Journal of Organometallic Chemistry, 445 (1993) 99–106

JOM 23108

Synthesis, structure and oxidative addition reactions of triscyclopentadienyluranium(III) nitrile complexes

Raymond Adam [a], Claude Villiers [a], Michel Ephritikhine [a], Monique Lance [b], Martine Nierlich [b] and Julien Vigner [b]

[a] *Laboratoire de Chimie de l'Uranium and* [b] *Laboratoire de Cristallochimie, Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA CE Saclay, F-91191 Gif sur Yvette (France)*

(Received July 2, 1992)

Abstract

The U^{III} nitrile complexes [U(cp)$_3$(NCR)] (cp = η-C_5H_5; R = Me, ^{n}Pr, ^{i}Pr or ^{t}Bu) have been prepared by treatment of [U(cp)$_3$(THF)] (THF, tetrahydrofuran) with the corresponding nitrile; the crystal structures of [U(cp)$_3$(NC^{n}Pr)] and [U(cp)$_3$(NC^{i}Pr)] have been determined. Reaction of [U(cp)$_3$(THF)] with benzonitrile at room temperature or thermolysis of the adducts [U(cp)$_3$(NCR)] (R = Me or ^{n}Pr) afforded an equimolar mixture of the U^{IV} compounds [U(cp)$_3$(CN)] and [U(cp)$_3$(R)] (R = Me, ^{n}Pr or Ph).

1. Introduction

Alkyl and aryl nitriles frequently form adducts with transition metal complexes and their reactions, such as hydrolysis or reduction, are greatly accelerated in the coordination sphere of the metal centre [1]. However, there are a few examples of organometallic or inorganic compounds which have been obtained by electron transfer from low valent metal species to a nitrile molecule. These are limited to the products of the reactions depicted by eqns. (1)–(3):

$$[M(L)_n] + RCN \longrightarrow [M(L)_2(R)(CN)] \quad (1)$$

(L = tertiary phosphine; M = Ni, Pd or Pt;
R = Me, Ph or C_6H_4F [2,3])

$$2[M](NCR) \longrightarrow [M]\text{–}N{=}C(R)\text{–}C(R){=}N\text{–}[M] \quad (2)$$

([M] = Ti(cp)$_2$Cl and R = CH$_2$Ph [4];
[M] = Ti(cp)$_2$(*o*-MeC$_6$H$_4$) and
R = Me, Ph or *o*-MeC$_6$H$_4$ [5])

$$2[M](NCMe) \longrightarrow [M]{=}N\text{–}C(Me){=}C(Me)\text{–}N{=}[M] \quad (3)$$

([M] = TaCl$_3$(NCMe)$_2$ or NbCl$_4$(NCMe)$^-$ [6])

The cyanoalkyl or cyanoaryl compounds of eqn. (1) have been prepared by oxidative addition of RCN to the [M^0(L)$_2$] moiety [2,3], whereas the imino or nitrene derivatives of eqns. (2) or (3) result from reductive coupling of two coordinated nitrile molecules [4–6].

Here we report the preparation and characterization of the compounds [U(cp)$_3$(NCR)] (cp = η-C_5H_5; R = Me, ^{n}Pr, ^{i}Pr or ^{t}Bu) and present the crystal structures of the two butyronitrile derivatives. These adducts were transformed at higher temperature into a mixture of the U^{IV} complexes [U(cp)$_3$(R)] and [U(cp)$_3$(CN)] and we describe the nature of these reactions.

2. Results and discussion

2.1. *Synthesis of the complexes [U(cp)$_3$(NCR)] (R ≡ Me, ^{n}Pr, ^{i}Pr or ^{t}Bu)*

The trivalent uranium(III) complex [U(cp)$_3$(THF)] (**1**) (THF, tetrahydrofuran) has already been used to prepare a series of Lewis base adducts [U(cp)$_3$(L)] [7a]; the organouranium(III) nitrile complexes [U(C$_5$H$_4$R)$_3$-(NCEt)] (R ≡ Me or SiMe$_3$) were obtained by treating the corresponding triscyclopentadienyluranium with propionitrile [7b]. The THF ligand of **1** was readily displaced by RCN in toluene, leading to the formation of the compounds [U(cp)$_3$(NCR)] (**2a**, R = Me; **2b**, R = ^{n}Pr; **2c**, R = ^{i}Pr; **2d**, R = ^{t}Bu); after filtration and evaporation of the solution, these compounds were isolated as red microcrystals in about 70% yield. A

Correspondence to: M. Ephritikhine.

