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Preparation and selected properties of organouranium(IV) salts of the general type $[(C_5H_5)_3U(NCR)_2][B(C_6H_5)_4]^*$

Hüseyin Aslan, Kenan Yünlü, R. Dieter Fischer

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

Gabriella Bombieri,

Universita' di Milano, Istituto di Chimica Farmaceutica e Tossicologica, Viale Abruzzi 42, I-20131 Milano (Italy)

and Franco Benetollo

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti 4, I-35100 Padova (Italy)

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Abstract

Salts of the type $[Cp_3U(NCR)_2][BPh_4]$ ($Cp = \eta^5-C_5H_5$), $R = CH_3$, **1**; $R = C_2H_5$, **2** or $R = n-C_3H_7$, **3**; $Ph = C_6H_5$) can be prepared either from the aqua salts, $[Cp_3U(OH_2)_2][BPh_4] \cdot xH_2O$, and nitrile in n-hexane, or, better, by a one-pot reaction from Cp_3UCl and $Na[BPh_4]$ in NCR/ H_2O mixtures. The NIR/VIS and the 1H NMR spectra of **1–3** strongly suggest a trigonal bipyramidal (tbp) configuration for the cation. This prediction has been fully confirmed by a single crystal X-ray study of **1**. The U–N(acetonitrile) distance in tbp-configured complexes ranges from 2.57 Å (in **1**) to 2.66 Å in $Cp_3U(NCS)(NCMe)$ (**4**), confirming the previously suggested “*trans* effect” in tbp-systems. The crystal and molecular structure of **4** has been re-examined for a single crystal obtained from a solution of $[N(n-C_4H_9)_4][Cp_3U(NCS)(NCBH_3)]$ in NCMe. The salts **1–3** lose readily BPh_3 (and NCR) when heated (up to $\geq 60^\circ C$) under a high vacuum or when dissolved in common solvents, such as toluene, CH_2Cl_2 , or THF). The ^{13}C NMR shifts of the Cp ring carbon atoms of **1** (δ 145.9 ppm) are another feature of the unusually weakly paramagnetic title compounds.

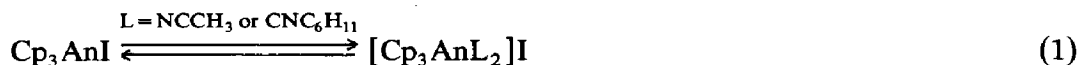
* Some of the results described here were presented at the Second International Conference on the Basic and Applied Chemistry of *f*-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon (Portugal), April 6–10, 1987; Abstract P(II) 8 [4].

Introduction

Although salts containing the cationic organouranium(IV) complexes $[\text{Cp}_3\text{U}(\text{NCR})_2]^+$, most probably having trigonal bipyramidal (tbp) configurations, have been mentioned in the literature ($\text{R} = \text{CH}_3$ [1–4]; $\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$ [2]), no general route to salts $[\text{Cp}_3\text{U}(\text{NCR})_2]\text{X}$ with an optimally stabilizing, metal-free, counter-anion X^- has previously been reported. We describe below three convenient routes to the tetraphenylborate salts. Both NMR and NIR/VIS spectroscopy in solution, and the growing of crystals of the salts suitable for crystallographic studies, were found to be hampered by the fact that some nitriles that serve as the axial ligands in the cationic complexes turn out to be the only suitable solvents. Facile exchange of nitrile ligands is not only inevitable in case of the title complexes, but it has been observed for other anions $[\text{Cp}_3\text{UXY}]^-$. The NCBH_3^- ligand, which is isoelectronic with NCCH_3 , undergoes particularly rapid exchange with NCCH_3 .

Preparation

Bohlander has briefly reported [5] that extremely labile organoactinoid(IV) salts involving tbp-configured cations along with an iodide counter-anion can be produced by the reaction shown in eq. 1, but the corresponding chlorides, Cp_3AnCl , show no tendency for replacement of Cl^- by L . Likewise, the expected salt



(An = U, Th, Np)

$[\text{Cp}_3\text{U}(\text{NCCH}_3)_2][\text{BPh}_4]$ containing the less nucleophilic BPh_4^- anion is not separated out when solutions of Cp_3UCl and $\text{Na}[\text{BPh}_4]$ in NCCH_3 are combined. However, when water is added slowly to the solution, two liquid phases are ultimately formed. The oily heavier layer, which is green, apparently contains all organouranium material in NCCH_3 solution (along with little H_2O), while the lighter, almost colourless layer, is essentially an aqueous solution of NaCl , with a little $\text{Na}[\text{BPh}_4]$ and NCCH_3 . We were unable to make crystalline $[\text{Cp}_3\text{U}(\text{NCCH}_3)_2][\text{BPh}_4]$ by controlled replacement of $\text{L} = \text{water}$ or isocyanide (vide infra), but well-shaped crystals of **1** formed at the phase boundary when the two-phase system was kept overnight at -25°C . The salt **1** was, however, obtained by evaporation of solvent from the pure green phase. Compound **3** was prepared in the same way as **1**, after addition of water to a solution of Cp_3UCl and $\text{Na}[\text{BPh}_4]$ in $\text{NC-n-C}_3\text{H}_7$ two different liquid phases again separated, but in this case the green nitrile layer was lighter than the uncoloured aqueous solution. Single crystals of **3** could not be obtained from this two-phase-system even at lower temperatures.

