Reactivity of the cationic uranium amide compound [U(η-C₅Me₅) ₂(NMe₂)(OC₄H₈)][BPh₄]

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Abstract

The cationic uranium amide compound [U(Cp*)₂(NMe₂)(THF)][BPh₄] **1** (Cp* = η-C₅Me₅, THF = tetrahydrofuran) was transformed into the heterocyclic metallacycle |(Cp*)₂U(O(CH₂)₄NMe₂(CH₂)₄O)||BPh₄| ·0.5THF **2** in the presence of a catalytic amount of the free amine NR₂H (R = Me, Et). Treatment of **1** with tBuNC afforded the isocyanide adduct [U(Cp*)₂(NMe₂)(CNtBu)₂][BPh₄] **4** whereas reactions with MeCN, CO₂ and CO gave the insertion compounds [U(Cp*)₂(NC{Me}{NMe₂})(THF)][BPh₄] **5**, [U(Cp*)₂(O₂CNMe₂)(THF)][BPh₄] **6** and [U(Cp*)₂(η²-CONMe₂)(THF)][BPh₄] **7**. The crystal structure of a THF solvate of **4** has been determined. © 1997 Elsevier Science S.A. © 1997 Elsevier Science S.A.

1. Introduction

Cationic metal complexes with dialkyl–amide ligands were unknown until we discovered an efficient and practical synthesis, by protonolysis of an M–NR₂ bond with the ammonium salt NR′₃HBPh₄. Thus, reaction (1) served to prepare a number of mono- and dicationic compounds of uranium and Group 4 elements, such as [M(NR₂)₃(THF)ₓ][BPh₄] (M = U, Ti, Zr, Hf; x = 0–3; R = Me or Et), [U(NEt₂)₂(THF)₃][BPh₄]₂ and a series of organometallic derivatives with cyclopentadienyl or cyclooctatetraene ligands [1–6].

$$[\{M\}(NR_2)_{n+1}] + NR'_3HBPh_4$$

$$\rightarrow [\{M\}(NR_2)_n][BPh_4] + NR_2H + NR'_3 \qquad (1)$$
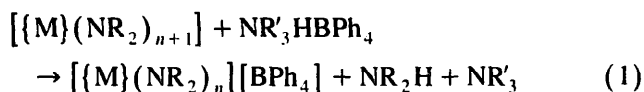
Electrophilic species of the type [{M}(NR₂)ₙ]⁺ are expected to be very reactive. Indeed, cationic complexes of the Group 4 elements with heteroatom ligands proved to be useful in stoichiometric and catalytic processes [7], and moreover, it is known that amide compounds exhibit a reactivity which is quite similar to that of their alkyl analogues: both complexes readily react with proton acidic substrates to give substitution derivatives and with unsaturated molecules to afford insertion products [8]. In this context, it seemed to us of interest to consider the potential of some uranium amide cations as precursors for the preparation of new cationic complexes [4]. Such compounds are quite uncommon, in particular in the series of the bispentamethylcyclopentadienyl complexes. This family, which was of fundamental importance in the development of organouranium chemistry [9], only contains three cationic derivatives: [U(Cp*)₂(THF)₂][BPh₄] (Cp* = η-C₅Me₅, THF = tetrahydrofuran) [6], [U(Cp*)₂(NR₂)(THF)][BPh₄] (R = Me, Et) [3] and [U(Cp*)₂(NEt₂)₂][BPh₄] [10] which are respectively in the +3, +4 and +5 oxidation states; the U(III) and U(IV) complexes were prepared by protonolysis of [U(Cp*)₂(N{SiMe₃}₂)] and [U(Cp*)₂(NR₂)₂] [reaction (1)]. Here we report on a number of derivatives obtained from [U(Cp*)₂(NMe₂)(THF)][BPh₄] which proved to be a unique entry into the class of the cationic bisCp* complexes of uranium.

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2. Results and discussion

2.1. Ring-opening reaction of THF promoted by [U(Cp*)₂(NMe₂)(THF)][BPh₄] 1

The electrophilicity of a metal complex is often evidenced by its ability to promote the ring-opening reaction of tetrahydrofuran [11,12]. Compound 1 was readily prepared in this solvent from [U(Cp*)₂(NMe₂)₂], by using reaction (1), and was easily isolated in a very good yield [3]. However, by keeping the reaction mixture for a longer period at room temperature, yellow microcrystals were progressively deposited from the red solution. The ¹H NMR spectrum exhibited, in addition to the two resonances attributed to the Cp* ligands (30 H) and NMe₂ groups (6 H), four signals of equal intensity (4 H) which suggested that a THF ring-opening reaction had occurred. The new compound,[(Cp*)₂U(O(CH₂)₄NMe₂(CH₂)₄O)]|BPh₄|
·0.5THF 2, was isolated and could be identified after X-ray diffraction analysis of the solvate obtained by crystallization from pyridine; the crystal structure was reported in our preliminary communication [13].

