(THF)]$ with one equivalent of either LiN(C_2H_5)₂ or LiN(C_6H_5)₂ proceeds readily and yields respectively, after simple workup, $[U(Tp^{Me2})Cl_2(NEt_2)]$ (3) and $[U(Tp^{Me2})Cl_2(NPh_2)]$ (4). The compounds are obtained as green and orange solids, respectively, in modest yield (eqn (2)).

$$\begin{split} & [U(Tp^{Me2})Cl_3] + LiNR_2 \rightarrow [U(Tp^{Me2})Cl_2(NR_2)] \\ & + LiCl: R = Et \mbox{ (3); Ph (4)} \end{split}$$

Compounds 3 and 4 are soluble in aromatic and ether type solvents, but poorly soluble in aliphatic hydrocarbons.

The IR spectra of **3** and **4** show the ν (B–H) stretching mode at 2540 cm⁻¹ consistent with a κ^3 -coordination mode of the Tp^{Me2} ligand.¹³

The room-temperature ¹H NMR spectra of both complexes were consistent with a C_s -symmetric coordination sphere, with the three pyrazolyl rings of the Tp^{Me2} ligand giving rise to two sets of resonances in the ratio 2 : 1. The amide ligands, NEt₂ and NPh₂, give rise to two and three resonances, respectively, with the expected intensity.

X-Ray quality crystals of 3 and 4 were grown by slow concentration of THF solutions. The ORTEP diagrams of compounds 3 and 4 are shown in Fig. 2 and 3. Both structures consist of discrete molecular units in which the metal centre is six-coordinate by the tridentate pyrazolylborate ligand, two chlorine atoms and the nitrogen atom of the amide ligand. Ignoring the short U–C(40) contacts in 3 and 4, the coordination geometry

	1	3	4
Formula	C ₂₆ H ₃₈ BN ₇ Cl ₂ SiU	$C_{19}H_{32}BN_7Cl_2U$	$C_{27}H_{32}BN_7Cl_2U$
$M_{\rm r}$	796.46	678.26	774.34
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P2_{1}/n$	PĪ
a/Å	20.948(3)	10.942(5)	8.1647(11)
b/Å	10.5300(10)	17.310(3)	10.2881(11)
c/Å	15.0120(10)	14.541(5)	18.947(2)
a/°			75.667(9)
β/°		109.01(3)	88.415(11)
y/°			78.416(10)
$V/\text{\AA}^3$	3311.4(6)	2603.9(14)	1510.2(3)
Ζ	4	4	2
$D_{\rm c}/{ m g~cm^{-3}}$	1.598	1.730	1.703
μ (Mo-K α)/mm ⁻¹	5.126	6.458	5.580
R_1	0.0682	0.0624	0.0792
wR_2	0.09310	0.01225	0.0855



Fig. 2 ORTEP diagram of $[U(Tp^{Me2})Cl_2(NEt_2)]$ (3) using 20% probability ellipsoids.



Fig. 3 ORTEP diagram of $[U(Tp^{Me2})Cl_2(NPh_2)]$ (4) using 30% probability ellipsoids.

around the uranium atom may be described as being octahedral. Comparative bond distances and angles are shown in Table 1.

The metrical parameters for the "UTp^{Me2}Cl₂" fragment in compounds 1, 3 and 4 compare favourably with those observed for other uranium (IV) complexes supported by one Tp^{Me2} ligand.^{4,6}