One alternative route to **1** and **2** (and probably also **3**) is the reaction of the solid salt $[\text{Cp}_3\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot 10\text{H}_2\text{O}$ (**5**) [2] with pure nitrile. A suspension of **5** in n -hexane reacts with nitriles to give non-uniform oily phases, but dissolution of **5** in the pure nitriles results in clear green solutions from which the analytically pure nitrile complexes are obtained after evaporation of the solvent. The nitrile com-

plexes **1** and **3** were prepared similarly from the previously described salt $[\text{Cp}_3\text{U}(\text{CN}-c\text{-C}_6\text{H}_{11})][\text{BPh}_4]$ (**6** ([2]) and RCN in *n*-hexane by (partial) replacement of nitrile by isocyanide [2].

The observations described above show that Cp_3UCl does not dissociate unless an efficient Lewis acid is present. In the absence of a conventional Lewis acids such as AlCl_3 , FeCl_3 , UO_2Cl_2 [6], or even BPh_3 , H_2O can solvate the Cl^- ions and so permit nitrile addition to the lower-coordinate uranium ion. In contrast to an earlier observation [7], no evidence for the formation of the *tbp*-configured adduct $\text{Cp}_3\text{UCl}(\text{NCCH}_3)$ was found.

The three salts **1–3** dissolve readily in anhydrous tetrahydrofuran or methylene chloride to give initially clear, green solutions from which a brown, air-sensitive decomposition product **7** separates after 5–10 minutes. While the elemental analysis of **7** is consistent with the formulation $\text{Cp}_3\text{UC}_6\text{H}_5$ (**8**), **7** is much less soluble than authentic **8** [8], so it cannot be characterized by NMR spectroscopy. Unexpectedly, solid samples of **7** did not display any *f–f* absorption bands in the near infrared and visible (NIR/VIS) spectral range. When suspended in benzene or toluene, salts **1–3** are converted into **7** almost immediately, without giving an intermediate green or brown solution. In all cases of solvent-induced decomposition, significant amounts of BPh_3 can be isolated from the solvent.

Only water- and oxygen-free alkanes are chemically completely inert towards solid **1–3**, yet, suspensions of **1–3** in *n*-hexane have been reported to react quickly with isocyanides to give exclusively the tetraphenylborates of the unexpected mixed-ligand cations $[\text{Cp}_3\text{U}(\text{NCR})(\text{CNR}')]^+$ [2]. Under high vacuum, solid samples of **1–3** decompose slowly above 40°C to give white sublimes of pure BPh_3 and a brownish-green residue. Analytically pure **7** was finally obtained, along with sublimed BPh_3 , from solid **5** at temperatures up to 120°C . Solid **1** remains virtually unaffected outside an inert gas atmosphere for almost 15 minutes, but its solution in CH_3CN immediately darkens when exposed to air. Solid **2** and **3**, however, decompose within some seconds in the air.

So far, only nitriles have turned out to be the satisfactory solvents for the salts **1–3**, although the ^1H NMR spectroscopic results (vide infra) suggest that usually rapid exchange of solvent molecules with the originally coordinated nitriles takes place. Interestingly, when NCCH_3 is present in excess it can even displace the iso-electronic NCBH_3^- anion from the initial anionic *tbp*-systems $[\text{Cp}_3\text{U}(\text{NCBH}_3)\text{X}]^-$. Thus from saturated solutions of the salts $[\text{NBu}_4][\text{Cp}_3\text{U}(\text{NCBH}_3)\text{X}]$ [9] with $\text{X} = \text{NCS}^-$ and NCBH_3^- , respectively, well-shaped crystals of the uncharged *tbp*-complex type $\text{Cp}_3\text{UX}(\text{NCCH}_3)$ are present after several weeks. These observations contrast with the reluctance of Cp_3UCl to react with pure NCCH_3 , but are reminiscent of the ready displacement of a chlorine ligand by NCCH_3 from $(\text{Ind})\text{AnCl}_3(\text{THF})_2$ systems (Ind = indenyl; An = U or Th) [10].