It was then clear that 2 resulted from the reaction of 1 with two molecules of tetrahydrofuran. In fact, complex 1, once isolated pure, was found to be inert towards THF and could be transformed into 2 only in the presence of free amine; the reaction was achieved by using either NMe₂H or NEt₂H (1 equivalent) and required respectively 6 and 10 days at 20°C to go to completion (NMR experiments). These facts indicated that the coordinated THF molecule in 1 did not undergo
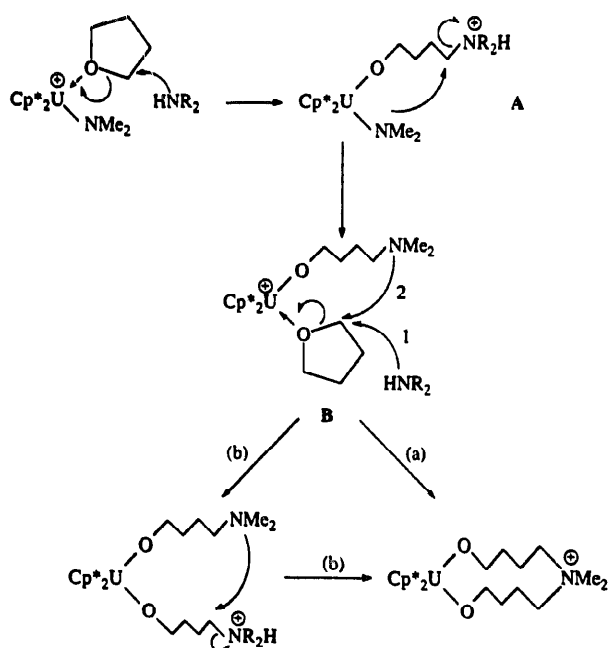

Scheme 1. Proposed mechanism for the formation of 2.

nucleophilic attack of the NMe₂ ligand but rather that of the free amine NR₂H. Similar reactions of NMe₃ with the zirconium cations [Zr(η-C₅H₅)₂(R)(THF)]⁺ afforded the ring-opened species [Zr(η-C₅H₅)₂(R)(O{CH₂}₄NMe₃)]⁺ [12]. Since 2 was obtained by treating 1 with either NMe₂H or NEt₂H, the first intermediate A in Scheme 1, [U(Cp*)₂(NMe₂)(O{CH₂}₄NR₂H)]⁺, should then rearrange into [U(Cp*)₂(O{CH₂}₄NMe₂(THF)]⁺, following nucleophilic substitution by the NMe₂ group and liberation of NR₂H. The coordinated THF in this second intermediate B would be attacked either by the amino group of the O(CH₂)₄NMe₂ ligand to give 2 directly [path (a)] or, as before, by NHR₂ to give [U(Cp*)₂(O{CH₂}₄NMe₂)(O{CH₂}₄NR₂H)]⁺ which would cyclize into the final product 2 [path (b)]. The free amine NR₂H plays a catalytic role in the formation of 2. The synthesis of 2 represents a novel ring-opening reaction of two THF molecules promoted by a single metal species; compound 2 is a unique heterocyclic metallacycle containing both oxygen and nitrogen atoms.
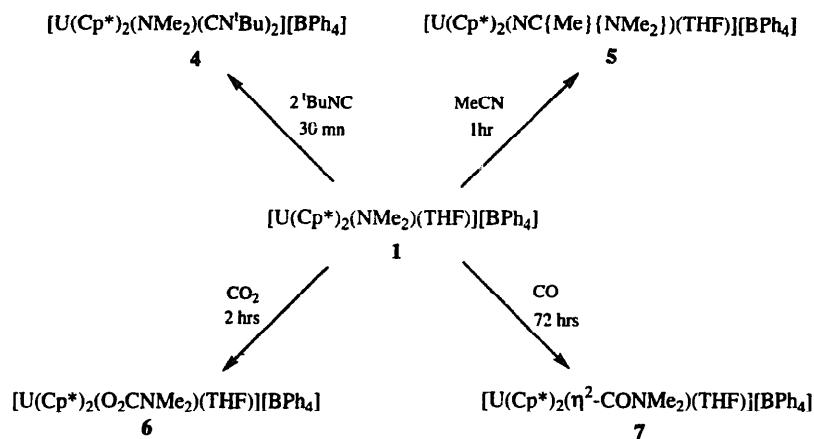
2.2. Reactions of 1 with proton acidic substrates