0022-328X/93/$6.00

slight excess of nitrile (about 5 equiv.) was necessary to shift the equilibrium depicted by eqn. (4); the nitrile ligand of 2 was also found to exchange easily with free RCN, but the formation of a 1:2 adduct [U(cp)$_3$(NCR)$_2$] was not observed.

$$[\mathrm{U(cp)_3(THF)}] + \mathrm{RCN} \rightleftarrows [\mathrm{U(cp)_3(NCR)}] + \mathrm{THF} \qquad (4)$$

(1) (**2a**, R = Me; **2b**, R = ^{n}Pr; **2c**, R = ^{i}Pr; **2d**, R = ^{t}Bu)

The compounds [U(C$_5$H$_4$Me)$_3$(NCR)] (R = Me or ^{n}Pr) were similarly prepared from [U(C$_5$H$_4$Me)$_3$(THF)]. The benzonitrile adduct [U(cp)$_3$(NCPh)] could not be observed because of its immediate oxidation into a mixture of the U^{IV} complexes [U(cp)$_3$(Ph)] and [U(cp)$_3$(CN)] (see below).

The compounds **2a**–**2d** have been characterized by elemental analyses and ^{1}H nuclear magnetic resonance (NMR) spectra (Table 1); the signals corresponding to the nitrile hydrogen atoms on the α and β positions are at about −45 and −10 ppm respectively, as previously observed for the derivatives [U(C$_5$H$_4$R)$_3$(NCEt)] (R = Me or SiMe$_3$) [7b]. It has also been noted [7b] that the ν(CN) IR absorption band of these triscyclopentadienyluranium(III) nitrile complexes is very weak and its frequency is not significantly different from that of the corresponding free nitrile.

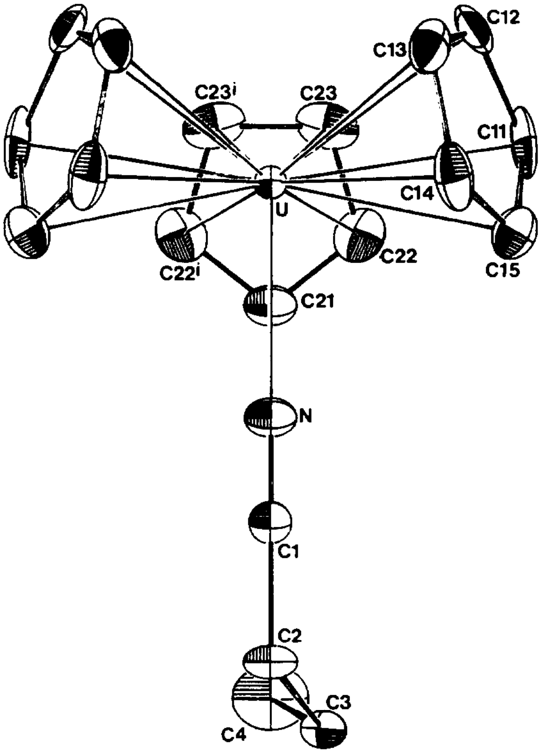


Fig. 1. ORTEP drawing of molecule **2b**. Atoms labelled "i" are related to corresponding unlabelled atoms by a mirror plane.

2.2. *Crystal structures of [U(cp)$_3$(NC^{n}Pr)] and [U(cp)$_3$(NC^{i}Pr)]*

ORTEP drawings [8] of **2b** and **2c** are shown in Figs. 1 and 2 respectively; selected bond lengths and angles

TABLE 1. Analytical and ^{1}H NMR data

Compound	Analyses [a]			NMR data [b]	
	C	H	N	Cp ligand	Nitrile ligand
[(U(cp)$_3$(NCMe)] (**2a**)	42.93 (43.04)	3.85 (3.80)	2.67 (2.95)	−14.32 (15H)	−42.20 (3H, Me)
[U(cp)$_3$(NC^{n}Pr)] (**2b**)	45.16 (45.42)	4.23 (4.38)	2.55 (2.79)	−14.36 (15H)	−44.48 (2H, α-CH$_2$) −9.36 (2H, β-CH$_2$) −7.49 (3H, Me)
[U(cp)$_3$(NC^{i}Pr)] (**2c**)	45.14 (45.42)	4.16 (4.38)	2.51 (2.79)	−14.32 (15H)	−42.09 (1H, CH) −10.78 (6H, Me)
[U(cp)$_3$(NC^{t}Bu)] (**2d**)	46.17 (46.51)	4.44 (4.65)	2.53 (2.71)	−14.19 (15H)	−11.35 (9H, Me)
[U(C$_5$H$_4$Me)$_3$(NCMe)]				−5.99 (6H) −13.54 (9H) −20.45 (6H)	−47.32 (3H, Me)
[U(C$_5$H$_4$Me)$_3$(NC^{n}Pr)]				−5.30 (6H) −12.30 (9H) −19.98 (6H)	−49.17 (3H, α-CH$_2$) −9.50 (2H, β-CH$_2$) −7.71 (2H, Me)

[a] Analytical data given as: found (required) in per cent. [b] At 30°C in toluene-d_8; δ relative to TMS. The signals are singlets with half-height widths between 10 and 30 · Hz, except those of the methylcyclopentadienyl compounds which are broader ($w_{1/2} \approx 70$ Hz).