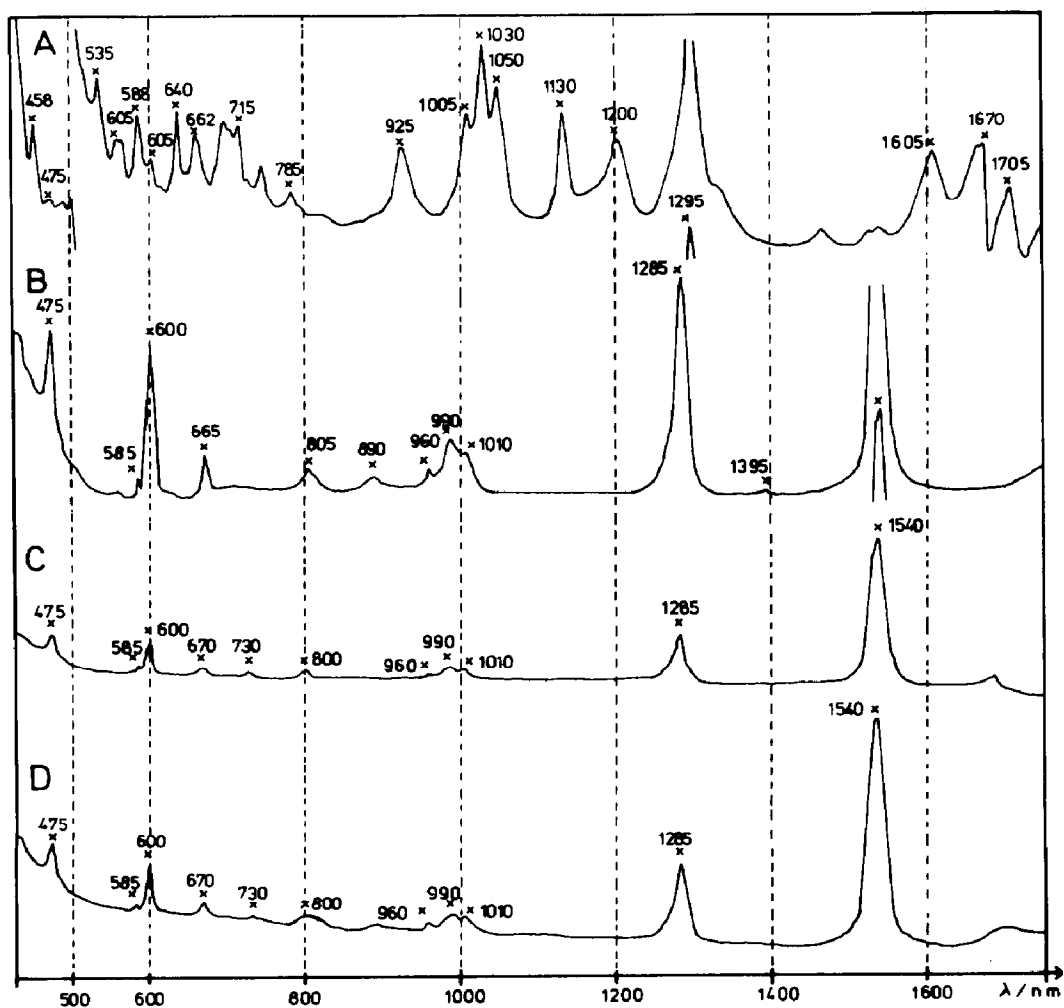
Spectroscopy

The infrared spectrum of **1** shows only one $\nu(\text{CN})$ absorption band (Table 1) the position of which clearly indicates NCCH_3 -coordination, but the IR-spectra of **2** and **3** suggest the presence of some free nitrile in the sample, and indicate significant lability of **2** and **3** even when embedded in KBr or Nujol.

Table 1

Infrared bands in the $\nu(\text{CN})$ region

Compound	$\nu(\text{CN})$ (cm^{-1}) of the complex		$\nu(\text{CN})$ (cm^{-1}) of free nitrile	
	KBr	Nujol		
1	2275 vs (2308 s) ^a		2253.5 s (2293.0) ^a	(NCMe) (NCMe)
2	2265 w 2250 m	2265 s 2240 m	2250 s	(NCEt)
3	2260 s	2270 w 2250 m	2258 s	(NCP ^r)

^a Fermi resonance.Fig. 1. NIR/VIS spectra (for solutions in CH_3CN): A, Cp_3UCl ; B, salt 1; C, salt 3, and D, salt 2.

The NIR/VIS absorption spectra of **1**, **2** and **3** in nitrile solution (Fig. 1) are fully consistent with the *tbp*-configuration [11], while the spectrum of a solution of Cp_3UCl in NCCH_3 shows that the dominant species is pseudotetrahedral Cp_3UCl .

The ^1H NMR spectra of CD_3CN solutions of **1**–**3** show three main features:

(a) The Cp protons give one relatively sharp singlet between -0.1 and -0.5 ppm i.e. at slightly lower fields than those for the Cp proton resonances of $\psi\text{-}T_d$ configured Cp_3UCl ($\text{THF-}d_8$ and CD_3CN , $\delta -2.7$ ppm). Although the resonances of the cationic *tbp*-systems are indicative of paramagnetism in the light of the isotropic shift value, Δ^{iso} , of ca. 6 ppm (diamagnetic reference: Cp_3ThCl), the δ (and Δ^{iso}) values for the Cp protons show practically no change when the temperature is varied in the range $230 \text{ K} < T < 305 \text{ K}$. This finding is consistent with earlier suggestions of a temperature independent paramagnetism for various *tbp*-configured $\text{Cp}_3\text{U}^{\text{IV}}$ derivatives [12].

(b) Whereas the methyl proton resonance of **1** is buried under the multiplet of the solvent, the initially metal-coordinated nitriles of **2** and **3** give clean multiplet patterns coinciding with those of the fully diamagnetic nitrile complexes $[\text{Cp}_2\text{M}(\text{NCR})\text{X}][\text{BPh}_4]$ ($\text{M} = \text{Ti}^{\text{IV}}$ or Zr^{IV} ; $\text{X} = \frac{1}{2}\text{O}$ and OH , respectively, $\text{R} = \text{C}_2\text{H}_5$ and $n\text{-C}_3\text{H}_7$ [13]). It seems reasonable to assume that practically all the initially present nitrile ligands have been replaced by solvent molecules at the paramagnetic centre.

(c) The phenyl protons of the BPh_4^- anion give resonance patterns composed of three close-lying sets of signals that are almost superimposable on those observed previously for the above-mentioned Ti^{IV} and Zr^{IV} complexes [13]. Again there is no evidence of an isotropic shift due to the paramagnetism of the complex.

The ^{13}C NMR spectrum of **1** (solvent: CD_3CN , room temperature) consists of four rather sharp singlets at 122.6, 126.9, 136.5, and 145.9 ppm. The first three signals can be respectively attributed to the ring C(2,6), C(3,5) and C(4) atoms, of the Ph groups in the BPh_4^- anion (e.g. $\text{Na}[\text{BPh}_4]$, δ 125.8, 129.8, 138.8 and 164.8 ppm [14a]), the singlet at 145.9 ppm cannot unambiguously be assigned to the *ipso*-C (C_i) atom of the BPh_4^- anion. This resonance could be expected to be a quartet with $J(^{13}\text{C}\text{-}^{11}\text{B})$ 49 Hz [14], but the influence of the electric quadrupole moment of the ^{11}B nucleus (at room temperature) is likely to lead to an absence of the *ipso*-C quartet at ca. 165 ppm [13,15].