Like the monocyclooctatetraene compound [U(η-C₈H₈)(NEt₂)(THF)₂][BPh₄] [4], complex 1 was rather inert towards proton acidic molecules unless these could be activated by prior coordination to the metal centre. Thus, 1 did not react with NEt₃HBPh₄, cyclopentadiene or phenylacetylene but in the presence of isopropanol, which has the same pK_a as phenylacetylene, it was readily transformed into the cation [U(Cp*)₂(OⁱPr)(THF)]⁺. This reaction likely proceeded by the intermediate formation of the adduct [U(Cp*)₂(NMe₂)(ⁱPrOH)]⁺, followed by proton transfer and elimination of NMe₂H. The cation [U(Cp*)₂(OⁱPr)(THF)]⁺ was detected by ¹H NMR but could not be isolated pure as it further reacted with ⁱPrOH in the presence of NMe₂H to give the neutral bisalkoxide [U(Cp*)₂(OⁱPr)₂] [14] which presumably resulted from deprotonation of [U(Cp*)₂(OⁱPr)(ⁱPrOH)]⁺ by the amine. Treatment of 1 with 2 equivalents of the alcohol gave [U(Cp*)₂(OⁱPr)₂] in almost quantitative yield [Eq. (2)]

$$[U(Cp^*)_2(NMe_2)(THF)][BPh_4] + 2^iPrOH$$

$$\rightarrow [U(Cp^*)_2(O^iPr)_2] + NMe_2H_2BPh_4 \qquad (2)$$
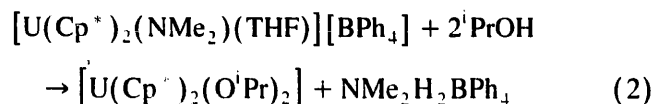
Attempts to prepare stable alkoxide cations of the type [U(Cp*)₂(OR)(THF)]⁺ in which a bulky OR group would prevent the coordination of a second molecule of alcohol have so far been unsuccessful; no reaction was observed between 1 and 2,6-diisopropyl phenol. However, it should not be concluded from these results that cationic alkoxide compounds could not be synthesized

[U(Cp*)₂(NMe₂)(CN^{t}Bu)₂][BPh₄]   [U(Cp*)₂(NC{Me}{NMe₂})(THF)][BPh₄]
           4   **5**

2 ^{t}BuNC   MeCN
30 mn   1hr

[U(Cp*)₂(NMe₂)(THF)][BPh₄]
1

CO₂   CO
2 hrs   72 hrs

[U(Cp*)₂(O₂CNMe₂)(THF)][BPh₄]   [U(Cp*)₂(η²-CONMe₂)(THF)][BPh₄]
            6   **7**

Scheme 2. Reactions of **1** with unsaturated molecules. All reactions in THF at room temperature.

from their amide precursors. Thus, the monocyclopentadienyl cationic complex [U(Cp*)(NMe₂)₂(THF)₂][BPh₄], made in situ by protonolysis of [U(Cp*)(NMe₂)₃] [10], reacted with 2 equivalents of ethanol to give [U(Cp*)(OEt)₂(THF)₂][BPh₄] **3** which was isolated as a pale green microcrystalline powder in 82% yield [Eq. (3)].

$$[U(Cp^*)(NMe_2)_2(THF)_2][BPh_4] + 2EtOH$$

$$\rightarrow [U(Cp^*)(OEt)_2(THF)_2][BPh_4] + 2NMe_2H$$
$$\mathbf{3}$$

(3)
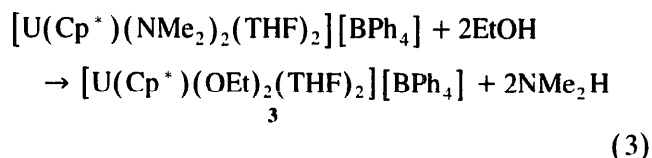
2.3. Reactions of 1 with unsaturated molecules

The reactions are summarized in Scheme 2. Orange crystals of [U(Cp*)₂(NMe₂)(CN^{t}Bu)₂][BPh₄] **4** were

isolated in 80% yield after addition of ^{t}BuNC to a solution of **1** in tetrahydrofuran. The isocyanide adduct **4** was quite stable, and insertion of ^{t}BuNC into the U–N bond was not observed, even after prolonged heating. However, reaction of **1** with cyclohexyl isocyanide was more complicated and the product(s), possibly insertion derivatives, have not been identified. It had previously been reported that the neutral amide complexes [U(η-C₅H₅)₂(NEt₂)₂] and [U(Cp*)₂(NEt₂)(Cl)] were inert towards ^{t}BuNC but reacted with CNC₆H₁₁ to give the iminoalkylamido insertion compounds [15].

Complex **1** was readily and cleanly transformed into the cationic amidino and carbamate derivatives [U(Cp*)₂(NC{Me}{NMe₂})(THF)][BPh₄] **5** (84%) and [U(Cp*)₂(O₂CNMe₂)(THF)][BPh₄] **6** (82%), by insertion of acetonitrile and carbon dioxide into the uranium–nitrogen bond. These reactions are identical to

Table 1
¹H NMR of compounds **1–7**[a]