As referred above, the U-N(4) distance of 2.04(2) Å in 1 is rather short. The bond distance of C(4) to the coordinated nitrogen N(4) (1.33(3) Å) in 1 is slightly longer than the value accepted for the N(sp²)-C(sp²) double bonds (1.28 Å),¹⁴ suggesting charge delocalisation from the N=C bond to the U-N bond. These structural features together with the almost linear U-N(4)-C(4) angle of 174.4° may corroborate the assumption made by other authors that there is significant ligand to metal π -bonding in the uranium ketimido interaction and, therefore, that these bonds have a significant uranium-nitrogen multiplebond character.9 This assumption was based on the U-N bond distances to the ketimide ligands $[U(C_5Me_5)_2(NCPh_2)_2]^{10}$ $(U-N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2\{NC(Ph)(CH_2Ph)\}_2]^9 (U-N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2\{NC(Ph)(CH_2Ph)]_2]^9 (U-N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2\{NC(Ph)(CH_2Ph)]_2]^9 (U-N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2\{NC(Ph)(CH_2Ph)]_2]^9 (U-N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2(N(av.) 2.182(8) \text{ Å}), [U(C_5Me_5)_2(N(av.) 2.182(8) \text{ Å})]_2$ $N(av.) 2.184(3) Å), [U(I){NC(Bu^t)(C_6H_2-2,4,6-Me_3)_3}(DME)]^{11}$ (U-N(av.) 2.189(25) Å) and $[U\{NC(Bu^{t})(C_{6}H_{2}-2,4,6-Me_{3})_{3}\}]_{2}$ - $(COT)^{11}$ (U–N(av.) 2.174(16) Å), that are shorter than those in the amide uranium(IV) complexes $[U(C_5Me_5)_2\{NH(C_6H_32,6 Me_{2}_{2}^{15}$ (U-N(av.) 2.267(6) Å), [U(C₅Me₅)(C₅Me₄CH₂NAd)- ${NH(Ad)}^{16}$ (U-N 2.231(6), 2.155(7) Å), $[U{Me_2Si(C_5Me_4)} (^{1}BuN)$ (NMe₂)₂]¹⁷ (U–N(av.) 2.210(7) Å) and [{U(NEt₂)₄}₂]¹⁸ (U-N(av.) 2.22(1) Å) and in the large U-N-C angles $([U(C_5Me_5)_2 - C_5Me_5)_2 - C_5Me_5)_2$ $(NCPh_2)_2]^{10}$ (173.4(6) and 176.5(5)°), $[U(C_5Me_5)_2\{NC-1, C_5Me_5\}_2]^{10}$ $(CH_2Ph)(Ph)_2]^9$ (162.4(3)°), $[UCp_3\{NC(Me)CH(PMePh_2)\}]^{12}$ $(163(1)^{\circ})$ and $[U(I)\{NC({}^{\prime}Bu)(C_{6}H_{2}\text{-}2,4,6\text{-}Me_{3})\}_{3}(DME)]^{11}$ (172.8(14), 171.4(17) and 160.4(13)^{\circ}).

The U–N(4) distance of 2.148(10) Å in **3**, is close to the corresponding distance in $[U(OC_6H_3-2,6-Bu^{1}_2)_3(NEt_2)]$ (2.16 Å)¹⁹ and $[U\{(SiMe_2NPh)_3-tacn\}(NEt_2)]$ (2.146(12) Å),²⁰ but significantly shorter than those usually found in other structurally characterized uranium(IV) alkylamido complexes, 2.220(5) Å in $[U\{(Me_3SiNCH_2CH_2)_3N\}(NEt_2)]$,²¹ 2.210(4) Å in $[U\{Me_2Si(C_5Me_4)(^{1}BuN)\}(NMe_2)_2]$,¹⁷ and 2.22(1) Å for the terminal U–N bonds in the dimeric $[\{U(NEt_2)_4\}_2]$.¹⁸

The two ethyl groups of the amide ligand are inequivalent. The U–N(4)–C(40) is more acute than the U–N(4)–C(42) angle by 27.5°. This distortion is a result of a close contact between the U and the N(4)–C(40) functionality. The U ··· C(40) distance of 2.942(13) Å may be compared with those of contacts to the methyl groups within the bis(trimethylsylilamide) ligands in $[U(SC_6H_3-2,6-Me_2){N(SiMe_3)_2}_3]^{22}$ (3.158 Å) and $[Th(NMePh)_2{N(SiMe_3)_2}_2]^{23}$ (3.073(10) and 3.064(10) Å). Inspection of the angles around the nitrogen atom coordinated to uranium reveals that the planarity of the substituents is maintained (sum of angles 359.7°).