The alternative assignment of the 145.9 ppm signal to the 15 equivalent Cp ring C atoms of the paramagnetic cation would imply a substantial decrease in the isotropic shift $\Delta_{\text{C}}^{\text{iso}}$ from -126 ppm for $\psi\text{-}T_d$ -configured Cp_3UCl [16] to only -27.5 ppm for the *tbp*-configured cation of **1**. Since the two geometry factors G_{C} and G_{H} of the (rapidly rotating) ring C- and H-atoms have the same sign ($G_{\text{C}} = -3.45 \times 10^{22} \text{ cm}^{-3}$; $G_{\text{H}} = -1.01 \times 10^{22} \text{ cm}^{-3}$ [17*]), while the signs of $\Delta_{\text{C}}^{\text{iso}}$ and $\Delta_{\text{H}}^{\text{iso}}$ differ, the isotropic shifts cannot both be exclusively due to magnetic dipolar interactions (i.e. $\Delta^{\text{iso}} \neq \Delta^{\text{dip}}$). If the latter assignment were correct, non-negligible contributions of the contact shift Δ^{con} (due to transfer of free electron spin density from the metal ion on to the ^{13}C - and ^1H -nuclei) to Δ^{iso} would be implied also. The spin transfer within a system with an energetically fairly isolated singlet (i.e. a “nonmagnetic”) ground state (as found for the *tbp*-system in question

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

[12]) can be interpreted theoretically only in terms of a sophisticated second-order treatment [18].

Experimental

All experiments were carried out under pure nitrogen in Schlenk-type glassware. Infrared spectra were recorded on the Perkin-Elmer spectrometers PE 577 and PE 325, NIR/VIS-spectra on a Cary 17I spectrometer, and NMR spectra (^1H or ^{13}C) on the Bruker WP 80 spectrometer.

Preparation of $[\text{Cp}_3\text{U}(\text{NCCH}_3)_2][\text{BPh}_4]$ (1): A clear solution of 1.53 g (4.48 mmol) NaBPh_4 in 30 ml NCCH_3 was added dropwise with stirring to a brown filtered solution of 2.1 g (4.48 mmol) Cp_3UCl in 50 ml NCCH_3 . No precipitation of NaCl took place during overnight stirring. Oxygen-free H_2O was added dropwise without stirring until no further dark-green oily drops separated from the bulk solution ($\text{H}_2\text{O}/\text{NCCH}_3 \approx 10/1$). The dark green homogeneous lower layer was separated from the almost colourless upper one, and the solvent evaporated off. The residue was washed with cold n-hexane and vacuum-dried at room temperature to give analytically pure 1. Yield: 2.68 g (72%). Elemental analysis: Found: C, 61.75; H, 4.88; N, 3.45; B, 1.37; U, 28.39. $\text{C}_{43}\text{H}_{41}\text{N}_2\text{BU}$ ($M = 833.81$) calcd.: C, 61.87; H, 4.95; N, 3.35; B, 1.29; U, 28.50%.

Preparation of $[\text{Cp}_3\text{U}(\text{NCC}_2\text{H}_5)_2][\text{BPh}_4]$ (2): Pure $([\text{Cp}_3\text{U}(\text{H}_2\text{O})_2][\text{BPh}_4] \cdot 10\text{H}_2\text{O})$ (5) or 1 (ca. 2 g) was dissolved in ca. 100 ml of oxygen-free NCC_2H_5 . The solution was filtered and the solvent evaporated off; and the green residue washed with cold n-hexane and vacuum-dried at room temperature to give 2 in practically quantitative yield; NMR: $\delta(^1\text{H})$ (CD_3CN): -0.27 (s, 15H, Cp), 1.30 (t, $J(\text{C}-\text{H})$ 7.2 Hz, 6H, CH_3), 2.34 (q, $J(\text{C}-\text{H})$ 7.2 Hz, 4H, CH_2), 6.87 (t, $J(\text{C}-\text{H})$ 7.2 Hz, 4H, *p*-Ph); 7.00 (t, $J(\text{C}-\text{H})$ 7.2 Hz, 8H, *m*-Ph), and δ 7.22 – 7.27 (m, 8H, *o*-Ph).

Preparation of $[\text{Cp}_3\text{U}(\text{NC-n-C}_3\text{H}_7)_2][\text{BPh}_4]$ (3): The procedure was similar to that for the preparation of 1 (vide supra). Solutions of 1.6 g (3.41 mmol) Cp_3UCl in 40 ml $\text{NC-n-C}_3\text{H}_7$ and 1.2 g (3.41 mmol) of NaBPh_4 in 50 ml of $\text{NC-n-C}_3\text{H}_7$ were mixed, and a total of 900 ml of H_2O was added dropwise to give a clean two-layer system. The green upper layer was separated and the solvent evaporated. The residue was washed with three 50 ml-proportions of n-hexane, and vacuum-dried to give 1.9 g (63%) of 3. Elemental analysis: Found: C, 63.49; H, 5.52; N, 3.17. $\text{C}_{47}\text{H}_{49}\text{N}_2\text{BU}$ ($M = 869.81$) calcd.: C, 63.36; H, 5.50; N, 3.14%.