Compound	Cp* ligands	Other ligands
[(Cp*)₂U(O(CH₂)₄NMe₂(CH₂)₄O)][BPh₄] · 0.5THF **2**	0.0 (34 H)[b]	16.92 (4 H, t, J = 7 Hz, α-CH₂)[c]; 7.8 and 7.1 (Ph and solvent resonances); 3.55 and 1.51 (2 H + 2 H, m, THF); 0.87 (6 H, NMe₂) −1.7 (4 H, m, δ-CH₂)[c]; −9.0 (4 H, m, γ-CH₂)[c]
[U(Cp*)(OEt)₂(THF)₂][BPh₄] **3**	−7.15 (15 H)	182 (4 H, CH₂); 74 (6 H, Me); 6.4 (20 H, Ph)
[U(Cp*)₂(NMe₂)(CN^{t}Bu)₂][BPh₄] **4**	2.85 (30 H)	88 (6 H, $w_{1/2}$ = 190 Hz, NMe₂); 7.0 (8 H, o-Ph); 6.7 and 6.5 (12 H, m- and p-Ph); −9.2 (18 H, $w_{1/2}$ = 70 Hz, ^{t}Bu)
[U(Cp*)₂(NC{Me}{NMe₂})(THF)][BPh₄] **5**	3.7 (30 H)	21.0 (3 H, Me); 13.8 and 10.6 (3 H + 3 H, $w_{1/2}$ = 50 Hz, Me) 6.3 (20 H, Ph)
[U(Cp*)₂(O₂CNMe₂)(THF)][BPh₄] **6**	14.4 (30 H)	5.8 (20 H, Ph); −15.9 (6 H, Me)
[U(Cp*)₂(η²-CONMe₂)(THF)][BPh₄] **7**	6.9 (30 H)	6.0 (20 H, Ph); −6.9 and −29.9 (3 H + 3 H, Me)

[a] At 30 °C, δ relative to TMS, in THF-d_8 except **2** in pyridine-d_5. When not specified, the signals are singlets with half-height widths between 10 and 30 Hz.

[b] The signals of the Cp* and β-CH₂ are overlapping.

[c] α, β, γ and δ are the positions of the carbon atoms of the metallacycle, with respect to the oxygen atoms; attribution was made after decoupling experiments.

Table 2
Elemental analyses of the compounds

Compound	Analyses % Found (Calc.)		
	C	H	N or B (3)
[(Cp*)₂U(O(CH₂)₄NMe₂(CH₂)₄O)][BPh₄] · 0.5THF **2**	63.69 (63.18)	7.12 (7.17)	1.29 (1.36)
[U(Cp*)(OEt)₂(THF)₂][BPh₄] **3**	59.44 (59.61)	6.49 (6.63)	1.33 (1.17)
[U(Cp*)₂(NMe₂)(CNᵗBu)₂][BPh₄] **4**	64.50 (64.79)	7.19 (7.18)	3.88 (4.05)
[U(Cp*)₂(NC{Me}{NMe₂})(THF)][BPh₄] **5**	63.15 (63.41)	6.75 (6.86)	2.76 (2.84)
[U(Cp*)₂(O₂CNMe₂)(THF)][BPh₄] **6**	61.78 (62.01)	6.56 (6.53)	1.35 (1.42)
[U(Cp*)₂(η²-CONMe₂)(THF)][BPh₄] **7**	62.89 (63.03)	6.52 (6.64)	1.41 (1.44)

those observed with $[U(\eta\text{-}C_8H_8)(NEt_2)(THF)_2][BPh_4]$ [4].

In contrast to $[U(\eta\text{-}C_8H_8)(NEt_2)(THF)_2][BPh_4]$, complex **1** reacted with carbon monoxide in THF to give the cationic carbamoyl compound $[U(Cp^*)_2(\eta^2\text{-}CONMe_2)(THF)][BPh_4]$ **7** which was isolated as red microcrystals in 72% yield. Such insertion of CO into a metal–nitrogen bond was first observed with the neutral actinide compounds $[M(Cp^*)_2(NR_2)_2]$ and $[M(Cp^*)_2(NR_2)(Cl)]$ (M = Th, U; R = Me, Et) [16].

2.4. Characterization of the compounds: X-ray crystal structure of a THF solvate of $[U(Cp^*)_2(NMe_2)(CN^tBu)_2][BPh_4]$

The new complexes **1–7** have been characterized by their IR and ^1H NMR spectra (Table 1), their elemental

analyses (Table 2) and, in the case of $[(Cp^*)_2U(O(CH_2)_4NMe_2(CH_2)_4O)]\|BPh_4\|$ ·pyridine [13] and $[U(Cp^*)_2(NMe_2)(CN^tBu)_2][BPh_4]$ · THF, by their X-ray crystal structure.