are listed in Table 2. The two molecules have a similar geometry which is classical for a $[U(cp)_3(L)]$ complex. The three Cp groups and the nitrile ligand form a distorted tetrahedron around uranium. The average U–C distances are 2.81(9) Å in **2b** and 2.76(5) Å in **2c**; the metal–ring centroid distances range from 2.51(1) to 2.58(2) Å and the ring centroid–uranium–ring centroid angles vary from 116.7(4)° to 120.2(4)°. The average ring centroid–metal–nitrogen atom angle is 97(4)° in **2b** and 98(1)° in **2c**. The single uranium–nitrogen bond length is 2.61(1) Å in **2b** and 2.551(9) Å in **2c**; while there are no other U^{III} nitrile complexes with which comparisons can be made, these values fall within the range of all previously determined U–N single-bond lengths [9]. The four atoms U, N, C(1) and C(2) of **2b** lie on a straight line located in the plane of symmetry of the complex; the n-butyl chain does not adopt the usual staggered conformation, the torsional angle C(1)–C(2)–C(3)–C(4) being −55(3)°, and this geometry certainly results from the packing of the molecule. In **2c** the U–N–C(1) angle is equal to 172.1(8)° and is similar to that found in the lanthanide compounds $[Ln(cp)_3(NCEt)]$ (168.3(4)° and 171.0(5)° for Ln = La and Yb respectively [10a]). It is note worthy that the space groups of **2b** (*Pnma*) and **2c** (*P*-1) appear to be the same as for the lanthanide analogues: *P*-1 for $[Ln(cp)_3(NCEt)]$ (Ln = La, Pr or Yb) [10a] and *P*-1 or *Pnma* for the two crystalline forms of $[Sm(cp)_3(NCMe)]$ [10b].

The nitrile molecule is not much affected by coordi-

TABLE 2. Selected bond lengths (Å) and bond angles (°)

$[U(cp)_3(NC^nPr)]$ (2b)					
U environment					
U–N	2.61(1)	U–C(11)	2.79(1)	U–C(12)	2.78(1)
U–C(13)	2.77(1)	U–C(14)	2.783(9)	U–C(15)	2.83(1)
U–C(21)	2.90(2)	U–C(22)	2.85(1)	U–C(23)	2.79(1)
U–1 [a]	2.53(2)	U–2	2.58(2)		
N–U–1	95.5(4)	N–U–2	100.7(4)		
U–N–C(1)	178(1)	1–U–1^{i} [b]	118.6(4)	1–U–2	118.4(4)
Nitrile ligand					
N–C(1)	1.11(1)	C(1)–C(2)	1.43(2)	C(2)–C(3)	1.45(2)
C(3)–C(4)	1.46(3)				
N–C(1)–C(2)	178(1)	C(1)–C(2)–C(3)	115(1)	C(2)–C(3)–C(4)	117(2)
Cp ligand					
⟨C–C⟩	1.38(3)	⟨C–C–C⟩	108(3)		
$[U(cp)_3(NC^iPr)]$ (2c)					
U environment					
U–N	2.551(9)				
U–C(11)	2.811(9)	U–C(21)	2.77(1)	U–C(31)	2.793(8)
U–C(12)	2.79(1)	U–C(22)	2.76(1)	U–C(32)	2.81(1)
U–C(13)	2.76(1)	U–C(23)	2.73(1)	U–C(33)	2.75(1)
U–C(14)	2.73(1)	U–C(24)	2.73(1)	U–C(34)	2.76(1)
U–C(15)	2.79(1)	U–C(25)	2.78(1)	U–C(35)	2.760(9)
U–1 [a]	2.53(1)	U–2	2.51(1)	U–3	2.52(1)
N–U–1	98.4(4)	N–U–2	97.8(3)	N–U–3	97.9(4)
1–U–2	117.3(4)	1–U–3	116.7(4)	2–U–3	120.2(4)
U–N–C(1)	172.1(8)				
Nitrile ligand					
N–C(1)	1.11(1)	C(1)–C(2)	1.49(2)	C(2)–C(3)	1.46(1)
C(2)–C(4)	1.41(1)				
N–C(1)–C(2)	179(1)	C(1)–C(2)–C(3)	110.9(9)	C(1)–C(2)–C(4)	114(1)
C(3)–C(2)–C(4)	120(1)				
Cp ligand					
⟨C–C⟩	1.37(5)	⟨C–C–C⟩	108(5)		

[a] 1, 2, 3 are the centroids of the cyclopentadienyl rings; [b] atom labelled "i" is related to corresponding unlabelled atom by a mirror plane.