Preparation of product "Cp₃UPh" (7): Salt 1 (0.4 g) was dissolved in 60 ml of THF. After 5 min brown flakes began to precipitate out. Most of the solute had separated after ca. 2 h, and the brown powder was filtered off, washed with THF until the THF remained colourless, and vacuum-dried at room temperature for 2 h. Elemental analysis: Found: C, 49.5; H, 3.98. $\text{C}_{21}\text{H}_{20}\text{U}$ ($M = 510.42$) calcd.: C, 49.4; H, 3.94%.

X-ray measurements and structure determination

The crystal data and details of the refinement are summarized in Table 2. $\text{Cp}_3\text{U}(\text{NCCH}_3)_2(\text{BPh}_4)$ (1) and $\text{Cp}_3\text{U}(\text{NCS})(\text{NCCH}_3)$ (4) are irregular prisms. They are sensitive to atmospheric moisture and so were placed in thin-walled Lindemann glass capillaries under an inert atmosphere in a glove box. They were centred on a four-circle Philips PW 1100 automated diffractometer with graphite monochro-

Table 2

Summary of crystal data collection

Compound	[Cp ₃ U(NCCH ₃) ₂](BPh ₄) (1)	Cp ₃ U(NCS)(NCCH ₃) (4)
Formula	C ₄₃ H ₄₁ N ₂ BU	C ₁₈ H ₁₈ N ₂ SU
<i>M</i>	834.7	532.4
Crystal colour	brown orange	green
Crystal size (mm)	1.7 × 0.72 × 0.48	0.1 × 0.24 × 0.28
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Crystal system	monoclinic	monoclinic
<i>a</i> (Å)	26.425(3)	11.658(2)
<i>b</i> (Å)	11.662(2)	14.438(3)
<i>c</i> (Å)	11.847(2)	10.198(2)
β (°)	95.2(3)	90.79(5)
<i>U</i> (Å ³)	3635.9	1716.4
<i>Z</i>	4	4
<i>D</i> _c (Mg m ⁻³)	1.52	2.06
<i>F</i> (000)	1640	992
Radiation (λ /Å)	(Mo- <i>K</i> _α (0.7107))	(Mo- <i>K</i> _α (0.7107))
Reflections measured	9555	4543
<i>T</i> (K)	293	293
scan method	$\theta/2 \theta$	$\theta/2 \theta$
scan speed (°/min)	1.80	3.0
scan width (°)	1.50	1.50
Background counts (s)	20	20
2 θ max (°)	56	56
σ -limit ($I > n\sigma(I)$)	<i>n</i> = 3	<i>n</i> = 3
Unique observed reflections ($I > 3\sigma(I)$)	5879	2053
Weighting scheme <i>w</i>	1.0 [$\sigma^2(F_0)$ + 0.003602(F_0) ²] ⁻¹	3.9470 [$\sigma^2(F_0)$ + 0.000221(F_0) ²] ⁻¹
<i>R</i> ($R = \Sigma F_0 - F_c / \Sigma F_0 $)	0.0542	0.0395
<i>R</i> _w ($R_w = \Sigma w^{1/2} (F_0 - F_c) / \Sigma w^{1/2} F_0 $)	0.070	0.0394
μ (Mo- <i>K</i> _α) (cm ⁻¹)	42.80	91.5

mated Mo-*K*_α radiation, the orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystals at random, varying each of the orientation angles θ and χ in the range of 120°, with the detector position varying between 2 θ 12° and 2 θ 18°. For determination of precise lattice parameters 25 strong reflections with 8° < θ < 16° were used.

The intensities of two standard reflections 513 and 821 for **1** and -422 and 33 - 3 for **4** were monitored every 180 minutes. There was no significant fluctuation in intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz and polarization effects and for absorption as described by North et al. [19]. The structure of **1** was solved by use of three-dimensional Patterson and Fourier syntheses and refined by full matrix least-squares with minimization of the function $\Sigma w(\Delta F)^2$, with anisotropic thermal parameters for the non hydrogen atoms except for those of the phenyl groups and isotropic for the remaining non hydrogen atoms. The phenyl rings were refined as rigid groups, and restricted to their normal geometry (*D*_{6h} symmetry, C-C 1.395 Å),

Table 3

Atomic coordinates ($\times 10^4$) and U_{iso} , $U_{\text{eq}}(\text{\AA}^2 \times 10^3)$ with e.s.d.'s in parentheses, ($U_{\text{eq}} = 1/3 \sum_i \Sigma_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$) for **1** and **4**