The infra-red spectrum of **4** exhibits a strong band at 2181 cm^{-1} which corresponds to the CN stretching vibration. This frequency, which is similar to that of 2190 cm^{-1} in the triscyclopentadienyl uranium cation $[U(\eta\text{-}C_5H_5)_3(CNC_6H_{11})(NCMe)]^+$ [17], is higher than in free ^tBuNC (2136 cm^{-1}) and suggests a major resonance contribution of hybrid C in the structure of **4**; this point has been confirmed by the X-ray diffraction analysis (vide infra). The increase of $\nu(CN)$ upon coordination is more important in these cationic uranium(IV) complexes than in the trivalent derivatives $[U(\eta\text{-}C_5H_4SiMe_3)_3(CNEt)]$ (9 cm^{-1}) [18] and $[U(\eta\text{-}C_5H_5)_3(CNC_6H_{11})]$ (25 cm^{-1}) [19], in agreement with
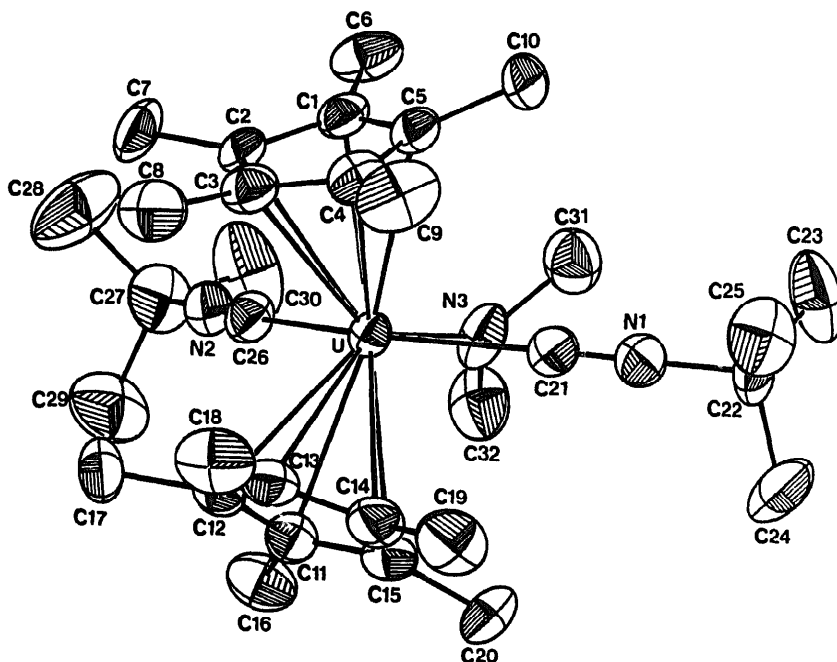

Fig. 1. ORTEP drawing of the cation $[U(Cp^*)_2(NMe_2)(CN^tBu)_2]^+$.

Table 3

Selected bond distances (Å) and angles (deg) with estimated standard deviations for [U(Cp*)$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$] · THF

U–N(3)	2.22(1)	U–C(21)	2.60(1)	U–C(26)	2.58(1)
U–C(1)	2.74(1)	U–C(2)	2.78(1)	U–C(3)	2.80(1)
U–C(4)	2.76(1)	U–C(5)	2.75(1)	U–C(11)	2.75(1)
U–C(12)	2.76(1)	U–C(13)	2.80(1)	U–C(14)	2.79(1)
U–C(15)	2.77(1)	U–1^a	2.49(1)	U–2^a	2.50(1)
C(21)–N(1)	1.14(1)	C(26)–N(2)	1.16(1)		
1–U–N(3)	115.5(4)	2–U–N(3)	113.6(4)		
1–U–C(21)	96.8(4)	2–U–C(21)	94.7(4)		
1–U–C(26)	94.4(4)	2–U–C(26)	96.8(4)		
1–U–2	130.9(4)	N(3)–U–C(21)	76.8(4)		
N(3)–U–C(26)	75.8(4)	C(21)–U–C(26)	152.5(4)		
U–C(21)–N(1)	169.7(6)	U–C(26)–N(2)	171.3(6)		
C(21)–N(1)–C(22)	179(1)	C(26)–N(2)–C(27)	178(1)		

^{a} 1 and 2 are the centroids of the C(1)–C(5) and C(11)–C(15) rings.

the more pronounced π acid character of the U(IV) centre.

$$[U]-C \equiv N^+ -^t Bu \leftrightarrow [U]^- \; :C=N-^t Bu$$
$$\quad C \qquad\qquad\qquad\qquad D$$

The crystals of the THF solvate of 4 are composed of discrete cation–anion pairs. The BPh$_4$ anion displays the expected geometry; an ORTEP drawing [20] of the cation is shown in Fig. 1 and selected bond distances and angles are listed in Table 3. The cation of 4 adopts the classical bent sandwich structure of [M(η-C$_5$R$_5$)$_2$(X)$_2$(Y)] compounds. The arrangement of the amide and two isocyanide ligands in the equatorial girdle is symmetrical, as observed in [U(η-C$_5$H$_5$)$_2$(NEt$_2$)(THF)$_2$]$^+$ [3] but in contrast to that found in the thorium alkyl compound [Th(Cp*)$_2$(Me)(THF)$_2$][BPh$_4$] [21]. The U, N(3), C(21) and C(26) atoms are coplanar within ±0.01 Å and this plane is almost perpendicular [88.7(3)°] to that defined by U, N(3) and the two centroids of the Cp* rings (±0.01 Å). The C(21)–U–C(26) angle [152.5(4)°] is similar to the Cl–U–Cl angle [151.0(1)°] in [U(Cp*)$_2$(Cl)$_2$(HNPPh$_3$)] [22]. The uranium–nitrogen distance [2.22(1) Å] is in the range of U–N bond lengths for terminally coordinated amide ligands and the geometry of the UNC$_2$ fragment is planar; these structural parameters are indicative of a π-interaction between U and N atoms. The U–C(isocyanide) bond distances, which are equal to 2.58(1) and 2.60(1) Å, may be compared with that of 2.57(3) Å in the uranium(III) complex [U(η-C$_5$H$_4$SiMe$_3$)$_3$(CNEt)] [18]. The linear arrangement of the isocyanide groups and the short C–N(^{t}Bu) bond distances [1.14(1) and 1.16(1) Å] confirm the deductions drawn from the IR studies.