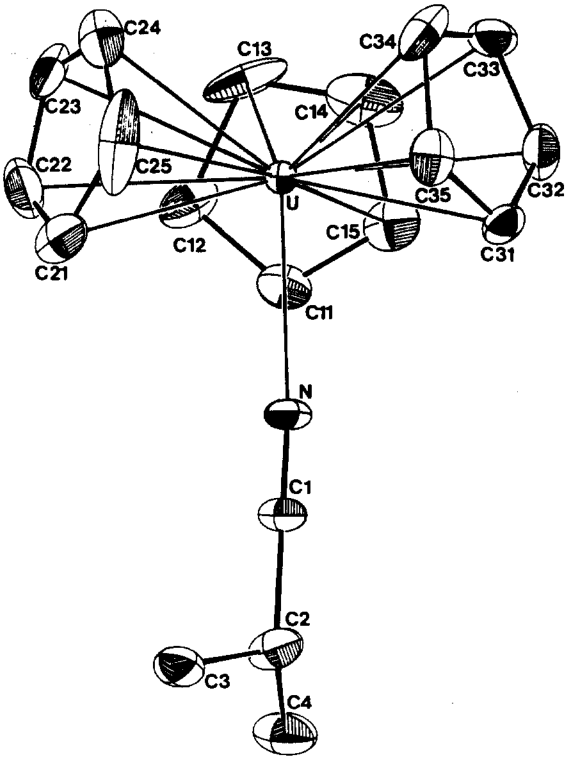


Fig. 2. ORTEP drawing of molecule **2c**.

nation since the C≡N distance is 1.11(1) Å in both compounds (1.158(2) Å in free nitrile [11]). These geometrical parameters confirm that in the complexes **2a**–**2d** the RCN ligand is σ bonded to the $U(cp)_3$ fragment.

2.3. Oxidative addition of RCN to triscyclopentadienyluranium

As we have already noted, the benzonitrile adduct $[U(cp)_3(NCPh)]$ could not be observed. The reaction of $[U(cp)_3(THF)]$ with 2 molar equiv. of PhCN was monitored by NMR spectroscopy. After 30 min at room temperature the spectrum exhibited resonances corresponding to the complex $[U(cp)_3(Ph)]$ in addition to those assigned to free nitrile and free THF; integration of the spectrum showed that the ratios $|U(cp)_3(Ph)|/|THF|$ and $|U(cp)_3(Ph)|/|PhCN|$ are equal to 0.5 and 0.3 respectively. Moreover, green microcrystals were deposited at the bottom of the tube and their IR spectrum revealed a band at 2110 cm^{-1} corresponding to the ν(CN) vibration of $[U(cp)_3(CN)]$; the insolubility of this cyano derivative was explained by its polymeric structure, ensured by bridging CN groups [12]. These results clearly indicate that **1** reacted with 0.5 equiv. of PhCN according to

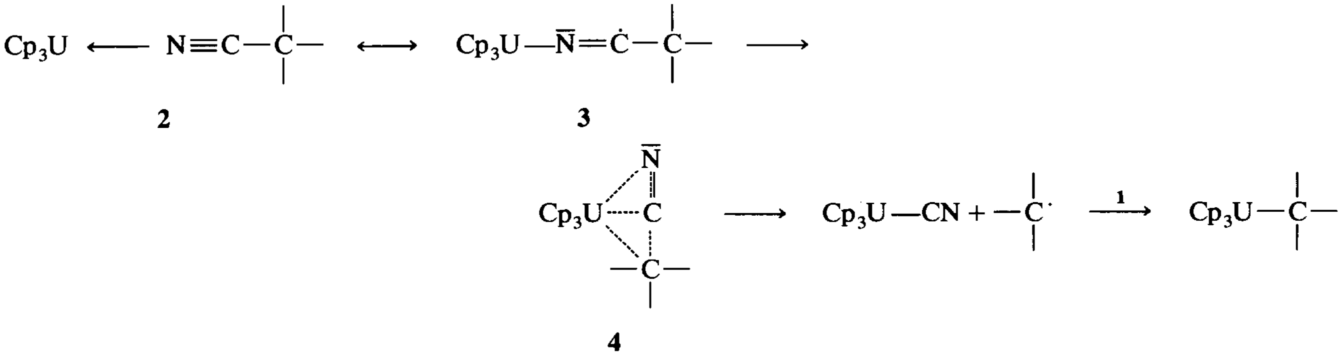
$$2[U(cp)_3(THF)] + PhCN \longrightarrow [U(cp)_3(Ph)] + [U(cp)_3(CN)] + 2\,THF \quad (5)$$

The adduct $[U(cp)_3(NCPh)]$ is certainly an intermediate in reaction (5) and so we examined the thermolysis of the nitrile compounds **2a**–**2d**. After 3 days at 80°C, solutions of the acetonitrile and butyronitrile derivatives **2a** and **2b** deposited green microcrystals of $[U(cp)_3(CN)]$, whereas the NMR spectra showed the formation of the alkyl complexes $[U(cp)_3(R)]$ ($R = Me$ or ^nPr) in about 50% yield and the presence of free nitrile (50% of the initially coordinated RCN). A similar transformation of $[U(C_5H_4Me)_3(NCMe)]$ into $[U(C_5H_4Me)_3(Me)]$ and $[U(C_5H_4Me)_3(CN)]$ was achieved after 3 days at room temperature. The green precipitate of $[U(cp)_3(CN)]$ was also formed by heating the isobutyronitrile and pivalonitrile adducts **2c** and **2d**, but the corresponding alkyl complexes $[U(cp)_3(^iPr)]$ and $[U(cp)_3(^tBu)]$ were not observed; under such thermal conditions these decompose into unidentified products [13].