The U–N(4) distance of 2.225(10) Å in 4 compares with those of 2.29(1), 2.27(10) and 2.267(6) Å in $[UCp_3(NPh_2)]_{,}^{24}$ $[U(NPh_2)_4]_{,}^{18}$ and $[U(C_5Me_5)_2\{NH(C_6H_3-2,6-Me_2)_2\}]_{,}^{15}$ respectively. The molecular structure of 4 also features one short contact to the carbon-*ipso* (C40) of one of the phenyl rings $(U \cdots C(40) 2.949 (13) \text{ Å})$. This interaction results in a decrease in the angle U–N(4)–C(40) to 105.5(8)° vs. U–N(4)–C(46) of 140.2(8)°, with the two phenyl groups which are attached to nitrogen occupying different positions relative to the "UTp^{Me2}Cl₂" core (Fig. 4).



Fig. 4 A B–U view of $[U(Tp^{Me2})Cl_2(NPh_2)]$ (4).

The most striking feature of the structures of the ketimide and the two amido complexes discussed above is the large differences of the U–N distances in these compounds.

The difference between the two U–N(4) distances in complexes **3** and **4** may be understood as the result of both steric and electronic effects: it is recognized that NPh₂ is larger than NEt₂, as can be immediately inferred from the dimeric structure presented by the complex [{U(NEt₂)₄}₂] in contrast with the monomeric structure of [U(NPh₂)₄],¹⁸ and the charge density on the N atom in the diethylamide ligand is expected to be larger than in the diphenylamide ligand due to the charge delocalisation effect of the phenyl groups.

The shorter U–N(4) distance in the ketimide complex 1 as compared to the corresponding distances in the amido complexes 3 and 4 may also be the consequence, apart from steric effects, of the intrinsic nature of the N atom which is

To be able to make a more thorough comparison of the U-N (and eventually Th-N) bond lengths in compounds containing ketimide and amide ligands, we need to take into account the different steric and/or electronic requirements of these ligands and also of the ancillary ligands. One way to sort out the steric effects that may contribute to the metal-ligand distances in a complex is to use a model proposed some years ago by Marçalo and Pires de Matos, based on a new definition of coordination number.25 In that work, the authors defined a steric coordination number (CN_s) based on the size of a ligand (as measured by the solid angle comprising the van der Waals' spheres of the atoms of the ligand) and used it to obtain the CNs of a compound, as the sum of the CN_s of all the ligands. From the analysis of a large number of structurally characterized lanthanide and actinide compounds, Marçalo and Pires de Matos derived a set of ligand effective radii r(N), which reflect the electronic and/or electrostatic contribution of the ligand to the metal-ligand bond length. These ligand effective radii together with the CN_s of a compound and Shannon's ionic radii $r(An^{4+})^{26}$ can be used in the comparison of the metal-ligand distances in compounds with different sets of ligands.

In Table 3 we show the results of an analysis, based on the model of Marçalo and Pires de Matos,²⁵ of a significant number of U(IV) and Th(IV) complexes containing amide and ketimide ligands. It should be noted that the large majority of these

compounds were not considered in the original work of the authors.²⁵ In Table 4 we present the CN_s of the ligands not included in ref. 25.

Several aspects can be highlighted from an inspection of the ligand effective radii (r(N)) presented in Table 3. The diphenylamido and arylamido ligands (average r(N) = 1.28(3) Å) form, as expected, longer bonds with the An metal centres as compared

Table 4 Steric coordination numbers (CN_s) of new ligands^a

Ligand	CNs
(SiMe ₂ NPh) ₃ -tacn	5.97
(Me ₂ Bu ^t SiNCH ₂ CH ₂) ₃ N	6.89
$Me_2Si(C_5Me_4)(Bu^tN)$	4.57
C ₅ Me ₄ CH ₂ NAd	4.17
NHPh	1.45
$NH(C_6H_4-4-Cl)$	1.45
$NH(C_6H_3-2,6-Me_2)$	1.72
NMePh	1.63
NHAd	1.59
NMe ₂	1.46
NC(Ph)(CH ₂ SiMe ₃)	1.52
$NC(Bu^{t})(C_{6}H_{2}-2,4,6-Me_{3})$	1.56
NC(Ph)(CH ₂ Ph)	1.37
NCPh ₂	1.44
NC(Me)(CHPMePh ₂)	1.47