In the IR spectrum of 5, no absorption corresponding to free or coordinated MeCN was visible in the 2000–2500 cm^{-1} region and the strong band at 1538 cm^{-1} was assigned to ν(CN) of the NC(Me)(NMe$_2$) ligand [4]. The rotation about the C–NMe$_2$ bond is slow on the

NMR scale, as shown by the two magnetically non-equivalent methyl groups; this restricted rotation can be explained by multiple CN bonding in hybrid F.

The strong band at 1566 cm^{-1} in the IR spectrum of 7 was attributed to the CO stretching vibration; this low ν(CO), which is comparable to those in the compounds [M(Cp*)$_2$(η^2-CONMe$_2$)(X)] (X = Cl, NR$_2$ or CONR$_2$) [16], is characteristic of the η^2-coordinated carbamoyl ligand. Since the THF ligand in 7 is labile and rapidly exchanging with the deuterated solvent, the observation of two magnetically non-equivalent Me groups in the NMR spectrum can be explained by the restricted rotation about the CN bond and therefore the significant contribution of hybrid I in the structure of 7.

3. Experimental details

3.1. General methods

All preparations and reactions were carried out under argon (less than 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove

box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuterated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The IR spectra were recorded in KBr plates on a Perkin–Elmer 1725X spectrometer. The ^{1}H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0).

The commercial reagents were dried by standard methods before use. Compounds **1** [3] and [U(Cp*)(NMe$_2$)$_3$] [10] were synthesized by published methods.

3.2. Synthesis of [(Cp*)$_2$U(O(CH$_2$)$_4$NMe$_2$(CH$_2$)$_4$O)][BPh$_4$] ·0.5THF **2**

Complex **1** was prepared as described in Ref. [3], from [U(Cp*)$_2$(NMe$_2$)$_2$] (303 mg, 0.51 mmol) and NEt$_3$HBPh$_4$ (206 mg, 0.49 mmol) in THF (20 ml) but the reaction mixture was stirred at 20 °C for 4 days. After filtration at −60 °C, the yellow microcrystalline powder of **2** was washed with diethyl ether (15 ml) and dried under vacuum (80 mg, 16%).

3.3. Reaction of **1** with ^{i}PrOH

An NMR tube was charged with **1** (7.8 mg, 8 μmol) in THF-d_8 (0.35 ml) and ^{i}PrOH (0.6 μl, 8 μmol) was introduced via a microsyringe. After 30 min at 20 °C, the spectrum of the orange solution showed that **1** was partially transformed into [U(Cp*)$_2$(O^{i}Pr)$_2$] (46%) and [U(Cp*)$_2$(O^{i}Pr)(THF-d_8)][BPh$_4$] (6%); δ 73.4 (1 H, CH), 7.02 (6 H, d, J = 6 Hz, Me) and 6.22 (30 H, Cp*). After addition of a second equivalent of ^{i}PrOH, the spectrum showed that **1** was completely transformed into [U(Cp*)$_2$(O^{i}Pr)$_2$]. This bisalkoxide complex was prepared by reaction of [U(Cp*)$_2$(Cl)$_2$] with NaO^{i}Pr or by treatment of [U(Cp*)$_2$(BH$_4$)$_2$] with ^{i}PrOH [14].

3.4. Synthesis of [U(Cp*)(OEt)$_2$(THF)$_2$][BPh$_4$] **3**

A 50 ml round-bottomed flask was charged with [U(Cp*)(NMe$_2$)$_3$] (155 mg, 0.31 mmol) and NEt$_3$HBPh$_4$ (122 mg, 0.30 mmol) and THF (20 ml) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 30 min at 20 °C and EtOH (35 μl, 0.60 mmol) was introduced via a microsyringe. After 90 min, the pale green solution was filtered and its volume reduced to 5 ml by evaporation. The pale green powder of **3** which precipitated upon addition of diethyl ether (20 ml) was filtered off, washed with diethyl ether (10 ml) and dried under vacuum (220 mg, 82%).

3.5. Synthesis of [U(Cp*)$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$] **4**

A 50 ml round-bottomed flask was charged with **1** (253 mg, 0.27 mmol) in THF (20 ml) and ^{t}BuNC (60 μl, 0.53 mmol) was introduced via a microsyringe. The reaction mixture was stirred at 20 °C for 30 min and after filtration, the volume of the orange solution was reduced to 10 ml by evaporation. The orange microcrystalline powder of **4** which precipitated upon addition of diethyl ether (25 ml) was filtered off and dried under vacuum (222 mg, 80%).