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}^*$
<i>Compound 1: [Cp₃U(NCCH₃)₂] [BPh₄]</i>				
U	1318.1(1)	1137.8(2)	1744.8(2)	42.2(1)
N(1)	1784(3)	-3301(7)	586(7)	66(3)
C(1)	1970(4)	-9791(9)	-6(8)	70(3)
C(2)	2193(4)	-1794(9)	-722(9)	78(4)
N(2)	861(3)	2626(7)	2892(7)	50(3)
C(3)	628(4)	3256(7)	3373(8)	66(3)
C(4)	306(5)	4101(9)	3935(11)	78(4)
C(5)	1030(10)	-1048(10)	2190(14)	112(8)
C(6)	1437(6)	-796(14)	3025(18)	121(8)
C(7)	1239(8)	-21(14)	3685(10)	115(8)
C(8)	739(7)	190(13)	3289(16)	113(7)
C(9)	621(6)	-434(17)	2391(15)	108(7)
C(10)	745(5)	2647(9)	396(9)	74(4)
C(11)	439(4)	1713(11)	534(9)	76(4)
C(12)	622(4)	800(9)	-56(9)	70(4)
C(13)	1040(4)	1177(10)	-575(8)	75(4)
C(14)	1112(4)	2325(12)	-258(9)	82(4)
C(15)	2005(5)	2887(12)	1745(15)	98(6)
C(16)	1958(5)	2736(13)	2862(15)	104(6)
C(17)	2163(7)	1628(15)	3170(14)	122(7)
C(18)	2354(5)	1209(13)	2198(20)	123(7)
C(19)	2234(6)	1974(19)	1382(15)	120(8)
B	-1323(3)	4568(7)	2090(7)	43(3)
C(20)	-1158(2)	4357(5)	734(4)	46(2)*
C(21)	-1519(2)	4387(5)	-202(4)	50(2)*
C(22)	-1370(2)	4204(5)	-1287(4)	60(2)*
C(23)	-861(2)	3991(5)	-1437(4)	60(2)*
C(24)	-501(2)	3960(5)	-501(4)	50(2)*
C(25)	-650(2)	4143(5)	584(4)	45(7)*
C(26)	-1973(2)	4644(4)	2090(4)	45(2)*
C(27)	-2227(2)	5534(4)	1491(4)	57(2)*
C(28)	-2756(2)	5592(4)	1422(4)	62(2)*
C(29)	-3031(2)	4760(4)	1952(4)	63(2)*
C(30)	-2777(2)	3870(4)	2551(4)	64(2)*
C(31)	-2248(2)	3811(4)	2620(4)	55(2)*
C(32)	-1096(3)	3427(5)	2895(5)	53(3)*
C(33)	-1067(3)	3536(5)	4071(5)	71(2)*
C(34)	-864(3)	2648(5)	4760(5)	91(3)*
C(35)	-691(3)	1651(5)	4272(5)	99(4)*
C(36)	-720(3)	1542(5)	3095(5)	79(3)*
C(37)	-922(3)	2430(5)	2406(5)	65(2)*
C(38)	-1068(2)	5778(4)	2681(4)	43(2)*
C(39)	-589(2)	6157(4)	2438(4)	54(2)*
C(40)	-387(2)	7161(4)	2933(4)	67(2)*
C(41)	-663(2)	7787(4)	3671(4)	75(3)*
C(42)	-1142(2)	7408(4)	3914(4)	79(3)*
C(43)	-1345(2)	6404(4)	3419(4)	64(2)*

Table 3 (continued)

Atom	x	y	z	U_{eq}/U_{iso}^*
<i>Compound 4: [Cp₃U(NCCH₃)(NCS)]</i>				
U	3273.0(3)	2498.4(6)	3599.3(4)	32.2(1)
N(1)	3120(11)	3196(8)	1420(11)	50(4)
C(1)	3111(12)	3513(10)	381(13)	47(5)
S(1)	3098(5)	3959(4)	-1097(5)	90(2)
N(2)	3415(11)	1727(9)	5962(13)	54(4)
C(2)	3389(12)	1377(10)	6968(16)	48(5)
C(3)	3324(16)	970(14)	8220(17)	72(7)
C(11)	3986(14)	1280(10)	1754(16)	56(5)
C(12)	2805(13)	1155(9)	1829(16)	50(5)
C(13)	2576(17)	720(10)	3040(18)	64(7)
C(14)	3616(19)	581(10)	3677(17)	75(7)
C(15)	4482(16)	926(11)	2917(17)	60(6)
C(21)	1216(14)	3412(12)	3159(17)	63(6)
C(22)	1688(15)	3818(11)	4283(20)	70(7)
C(23)	1686(13)	3181(11)	5264(18)	61(6)
C(24)	1213(14)	2343(7)	4802(18)	48(5)
C(25)	917(12)	2523(13)	3494(14)	60(4)
C(31)	5554(14)	2955(13)	3436(16)	62(5)
C(32)	5018(15)	3757(13)	3087(17)	68(6)
C(33)	4442(13)	4098(12)	4170(21)	68(7)
C(34)	4631(13)	3502(11)	5239(17)	60(5)
C(35)	5338(11)	2797(11)	4791(15)	54(5)

by the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen atom contributions (for the phenyl and cyclopentadienyl groups) were introduced in calculated positions ($d(C-H)$ 0.95 Å and U_{iso} 0.08 Å²) and allowed to “ride” on their bonded atoms.

The structure of **4** was solved by the same procedures as **1** and refined by full matrix least-squares with anisotropic thermal parameters for all non hydrogen atoms. Hydrogens were in calculated positions as for **1**, with U_{iso} 0.07 Å².

The anomalous dispersion terms [20] for U were taken into account in the refinements. Atomic scattering factors were from ref. 20.

Data processing and computation were carried out with the SHELX 76 program package [21] and the PARST program was used for geometry calculations [22].

Discussion

The final positional parameters for **1** and **4** are presented in Table 3. Tables of hydrogen coordinates, thermal parameters, and observed and calculated structure factors ($\times 10$) are available from the authors.