^a Not considered in original work; ref. 25

Complex	d(An–N)/Å	CNs	$r(An^{4+})/Å$	<i>r</i> (N)/Å	Ref.
$[UTp^{Me2}Cl_2(NPh_2)]$	2.225(10)	7.34	0.964	1.26	This work
$[U(NPh_2)_4]$	2.27(10)	7.16	0.954	1.32	a
$[UCp_3(NPh_2)]$	2.29(1)	7.91	0.994	1.30	Ь
$[U(C_5Me_5)_2(NHPh)_2]$	2.250(4)	7.88	0.993	1.26	с
$[U(C_5Me_5)_2 \{NH(C_6H_3-2,6-Me_2)\}]_2$	2.267(6)	8.42	1.021	1.25	d
$[U(C_5Me_5)_2Cl{NH(C_6H_4-4-Cl)}]$	2.237(3)	7.43	0.969	1.27	e
$[Th{N(SiMe_3)_2}_2(NMePh)_2](Th-NMePh)]$	2.302(10)	7.60	1.023	1.28	ſ
$[UH{N(SiMe_3)_2}_3]$	2.237(9)	7.31	0.962	1.27	g
$[U(OC_6H_3-2,6-Bu_2^t){N(SiMe_3)_2}_3]$	2.285(12)	8.92	1.048	1.24	h
$[UCl_2(DME)\{N(SiMe_3)_2\}_2]$	2.235(12)	8.12	1.005	1.23	i
$[Th(COT){N(SiMe_3)_2}_2]$	2.335(25)	7.78	1.032	1.30	j
$[Th(BH_4){N(SiMe_3)_2}_3]$	2.32(2)	7.93	1.040	1.28	k
$[Th{N(SiMe_3)_2}_2(NMePh)_2](Th-N(SiMe_3)_2)$	2.314(20)	7.60	1.023	1.29	ſ
$[UTp^{Me^2}Cl_2(NEt_2)]$	2.154(10)	7.22	0.958	1.20	This work
$[U{(SiMe_2NPh)_3-tacn}(NEt_2)]$	2.146(12)	7.64	0.980	1.17	1
$[U(OC_6H_3-2,6-Bu_2^t)_3(NEt_2)]$	2.162(5)	8.90	1.047	1.12	m
$[U{(Me_2Bu^{t}SiNCH_2CH_2)_3N}(NEt_2)]$	2.220(5)	8.56	1.029	1.19	n
$[U{Me_2Si(C_5Me_4)(Bu^tN)}(NMe_2)_2]$	2.210(7)	7.49	0.972	1.24	0
$[U(C_5Me_5)(C_5Me_4CH_2NAd)(NHAd)]$	2.155(7)	8.25	1.012	1.14	р
$[U(NEt_2)_3(THF)_3][BPh_4]$	2.18(3)	8.64	1.033	1.15	q
$[U(NEt_2)_2(py)_5][BPh_4]_2$	2.202(20)	9.29	1.067	1.13	q
$[U(C_5Me_5)(NEt_2)_2(THF)_2][BPh_4]$	2.175(15)	8.25	1.012	1.16	r
$[U(COT)(NEt_2)(THF)_3][BPh_4]$	2.18(2)	8.74	1.038	1.14	S
$[U(C_5Me_5)_2(NMe_2)(CNBu^{t})_2][BPh_4]$	2.22(1)	8.40	1.020	1.20	t
$[UTp^{Me^2}Cl_2\{NC(Ph)(CH_2SiMe_3)\}]$	2.04(2)	7.07	0.950	1.09	This work
$[UI{NC(Bu^{t})(C_{6}H_{2}-2,4,6-Me_{3})}_{3}(DME)]$	2.189(25)	7.46	0.970	1.22	u
$[U{NC(Bu^{t})(C_{6}H_{2}-2,4,6-Me_{3})}_{3}]_{2}(COT)$	2.174(16)	8.12	1.005	1.17	u
$[U(COT){NC(Bu^{t})(C_{6}H_{2}-2,4,6-Me_{3})}_{3}][Na(OEt_{2})]$	2.225(5)	8.12	1.005	1.22	u
$[U(C_5Me_5)_2\{NC(Ph)(CH_2Ph)\}_2]$	2.184(3)	7.79	0.988	1.20	v
$[U(C_5Me_5)_2(NCPh_2)_2]$	2.182(8)	7.86	0.992	1.19	w
$[Th(C_5Me_5)_2\{NC(Ph)(CH_2Ph)\}_2]$	2.256(8)	7.79	1.033	1.22	v
$[Th(C_5Me_5)_2(NCPh_2)_2]$	2.262(8)	7.86	1.036	1.23	v
$[UCp_3{NC(Me)(CHPMePh_2)}]$	2.06(1)	7.59	0.977	1.08	x