3.6. Synthesis of [U(Cp*)$_2$(NC{Me}{NMe$_2$})(THF)]-[BPh$_4$] **5**

A 50 ml round-bottomed flask was charged with **1** (183 mg, 0.19 mmol) in THF (20 ml) and MeCN (10.5 μl, 0.20 mmol) was introduced via a microsyringe. The reaction mixture was stirred at 20 °C for 1 h and

Table 4
Crystallographic data and details for [U(Cp*)$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$]·THF

Crystal data	
Formula	C$_{60}$H$_{82}$BN$_3$OU
M	1110.18
Crystal dimensions (mm^3)	0.60×0.40×0.20
Colour	orange
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.564(3)
b (Å)	14.724(4)
c (Å)	15.966(5)
α (deg)	100.65(2)
β (deg)	103.68(2)
γ (deg)	90.13(2)
V (Å^3)	2817(3)
Z	2
d_{calc} (g cm^{-3})	1.309
μ(Mo Kα) (cm^{-1})	27.691
F(000)	1136
Data collection	
Temperature (K)	294
θ limits (deg)	1, 20
Scan type	ω, 2θ
Scan width	0.8 + 0.35 tan θ
Range of abs. trans.	0.695, 0.999
Range of h, k, l	−12 to 12, 0 to 14, −15 to 15
Reflections collected	
Total	5748
Unique	5244
With $I > 3\sigma(I)$	4333
Number of parameters	550
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.068
$R_w = [\Sigma w\|\|F_o\|-\|F_c\|\|^2/ \Sigma w(\|F_o\|)^2]^{1/2}$	0.049
Max. residual electron density (e Å^{-3})	0.793

Table 5

Fractional atomic coordinates, thermal parameters and their estimated standard deviations for [U(Cp *)$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$]·THF

Atom	x	y	z	B_{eq}^*
U	0.04451(4)	0.22610(3)	0.23836(3)	3.994(9)
O	0.394	0.720	0.504	15.0
N(1)	−0.1626(8)	0.3522(6)	0.1010(6)	6.0(3)
N(2)	0.2635(8)	0.0551(7)	0.2436(6)	5.7(3)
N(3)	0.0585(9)	0.1806(7)	0.1013(6)	6.7(3)
C(1)	−0.0695(9)	0.0651(7)	0.2318(7)	5.0(3)
C(2)	−0.0087(9)	0.0869(8)	0.3200(7)	5.3(3)
C(3)	−0.050(1)	0.1668(8)	0.3628(7)	5.9(3)
C(4)	−0.1372(9)	0.1958(8)	0.3006(8)	5.8(3)
C(5)	−0.1514(9)	0.1326(8)	0.2207(7)	5.1(3)
C(6)	−0.060(1)	−0.0220(8)	0.1666(8)	6.9(3)
C(7)	0.073(1)	0.0244(9)	0.3668(8)	7.8(4)
C(8)	−0.021(1)	0.198(1)	0.4630(8)	9.2(4)
C(9)	−0.214(1)	0.272(1)	0.322(1)	9.4(4)
C(10)	−0.252(1)	0.125(1)	0.1432(9)	7.7(4)
C(11)	0.2388(9)	0.3304(8)	0.2924(7)	5.3(3)
C(12)	0.209(1)	0.3228(8)	0.3719(8)	5.8(3)
C(13)	0.116(1)	0.3759(8)	0.3776(8)	6.0(3)
C(14)	0.088(1)	0.4158(8)	0.3021(9)	6.7(4)
C(15)	0.164(1)	0.3879(8)	0.2491(8)	5.4(4)
C(16)	0.347(1)	0.299(1)	0.2698(9)	7.6(4)
C(17)	0.275(1)	0.2764(9)	0.4443(8)	7.4(4)
C(18)	0.073(1)	0.404(1)	0.4599(9)	8.9(4)
C(19)	0.002(1)	0.4898(9)	0.290(1)	9.7(5)
C(20)	0.168(1)	0.423(1)	0.1650(9)	9.4(4)
C(21)	−0.1043(9)	0.3174(8)	0.1499(7)	5.4(3)
C(22)	−0.238(1)	0.3962(9)	0.0353(8)	6.7(4)
C(23)	−0.277(1)	0.320(1)	−0.046(1)	10.8(5)
C(24)	−0.169(1)	0.473(1)	0.019(1)	11.2(5)
C(25)	−0.331(1)	0.432(1)	0.077(1)	9.2(5)
C(26)	0.1979(9)	0.1093(8)	0.2499(7)	5.3(3)
C(27)	0.347(1)	−0.0139(9)	0.232(1)	7.7(4)
C(28)	0.335(1)	−0.085(1)	0.287(1)	13.0(6)
C(29)	0.458(1)	0.039(1)	0.266(1)	10.5(6)
C(30)	0.324(1)	−0.053(1)	0.134(1)	11.9(6)
C(31)	−0.037(1)	0.143(1)	0.0293(9)	7.4(4)
C(32)	0.159(1)	0.177(1)	0.0677(9)	8.5(4)
C(33)	0.3010(9)	0.1587(7)	0.6943(7)	4.8(3)
C(34)	0.246(1)	0.0709(8)	0.6801(8)	5.9(3)
C(35)	0.257(1)	−0.0021(9)	0.6140(9)	6.5(4)
C(36)	0.322(1)	0.0087(9)	0.5559(8)	6.6(4)
C(37)	0.377(1)	0.0950(9)	0.5684(8)	6.5(3)
C(38)	0.366(9)	0.1684(8)	0.6359(7)	5.5(3)
C(39)	0.3349(9)	0.3400(7)	0.7564(7)	4.9(3)
C(40)	0.266(1)	0.3947(8)	0.7046(7)	5.8(3)
C(41)	0.309(1)	0.4749(8)	0.6844(8)	6.9(4)
C(42)	0.420(1)	0.5017(9)	0.7188(9)	8.2(4)
C(43)	0.488(1)	0.449(1)	0.769(1)	8.3(4)
C(44)	0.445(1)	0.3682(9)	0.7882(9)	7.1(4)
C(45)	0.3530(9)	0.2234(8)	0.8713(7)	5.3(3)
C(46)	0.379(1)	0.2966(9)	0.9453(8)	6.4(4)
C(47)	0.425(1)	0.282(1)	1.0303(8)	7.8(4)
C(48)	0.449(1)	0.191(1)	1.0426(9)	8.9(4)
C(49)	0.424(1)	0.117(1)	0.9719(9)	8.3(4)
C(50)	0.3763(9)	0.1334(9)	0.8863(8)	6.7(3)
C(51)	0.1554(9)	0.2510(7)	0.7737(7)	4.5(3)
C(52)	0.074(1)	0.2295(8)	0.6953(8)	6.1(3)
C(53)	−0.039(1)	0.2414(9)	0.6928(9)	7.1(4)
C(54)	−0.070(1)	0.2745(8)	0.7714(9)	6.9(4)
C(55)	0.009(1)	0.2957(9)	0.8497(8)	6.9(4)
C(56)	0.120(1)	0.2837(8)	0.8503(7)	5.7(3)
C(57)	0.405	0.628	0.527	15.0