The nitrile compounds $[U(cp)_3(NCR)]$ are therefore oxidized according to

$$2[U(cp)_3(NCR)] \longrightarrow [U(cp)_3(R)] + [U(cp)_3(CN)] + RCN \quad (6)$$

($R = Me$, ^nPr or Ph)



2

3

4

Schema 1. Postulated mechanism for the oxidative addition of RCN to $U(cp)_3$.

The order of reactivity of RCN (PhCN > MeCN) is opposite to that invariably encountered for the oxidative addition of organic halides to transition metal complexes, and in particular for the reaction of RX with [U(cp)$_3$(THF)], which gave a mixture of [U(cp)$_3$(R)] and [U(cp)$_3$(X)] (R = primary or secondary alkyl or Ph; X = halogen) [14]. It seems likely that **3**, which is a canonical form of the adduct **2** (Scheme 1), plays an important role in reaction (6). The metallic centre in **3** is in the 4+ oxidation state as a result of electron transfer from the trivalent species U(cp)$_3$ to the RCN ligand, and this electron transfer should be straightforward in the case of the benzonitrile molecule, which is much more easily reduced than the alkyl nitriles [15]. This reduction of the nitrile ligand would also be made easier by increasing the electron density on the metal, and the electron-richer adduct [U(C$_5$H$_4$Me)$_3$(NCMe)] was found to be more reactive than [U(cp)$_3$(NCMe)].

On the other hand, Turco and coworkers have noted the distinct behaviour of nitriles and organic halides in their oxidative addition to Ni^0 complexes [3] as well as the different stabilities of the halogeno and cyano derivatives [Ni(L)$_2$(X)(R)] (X = Cl or CN) towards reductive elimination [16]. These differences have been accounted for by the peculiar bonding properties of the cyanide fragment, which would allow the formation of an easily accessible intermediate or transition state with a π-bonded CN group. Stable complexes with π-coordinated nitrile ligands have been reported and two of these, [Fe$_3$(CO)$_9$(NC^{n}Pr)] [17] and [{Ni(PPh$_3$)(NCPh)}$_4$] [18], have been characterized crystallographically. The involvement of such an intermediate or transition state **4** in reaction (6) could explain how the nitrile adduct [U(cp)$_3$(NCR)] is transformed into the cyano derivative [U(cp)$_3$(CN)]. After cleavage of the R–CN bond, the radical R$^\cdot$ should be trapped by U(cp)$_3$, as it is captured during the reaction of **1** with organic halides, which was shown to proceed by a halogen atom abstraction oxidative addition mechanism [14]. It is noteworthy that during the transformation **2** → **4** the metal complex is formally oxidized by two units. Uranium compounds in the 5+ oxidation state, although not common, are well known; in particular, the triscyclopentadienyluranium(V) imide complexes [U(cp)$_3$(NR)] have been isolated [19] and the U$^\text{V}$ intermediates [U(cp)$_3$(R)(R')] were postulated to account for the distribution of the products [U(cp)$_3$(R)] and [U(cp)$_3$(R')] obtained by oxidation of [U(cp)$_3$(R)]$^-$ by a variety of alkyl halides R'X [20]. However, if these considerations are justified, the reaction of titanium(III) nitrile compounds would follow a different route from that depicted by eqn. (6), since a Ti$^\text{V}$ species analogous to **4** is not attainable. In fact, the adducts [Ti](NCR) afford the complexes [Ti]–N=C(R)–C(R)=N–[Ti] ([Ti] = Ti(cp)$_2$X) via coupling of the species [Ti]–N=C–R, and breaking of the R–CN bond was not observed [4,5,21*].

3. Experimental details

3.1. General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (Germany). IR spectra were recorded in Nujol mulls on a Perkin-Elmer 782 instrument and ^{1}H NMR spectra on a Bruker W 60 (FT) spectrometer. Deuterated solvents were dried over Na–K alloy. The chemical shifts are relative to tetramethylsilane ($\delta = 0$). ^{1}H NMR spectra and analytical data are given in Table 1.

All experiments were carried out under argon (less than 5 ppm O$_2$ and water) in Schlenk-type glassware on a high vacuum line or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and were distilled immediately before use. The nitriles (Fluka or Prolabo) were distilled over P$_2$O$_5$. [U(cp)$_3$(THF)] [22] and [U(C$_5$H$_4$Me)$_3$(Cl)] [23] were prepared by published methods; [U(C$_5$H$_4$Me)$_3$(THF)] [24] was synthesized in a manner similar to that of **1** by Na(Hg) reduction of [U(C$_5$H$_4$Me)$_3$(Cl)].

3.2. Synthesis of the nitrile compounds [U(cp)$_3$(NCR)] (2a–2d)

[U(cp)$_3$(NCMe)] (2a)

A 50 ml round-bottomed flask was charged with **1** (170 mg, 0.34 mmol) and toluene (20 ml) was condensed into it under vacuum at −78°C. Acetonitrile (176 μl, 3.4 mmol) was introduced via a gas-tight microsyringe into the solution at 20°C. The mixture was stirred for 10 min and after filtration the solvent was evaporated off, leaving a red powder of **2a** (100 mg, 63%).