^a Ref. 18. ^b Ref. 24. ^c R. C. Schnabel, D. S. Arney and C. J. Burns, manuscript in preparation, cited in D. S. J. Arney and C. J. Burns, *J. Am Chem. Soc.*, 1995, **117**, 9448. ^d Ref. 15. ^c R. G. Peters, B. L. Scott and C. J. Burns, *Acta Crystallogr., Sect. C*, 1999, **55**, 1482. ^J Ref. 23. ^s R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1981, **20**, 622. ^h J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van Der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, **114**, 10811. ⁱ L. G. McCullough, H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1981, **20**, 622. ^h J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van Der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, **114**, 10811. ⁱ L. G. McCullough, H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.* 1981, **20**, 2869. ^j T. M. Gilbert, R. R. Ryan and A. P. Sattelberger, *Organometallics*, 1988, **7**, 2514. ^k H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem. Inorg. Chem.*, 1979, **18**, 1221. ^l Ref. 20. ^m Ref. 19. ⁿ Ref. 11. ^e Ref. 16. ^e J. C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1995, 3019. ^l J. C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1995, 3027. ^s C. Boisson, J. C. Berthet, M. Ephritikhine, *M. Lance and M. Nierlich, J. Organomet. Chem.*, 1996, **522**, 249. ^l C. Boisson, J. C. Berthet, M. Lance, M. Nierlich and M. Ephritikhine, *J. Organomet. Chem.*, 1997, **548**, 9. ^w Ref. 11. ^v Ref. 10. ^s Ref. 12.

with the dialkylamido and alkylamido ligands (average r(N) =1.17(4) Å), and the disilylamido ligand forms also longer bonds (average r(N) = 1.27(3) Å), probably reflecting a lower basicity as compared to the dialkylamides (this difference was already apparent in the early work of Marçalo and Pires de Matos,25 which included also lanthanide compounds). According to this analysis, compounds 3 and 4 seem to have unexceptional U-N bond lengths to the diphenylamido and diethylamido ligands. Surprisingly, the ketimide ligands, with the exceptions of compound 1 and of [UCp₃{NC(Me)(CHPMePh₂)}],¹² seem to form bonds that are slightly longer (excluding the indicated compounds) than the ones formed by dialkylamido and alkylamido ligands, as an average r(N) = 1.21(2) Å is obtained for the ketimide compounds and, as indicated above, an average r(N) = 1.17(4) Å is obtained for the dialkylamide and alkylamide complexes.

Although the steric coordination number model is approximate due to a number of limitations,²⁵ particularly the average nature of the CN_s of the ligands (which can be affected for instance by the presence of agostic interactions like in compounds **3** and **4**), we think that it is reliable enough to show that we are in the presence of significant differences among the several structurally characterized An(IV) complexes containing ketimide ligands, that may be not steric in origin.