Table 5 (continued)

Atom	x	y	z	B_{eq}^*
C(58)	0.336	0.569	0.456	15.0
C(59)	0.317	0.609	0.387	15.0
C(60)	0.341	0.711	0.415	15.0
B	0.286(1)	0.2413(9)	0.7732(8)	4.8(3)

* $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

after filtration, the volume of the red–orange solution was reduced to 10 ml by evaporation. The red–orange microcrystalline powder of **5** which precipitated upon addition of diethyl ether (25 ml) was filtered off and dried under vacuum (150 mg, 84%).

3.7. Synthesis of [U(Cp*)$_2$(O$_2$CNMe$_2$)(THF)][BPh$_4$] 6

A 50 ml round-bottomed flask was charged with **1** (123 mg, 0.13 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum; the flask was pressurised with CO$_2$ (1 atm). The reaction mixture was stirred for 2 h at room temperature and after filtration, the volume of the bright red solution was reduced to 10 ml by evaporation. The red microcrystalline powder of **6** which precipitated upon addition of diethyl ether (25 ml) was filtered off and dried under vacuum (105 mg, 82%).

3.8. Synthesis of [U(Cp*)$_2$(η^2-CONMe$_2$)(THF)][BPh$_4$] 7

A 50 ml round-bottomed flask was charged with **1** (189 mg, 0.20 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum; the flask was pressurised with CO (1 atm). The reaction mixture was stirred for 72 h at room temperature and after filtration, the volume of the bright red solution was reduced to 10 ml by evaporation. The red microcrystalline powder of **7** which precipitated upon addition of diethyl ether (25 ml) was filtered off and dried under vacuum (140 mg, 72%).

3.9. X-ray crystal structure of [U(Cp*)$_2$(NMe$_2$)(CN^{t}Bu)$_2$][BPh$_4$]·THF

Crystals of a THF solvate of **4** were obtained by slow diffusion of pentane into a THF solution of **4**. A selected single crystal was introduced into a thin-walled Lindeman glass tube in the glove box. Data were collected at 21 °C on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator [λ(Mo Kα) = 0.70073 Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour; a decay was observed (2.7% in 75 h) and linearly corrected. The data

were corrected for Lorentz polarization effects and absorption [23]. The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F with anisotropic thermal parameters. A THF molecule, found in the last Fourier difference, was introduced at fixed positions; H atoms were not introduced. All calculations were performed on a Vax 4200 computer with the Enraf–Nonius MolEN system [24]. Analytical scattering factors for neutral atoms [25] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data are given in Table 4 and final positional parameters in Table 5.

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