[U(cp)$_3$(NC^{n}Pr)] (2b), [U(cp)$_3$(NC^{i}Pr)] (2c) and [U(cp)$_3$(NC^{t}Bu)] (2d)

These complexes were prepared as described for **2a**. Reaction of **1** (202 mg, 0.40 mmol) with ^{n}PrCN (174 μl, 2.0 mmol) gave **2b** (141 mg, 70%); reaction of **1** (170 mg, 0.34 mmol) with ^{i}PrCN (154 μl, 1.70 mmol) gave **2c** (135 mg, 80%) and treatment of **1** (114 mg, 0.23 mmol) with ^{t}BuCN (122 μl, 1.42 mmol) afforded **2d** (80 mg, 69%).

---

* Reference number with asterisk indicates a note in the list of references.

[U(C_5H_4Me)$_3$(NCMe)] and [U(C_5H_4Me)$_3$(NC^{n}Pr)]

These compounds were prepared as described for **2a**, using [U(C_5H_4Me)$_3$(THF)] instead of **1**. Yields about 70%.

3.3. Reaction of [U(cp)$_3$(THF)] with benzonitrile

An NMR tube was charged with **1** (10 mg) in toluene-d_8 (0.4 ml) and 2 molar equiv. of PhCN (4 μl) was added at room temperature via a gas-tight syringe. The solution turned from brown to red and after 30 min green microcrystals were deposited. The spectrum of the solution showed signals corresponding to [U(cp)$_3$(Ph)] [25], free PhCN and free THF. Integration of the spectrum indicated that $|U(cp)_3(Ph)|/|THF| = 0.5$ and $|U(cp)_3(Ph)|/|PhCN| = 0.3$. The IR spectrum of the green product showed a band at 2110 cm^{-1}.

3.4. Thermolysis of [U(cp)$_3$(NCR)]

In these experiments the alkyl products [U(cp)$_3$(R)] were identified by their ^{1}H NMR spectra, which were identical to those of authentic samples and/or those described in the literature [13].

(a) An NMR tube was charged with **2a** (10 mg) in toluene-d_8 (0.4 ml). After heating at 80°C for 1 day, green microcrystals of [U(cp)$_3$(CN)] were formed on the walls of the tube and the spectrum exhibited signals corresponding to an equimolar mixture of [U(cp)$_3$(Me)] and free MeCN.

(b) Thermolysis of **2b** was conducted as for **2a**. After 1 day at 80°C 80% of **2b** had reacted and after 3 days the reaction was complete. Green microcrystals were deposited and the NMR spectrum of the red solution showed signals corresponding to an equimolar mixture of [U(cp)$_3$^{n}Pr)] and ^{n}PrCN. Another experiment was done in the presence of hexamethylbenzene as internal standard; integration of the spectrum showed that [U(cp)$_3$^{n}Pr)] was formed in about 50% yield.

(c) An NMR tube was charged with **2c** or **2d** (10 mg) in toluene-d_8 (0.4 ml). After heating at 80°C for 4 days, the solution deposited a greenish powder and the spec-

TABLE 3. Crystallographic data and experimental details for compounds **2b** and **2c**

		[U(cp)$_3$(NC^{n}Pr)] (**2b**)	[U(cp)$_3$(NC^{i}Pr)] (**2c**)
Crystal data			
Crystal dimensions (mm)		0.30 × 0.25 × 0.10	0.30 × 0.25 × 0.10
Colour		Red	Red
Crystal system		Orthorhombic	Triclinic
Space group		*Pnma*	*P*-1
a (Å)		8.304(2)	8.422(2)
b (Å)		10.239(2)	10.469(2)
c (Å)		20.624(4)	11.297(2)
α (°)		90	63.07(2)
β (°)		90	88.90(2)
γ (°)		90	85.24(2)
V (Å^3)		1753(1)	884.8(7)
Z		4	2
D_{calc} (g cm^{-3})		1.903	1.886
μ(Mo Kα) (cm^{-1})		87.72	86.93
Data collection			
θ limits (°)		1, 20	1, 20
Scan type		ω–2θ	ω–θ
Scan width		0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
Range absc. trans.		0.568, 1.425	0.879, 1.176
Range	h	−8, 0	−8, 8
	k	0, 20	0, 10
	l	0, 10	−10, 10
Reflections collected	total	1187	1759
	unique	1006	1637
	with $I > 3\sigma(I)$	704	1422
Final values			
	$R(F) = \Sigma \lvert F_o \rvert - \lvert F_c \rvert / \Sigma \lvert F_o \rvert$	0.035	0.022
	$R_w(F) = [\Sigma w \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert^2 / \Sigma w(\lvert F_o \rvert)^2]^{1/2}$	0.046	0.028
	max. residual (e Å^{-3})	< 1	< 1

TABLE 4. Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d.s for compound **2b**