Conclusions

Nitriles insert into the U–C bond of $[U(Tp^{Me2})Cl_2(CH_2SiMe_3)]$ to give the ketimide complexes $[U(Tp^{Me2})Cl_2\{NC(R)-(CH_2SiMe_3)\}]$. The molecular structure of the compound with R = Ph revealed a short U–N bond length to the ketimide ligand that was compared to the U–N bond distances in amide complexes based on the same ligand arrangement, also prepared and structurally characterized in this work. A detailed analysis of the U–N bond lengths in these compounds and of other known U–N (and Th–N) distances in amide and ketimide actinide(IV) complexes confirmed the short character of the U–N bond length in $[U(Tp^{Me2})Cl_2\{NC(Ph)(CH_2SiMe_3)\}]$ and showed that the U–N bond distances in some of the U(IV) and Th(IV) complexes containing ketimide ligands described in the literature are unexpectedly long.

Experimental

General considerations

All preparations and subsequent manipulations were carried out using standard Schlenk line and dry-box techniques in an atmosphere of dinitrogen. Benzonitrile, acetonitrile, THF, toluene and *n*-hexane were dried by standard methods and degassed prior to use. LiNPh₂ and LiNEt₂ were synthesized by addition of *n*-BuLi to solutions of the amines in *n*-hexane, at 0 °C. Benzened₆ was dried over Na and distilled. [U(Tp^{Me2})Cl₃(THF)]⁴, and [U(Tp^{Me2})Cl₂(CH₂SiMe₃)]⁶ were prepared as previously reported. 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-d₆, 7.15 ppm). Carbon, hydrogen and nitrogen analyses were performed in-house using a EA110 CE Instruments automatic analyser.

Synthetic procedures

[U(Tp^{Me2})Cl₂{NC(Ph)(CH₂SiMe₃)}] 1. Benzonitrile (21 μL, 0.20 mmol) was added to a solution of [U(Tp^{Me2})Cl₂(CH₂SiMe₃)] (141 mg, 0.20 mmol) in toluene. The solution was stirred for 18 h. The solvent was removed under vacuum to yield **1** (137 mg, 86%) as a dark reddish solid (Found: C, 38.7; H, 5.0; N 12.2%. UCl₂BSiC₂₆H₃₈N₇ requires C, 39.2; H, 4.8; N, 12.3%); v_{max} (film)/cm⁻¹ 2540 (B–H), 1605 (C=N), 260 (U–Cl); λ_{max} (toluene)/nm: 540, 605, 640 (sh), 670 (sh), 680, 840, 880, 940, 1000 (sh), 1040 (sh), 1070 (sh), 1095, 1110, 1150 (sh), 1320, 1580,

1950; $\delta_{\rm H}$ (300 MHz, C₆D₆, Me₄Si) 55.8 (2H, CH₂SiMe₃), 42.5 (1H, H-4), 35.8 (3H, Me-pz), 34.8 (2H, doublet, H-*o*), 18.7 (3H, Me-pz), 13.7 (2H, triplet, H-*m*), 12.7 (1H, triplet, H-*p*), 11.2 (9H, CH₂SiMe₃), -5.8 (6H, Me-pz), -10.7 (2H, H-4), -24.5 (6H, Me-pz). Dark orange crystals of **1** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a toluene solution.

[U(Tp^{Me2})Cl₂{NC(Me)(CH₂SiMe₃)}] 2. The compound was synthesized as described for **1** by using 135 mg (0.19 mmol) of [U(Tp^{Me2})Cl₂(CH₂SiMe₃)] and 9 μL (0.19 mmol) of acetonitrile. Compound **2** (121 mg, 85%) was obtained as a dark yellow microcrystalline solid (Found: C, 35.2; H, 5.2; N, 12.8%. UCl₂BSiC₂₁H₃₆N₇ requires C, 34.3; H, 5.0; N, 13.3%); v_{max} (film)/cm⁻¹ 2540 (B–H), 1605 (C=N), 255 (U–Cl); λ_{max} (toluene)/nm: 570, 600, 650 (sh), 660 (sh), 680, 840, 935, 995 (sh), 1060 (sh), 1110, 1145 (sh), 1210; δ_{H} (300 MHz, C₆D₆, Me₄Si) 55.1 (2H, CH₂SiMe₃), 47.5 (3H, CH₃CN), 43.7 (1H, H-4), 40.5 (3H, Me-pz), 18.3 (3H, Me-pz), 11.2 (9H, CH₂SiMe₃), -6.7 (6H, Me-pz), -11.2 (2H, H-4), -24.6 (6H, Me-pz).