Atom	x	y	z	B (Å^2) [a]
U	0.2221(1)	0.250	0.10022(4)	2.92(2)
N	0.313(2)	0.250	−0.0207(9)	4.8(6)
C(1)	0.348(3)	0.250	−0.073(1)	4.0(6)
C(2)	0.400(4)	0.250	−0.139(1)	5.6(8)
C(3)	0.286(5)	0.305(3)	−0.185(2)	7(1)
C(4)	0.124(3)	0.250	−0.184(2)	10(1)
C(11)	0.240(3)	0.519(2)	0.121(1)	7.7(7)
C(12)	0.292(3)	0.461(2)	0.1798(9)	8.1(6)
C(13)	0.438(3)	0.407(2)	0.167(1)	6.7(6)
C(14)	0.475(2)	0.428(2)	0.103(1)	6.3(5)
C(15)	0.356(2)	0.498(2)	0.075(1)	5.7(5)
C(21)	−0.077(4)	0.250	0.028(2)	7(1)
C(22)	−0.085(3)	0.356(3)	0.069(1)	8.0(7)
C(23)	−0.093(2)	0.318(3)	0.134(1)	8.1(8)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$.

trum exhibited a number of paramagnetic signals which were not assigned.

3.5. Thermolysis of [U(C_5H_4Me)$_3$(NCMe)]

An NMR tube was charged with [U(C_5H_4Me)$_3$(NCMe)] (10 mg) in toluene-d_8 (0.5 ml). After 3 days at 20°C green microcrystals were deposited and the spectrum showed the formation of [U(C_5H_4Me)$_3$(Me)]. The latter was prepared by treating [U(C_5H_4Me)$_3$(Cl)] (10 mg) with LiMe (12.5 μl of a 1.6 M solution in Et_2O) in diethyl ether (0.5 ml). After 2 h the solvent was evaporated off and replaced by THF-d_8. The spectrum of the red solution showed signals corresponding to the methyl compound. δ: (30°C): 7.10 and −9.86 (s, 6H + 6H, CH), −5.08 (s, 9H, C_5H_4Me), −189.6 (s, 3H, U–Me).

TABLE 5. Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d.s for compound **2c**

Atom	x	y	z	B (Å^2) [a]
U	0.17993(3)	0.32924(3)	0.29729(3)	3.374(7)
N	0.227(1)	0.1964(8)	0.5482(7)	5.9(2)
C(1)	0.262(1)	0.147(1)	0.6551(8)	5.7(3)
C(2)	0.312(1)	0.081(1)	0.798(1)	7.9(4)
C(3)	0.434(1)	0.161(1)	0.819(1)	8.7(4)
C(4)	0.184(1)	0.037(1)	0.886(1)	9.8(4)
C(11)	−0.125(1)	0.293(1)	0.407(1)	6.9(3)
C(12)	−0.129(1)	0.433(1)	0.319(1)	8.8(4)
C(13)	−0.121(1)	0.438(1)	0.190(1)	11.3(5)
C(14)	−0.112(1)	0.306(2)	0.211(1)	11.2(5)
C(15)	−0.115(1)	0.215(1)	0.342(1)	8.5(4)
C(21)	0.336(1)	0.511(1)	0.364(1)	9.5(4)
C(22)	0.204(2)	0.585(1)	0.310(1)	10.4(4)
C(23)	0.204(2)	0.619(1)	0.187(1)	9.9(4)
C(24)	0.329(1)	0.573(1)	0.154(1)	8.6(3)
C(25)	0.435(1)	0.494(1)	0.265(2)	14.5(5)
C(31)	0.346(1)	0.0669(9)	0.3482(9)	6.0(3)
C(32)	0.225(1)	0.0751(9)	0.270(1)	8.0(3)
C(33)	0.244(2)	0.182(1)	0.151(1)	10.7(4)
C(34)	0.385(1)	0.244(1)	0.147(1)	11.6(3)
C(35)	0.446(1)	0.1668(9)	0.280(1)	7.2(3)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$.

3.6. X-Ray crystal structure determinations

Crystals of **2b** and **2c** were obtained by slow diffusion of pentane into a toluene solution of the complex. A selected single crystal was introduced into a thin-walled Lindemann glass tube in a glove-box. Data were collected at room temperature on an Enraf–Nonius diffractometer equipped with a graphite monochromator (λ = 0.71073 Å). The cell parameters were obtained by 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 (12% in 15 h for **2b** and 16% in 27 h for **2c**) and was corrected linearly. The data were corrected for Lorentz polarization effects and absorption [26]. The structure was solved by the heavy atom method and refined by full-matrix least squares on F with anisotropic thermal parameters. H atoms of **2c** and H atoms of the Cp ligands of **2b**, introduced at calculated positions (C–H = 0.95 Å, B = 6 Å^2), were not refined but constrained to ride on their C atoms. In **2b** the U atom lies on the mirror plane as do the N, C(1), C(2) and C(4) atoms of the nitrile molecule; C(3) was introduced in refinements with an occupation factor of 0.5. All calculations were performed on a Micro Vax II computer with the Enraf–Nonius MOLEN system [27]. Analytical scattering factors for neutral atoms [28] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3; final position and thermal parameters for **2b** and **2c** are listed in Tables 4 and 5 respectively.