 $[U(Tp^{Me2})Cl_2(NEt_2)]$ 3. A solution of LiNEt₂ (23 mg, 0.29 mmol) in toluene was slowly added to a suspension of [U(Tp^{Me2})Cl₃(THF)] (206 mg, 0.29 mmol) in the same solvent. The mixture was stirred for 3 h during which time the light-green suspension became bright green. The solution was centrifuged and the toluene solution was concentrated under reduced pressure (5 ml). Addition of n-hexane results in deposition of 3 (81 mg, 42%) as a green powder (Found: C, 34.6; H, 4.8; N, 14.5%. UCl₂BC₁₉H₃₂N₇ requires C, 33.6; H, 4.7; N, 14.5%); $v_{\text{max}}(\text{film})/\text{cm}^{-1}$: 2540 (B–H), 255 (U–Cl); $\lambda_{\text{max}}(\text{toluene})/\text{nm}$: 610, 647, 664, 730, 780, 935, 993, 1070, 1080 (sh), 1120, 1150 (sh), 1275; $\delta_{\rm H}$ (300 MHz, C₆D₆, Me₄Si): 118.52 (4H, CH₂(NEt₂)), 74.66 (3H, Me-pz), 47.43 (1H, H-4), 38.98 (6H, CH₃(NEt₂)), 13.40 (3H, Me-pz), -11.18 (6H, Me-pz), -12.38 (2H, H-4), -26.44 (6H, Me-pz). Green needles of 3 suitable for X-raydiffraction analysis were grown by slow concentration of a THF solution.

[U(Tp^{Me2})Cl₂(NPh₂)] 4. Compound 4 was synthesized by slow addition of a solution of LiNPh₂ (61 mg, 0.35 mmol) in THF to a solution of [U(Tp^{Me2})Cl₃(THF)] (250 mg, 0.35 mmol) in the same solvent. The green solution turned immediately to brown-red. After stirring for 2 h the solvent was removed under vacuum and the resulting solid extracted in toluene to separate the LiCl. Removal of the solvent gave an orange solid that was further washed with hexane and vacuum dried to yield 4 (162 mg, 60%) (Found: C, 42.3; H, 4.3; N, 12.1%. UCl₂BC₂₇H₃₂N₇ requires C, 41.9; H, 4.1; N, 12.7%); v_{max} (film)/cm⁻¹: 2540 (B–H), 265 (U– Cl); λ_{max} (toluene)/nm: 623, 648, 664, 671, 683, 728, 774, 932, 946, 989, 1020, 1060, 1098, 1136, 1164; $\delta_{\rm H}$ (300 MHz, C₆D₆, Me₄Si): 43 (3H, Me-pz), 33 (1H, H-4), 21 (4H, H-o), 12.4 (4H, H-m), 9.6 (3H, Me-pz), 7 (2H, H-p), -6.2 (6H, Me-pz), -10 (2H, H-4), -14.4 (6H, Me-pz). Golden crystals of 4 were grown by slow concentration of a THF solution.

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-monochromatized Mo-K α radiation ($\lambda = 0.71069$ Å) in the ω -2 θ scan mode. Data were corrected²⁷ for Lorentz and polarization effects, and for absorption by empirical corrections based on Ψ scans.

The structure of **1** was solved using Patterson methods and successive difference Fourier techniques and refined by fullmatrix least squares refinements on F^2 using SHELX-97.²⁸ The structures of **3** and **4** were solved by direct methods using SIR97²⁹ and refined by full-matrix least-squares refinements on F^2 using SHELXL-97²⁸ and the winGX software package.³⁰ The contributions of the hydrogen atoms were included in calculated positions. The drawings were made with ORTEP-3.³¹ A summary of the crystallographic data is given in Table 2. CCDC reference numbers 276941 (1), 276942 (3) and 276943 (4).

See http://dx.doi.org/10.1039/b509229a for crystallographic data in CIF or other electronic format.

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