References

1 H. E. Endres, in G. Wilkinson, R. G. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, Chap. 13.7; R. W. Hay, in G. Wilkinson, R. G. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, Vol. 6, Pergamon, Oxford, 1987, Chap. 61.4.

2 D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Pesson and E. L. Muetterties, *J. Am. Chem. Soc.*, *93* (1971) 3543; G. W. Parshall, *J. Am. Chem. Soc.*, *96* (1974) 2360; J. L. Burmeister and L. M. Edwards, *J. Chem. Soc. A*, (1971) 1663.

3 A. Morvillo and A. Turco, *J. Organomet. Chem.*, *208* (1981) 103.

4 F. Rehbaum and K. H. Thiele, *J. Organomet. Chem.*, *410* (1991) 327.

5 E. J. M. De Boer and J. H. Teuben, *J. Organomet. Chem.*, *140* (1977) 41; *153* (1978) 53.

6 F. A. Cotton and W. T. Hall, *J. Am. Chem. Soc.*, *101* (1979) 5094.

7 (a) T. J. Marks and R. D. Ernst, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*,

Vol. 3, Pergamon, Oxford, 1982, Chap. 21; B. E. Bursten, L. F. Rhodes and R. J. Strittmatter, *J. Am. Chem. Soc., 111* (1989) 2756, and references cited therein; (b) J. G. Brennan, *Thesis*, University of California, Berkeley, 1985.

8 C. K. Johnson, ORTEP II, *Rep. ORNL 5138*, 1976 (Oak Ridge National Laboratory, TN).

9 R. E. Cramer, U. Engelhardt, K. T. Higa and J. W. Gilje, *Organometallics, 6* (1987) 41, and references cited therein.

10 (a) M. R. Spirlet, J. Rebizant, C. Apostolidis and B. Kanellakopulos, *Inorg. Chim. Acta, 139* (1987).211; (b) M. Adam, H. Schultze and R. D. Fischer, *J. Organomet. Chem., 429* (1992) C1.

11 *Handbook of Chemistry and Physics*, 63rd edn., CRC Press, Boca Raton, 1982, p. F-180.

12 K. W. Bagnall, M. J. Plews, D. Brown, R. D. Fischer, E. Klähne, G. W. Langraf and G. R. Sienel, *J. Chem. Soc., Dalton Trans.*, (1982) 1999.

13 T. J. Marks, A. M. Seyam and J. R. Kolb, *J. Am. Chem. Soc., 95* (1973) 5529.

14 C. Villiers and M. Ephritikhine, *J. Organomet. Chem., 393* (1990) 339.

15 R. F. Muraca, in I. M. Kolthoff and P. J. Elving (eds.), *Treatise on Analytical Chemistry*, Part II, Vol. 16, Section B-2, Wiley, New York, 1980, p. 407; C. K. Mann, in A. J. Bard (ed.), *Electroanalytical Chemistry*, Vol. 3, Dekker, New York, 1969, p. 57.

16 G. Favero, M. Gaddi, A. Morvillo and A. Turco, *J. Organomet. Chem., 149* (1978) 395; G. Favero, A. Morvillo and A. Turco, *J. Organomet. Chem., 162* (1978) 99.

17 M. A. Andrews, C. B. Knobler and H. D. Kaesz, *J. Am. Chem. Soc., 101* (1979) 7260.

18 I. W. Bassi, C. Benedicenti, M. Calcaterra, R. Intrito, G. Rucci and C. Santini, *J. Organomet. Chem., 144* (1978) 223.

19 J. G. Brennan and R. A. Andersen, *J. Am. Chem. Soc., 107* (1985) 514.

20 C. Villiers and M. Ephritikhine, *New J. Chem., 15* (1991) 565.

21 Another mechanism involving the binuclear species $(cp)_3U$–N=C(R)–U$(cp)_3$ has been proposed by the referee. In this case no U^{V} intermediate should be implied and the reaction $[Ti^{III}](NCR) \rightarrow [Ti^{IV}]$–R + $[Ti^{IV}]$–CN should be possible.

22 J. F. Le Maréchal, C. Villiers, P. Charpin, M. Nierlich, M. Lance, J. Vigner and M. Ephritikhine, *J. Organomet. Chem., 379* (1989) 259.

23 A. Dormond, C. Duval-Huet and J. Tirouflet, *J. Organomet. Chem., 209* (1981) 341.

24 J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem., 25* (1986) 1756.

25 G. Brandi, M. Brunelli, G. Lugli and A. Mazzei, *Inorg. Chim. Acta, 7* (1973) 319.

26 N. Walker and D. Stuart, *Acta Crystallogr. A, 39* (1983) 158.

27 MOLEN, An Interactive Structure Solution Procedure, Enraf–Nonius, Delft, 1990.

28 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974 (present distributor: Kluwer, Dordrecht).