Figure 2 shows the stereochemistry of the [UCp₃(NCCH₃)₃] cation and BPh₄⁻ anion and the atom numbering scheme. Relevant interatomic distances and bond angles are listed in Table 4. The coordination around uranium reflects the trigonal bipyramidal geometry characteristic of such compounds, having the three Cp ligands in equatorial positions, with the monodentate neutral or charged ligands in

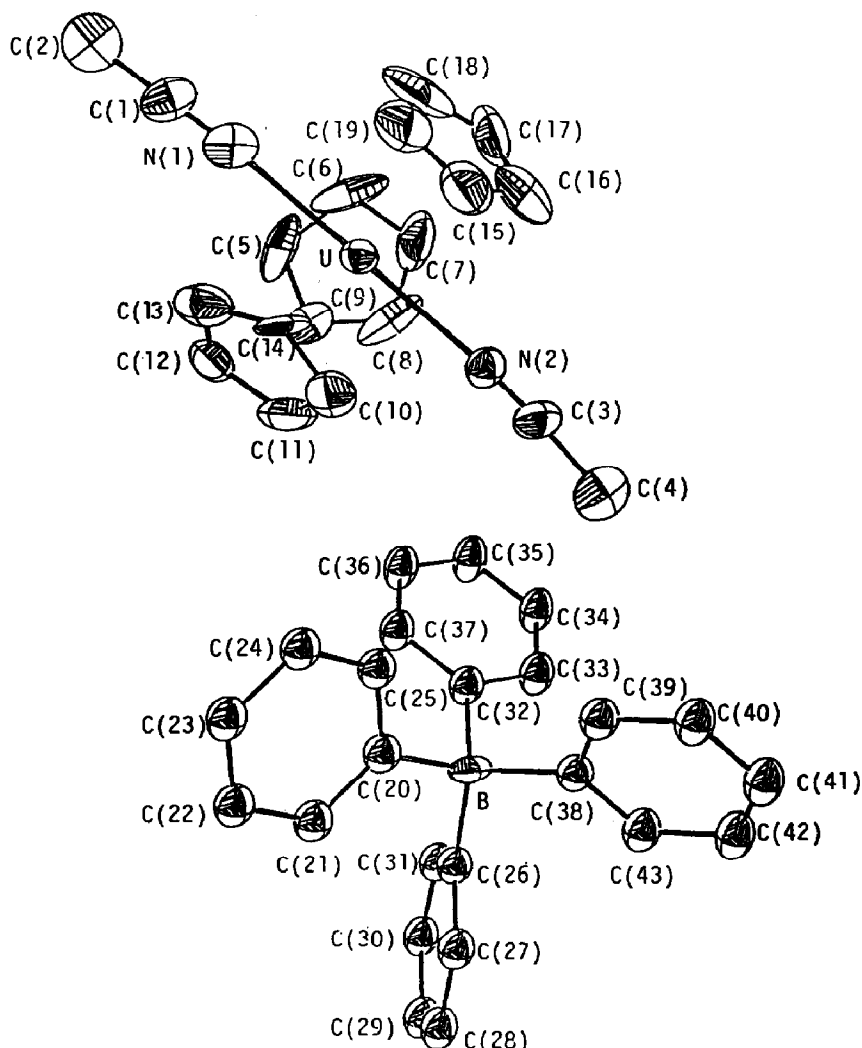


Fig. 2. ORTEP drawing of the asymmetric units in **1** (the $[\text{U}(\text{Cp})_3(\text{NCCH}_3)_2]^+$ cation, the $[\text{BPh}_4]^-$ anion) with the atom numbering system. (Thermal ellipsoids are at 40% probability level).

axial positions. The two axial NCCH_3 groups are collinear $\text{N}(1)\text{--U--N}(2)$ $179.2(3)^\circ$, and the average M--U--N angle is 89.8° , as in analogous species [1,23]. The mean U--N bond distance $2.57(1)$ Å is only slightly shorter than those $2.60(2)$ and $2.63(2)$ Å in $[\text{Cp}_3\text{U}(\text{NCCH}_3)_2]_2[\text{UO}_2\text{Cl}_4]$ in its butadiene [1] and acetonitrile clathrate, respectively [12], while the U--M ($\text{M} = \text{Cp}$ ring centre) distances are not influenced by the nature of the counter anion (mean value 2.47 Å in the three examples). In the $(\text{BPh}_4)^-$ anion the B--C distances range from $1.69(1)$ to $1.72(1)$ Å with a mean value of $1.71(1)$ Å, consistent with literature data, and the C--B--C angles do not deviate significantly from the tetrahedral value.

The structure of **4** was redetermined because the crystals we obtained were of good quality, and the refinement of the structure was carried out without the constraints used in the old refinement [7]. (In the Cp rings were given idealized geometries and, more importantly, the N--C and C--C bond distances in the NCCH_3 and NCS ligands were fixed.)

Table 4

Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses for **1**

U–N(1)	2.576(9)	N(1)–C(1)	1.17(1)	C(1)–C(2)	1.44(1)	B–C(20)	1.72(1)	B–C(32)	1.71(1)
U–N(2)	2.572(8)	N(2)–C(3)	1.14(1)	C(3)–C(4)	1.50(1)	B–C(26)	1.72(1)	B–C(38)	1.69(1)

Ring A		Ring B		Ring C	
C(5)–C(6)	1.42(3)	C(10)–C(11)	1.37(2)	C(15)–C(16)	1.35(4)
C(6)–C(7)	1.33(3)	C(11)–C(12)	1.38(2)	C(16)–C(17)	1.44(4)
C(7)–C(8)	1.38(3)	C(12)–C(13)	1.39(2)	C(17)–C(18)	1.39(5)
C(8)–C(9)	1.30(2)	C(13)–C(14)	1.46(3)	C(18)–C(19)	1.33(5)
C(9)–C(5)	1.34(3)	C(14)–C(10)	1.35(3)	C(19)–C(15)	1.32(4)

Averages:

U–C 2.73, C–C 1.37, U–M 2.47

U–N(1)–C(1)	175.0(8)	U–N(2)–C(3)	175.4(8)
N(1)–C(1)–C(2)	179(1)	N(2)–C(3)–C(4)	177(1)
N(1)–U–N(2)	179.2(3)		
C(20)–B–C(26)	110.1(5)	C(26)–B–C(32)	109.8(5)
C(20)–B–C(32)	107.6(5)	C(26)–B–C(38)	108.6(5)
C(20)–B–C(38)	112.5(5)	C(32)–B–C(38)	108.2(5)
M _A –U–M _B ^a	119.08(4)	M _A –U–M _C	120.02(3)
M _B –U–M _C	120.89(2)		
N(1)–U–M _A	90.3(2)	N(2)–U–M _A	90.4(2)
N(2)–U–M _A	90.2(2)	N(2)–U–M _B	89.7(2)
N(1)–U–M _C	88.8(2)	N(2)–U–M _C	90.6(2)

Ring A		Ring B		Ring C	
C(6)–C(5)–C(9)	110(2)	C(11)–C(10)–C(14)	108(1)	C(16)–C(15)–C(19)	108(2)
C(5)–C(6)–C(7)	104(2)	C(10)–C(11)–C(12)	108(1)	C(15)–C(16)–C(17)	107(1)
C(6)–C(7)–C(8)	110(1)	C(11)–C(12)–C(13)	108(1)	C(16)–C(17)–C(18)	105(2)
C(7)–C(8)–C(9)	109(2)	C(12)–C(13)–C(14)	106(1)	C(17)–C(18)–C(19)	107(2)
C(8)–C(9)–C(5)	108(2)	C(13)–C(14)–C(10)	109(1)	C(18)–C(19)–C(15)	113(2)

Averages: C–C–C 108, M–U–M' 120, N(1)–U–M 89.8, N(2)–U–M 90.2

^a M = Centre of a C₅H₅ ring.

Figure 3 shows an ORTEP drawing [24] of the molecule, Table 3 lists atomic parameters, and Table 5 selected interatomic distances and angles. The values in square brackets are those found previously [17]. The new refinement confirms the significant difference of 0.22 Å between U–N_{NCS} and U–N_{NCCH₃}, and allows a better analysis of the U–N_{NCCH₃} bond distances (see Table 6). It can be seen that in the compounds with the characteristic trigonal bipyramidal geometry having monodentate ligands in axial positions, the longest U–N_{NCCH₃} distance is *trans* to the NCS moiety. The different coordination geometry in the indenyl derivative (pentagonal bipyramidal) [10] having NCM_e ligands in the basal plane does not significantly affect the U–N_{NCCH₃} bond distances, (at least within the limits of esd, which are unfortunately rather high for the reported compounds), which are all comparable. The bulks of the various ligands seem to be more important in determining the coordination number and geometry around the central metal ion than in influencing the bond distances.

Table 5

Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses for 4

U–N(1)	2.44(1)	[2.41(2)]	N(2)–C(1)	1.15(2)	[1.20(2)] ^b	C(1)–S(1)	1.64(1)	[1.62(2)]
U–N(2)	2.66(1)	[2.68(2)]	N(2)–C(2)	1.14(2)	[1.16(2)] ^b	C(2)–C(3)	1.41(2)	[1.47(3)]
Ring A			Ring B			Ring C		
C(11)–C(12)	1.39(2)		C(21)–C(22)	1.39(3)		C(31)–C(32)	1.36(3)	
C(12)–C(13)	1.41(2)		C(22)–C(23)	1.36(3)		C(32)–C(33)	1.39(3)	
C(13)–C(14)	1.38(3)		C(23)–C(24)	1.41(2)		C(33)–C(34)	1.40(3)	
C(14)–C(15)	1.37(3)		C(24)–C(25)	1.40(2)		C(34)–C(35)	1.39(2)	
C(15)–C(11)	1.41(2)		C(25)–C(21)	1.37(3)		C(35)–C(31)	1.43(2)	
Averages:								
U–C 2.74, C–C 1.39, U–M 2.47								
U–N(1)–C(1)		176(1)	U–N(2)–C(2)		174(1)			
N(1)–C(1)–S(1)		180(1)	N(2)–C(2)–C(3)		178(2)			
N(1)–U–N(2)		179.2(4)						
M _A –U–M _B		119.50(4)	M _A –U–M _C		119.44(4)			
M _B –U–M _C		120.76(3)						
N(1)–U–M _A		91.5(3)	N(2)–U–M _A		88.2(3)			
N(1)–U–M _B		92.2(3)	N(2)–U–M _B		87.4(3)			
N(1)–U–M _C		91.8(3)	N(2)–U–M _C		88.9(3)			
Ring A			Ring B			Ring C		
C(12)–C(1)–C(15)	108(1)		C(22)–C(21)–C(25)	107(1)		C(32)–C(31)–C(35)	108(2)	
C(11)–C(12)–C(13)	108(1)		C(21)–C(22)–C(23)	108(2)		C(31)–C(32)–C(33)	109(2)	
C(12)–C(13)–C(14)	107(2)		C(22)–C(23)–C(24)	110(2)		C(32)–C(33)–C(34)	109(2)	
C(13)–C(14)–C(15)	109(2)		C(23)–C(24)–C(25)	104(1)		C(33)–C(34)–C(35)	106(1)	
C(14)–C(15)–C(11)	108(2)		C(14)–C(25)–C(21)	110(1)		C(34)–C(35)–C(31)	108(1)	
Averages:								
C–C–C 108, M–U–M' 120, N(1)–U–M 91.8, N(2)–U–M 88.2								

^a M = centre of a C₅H₅ ring. ^b Rigid refinement [7].

Table 6

Selected structural parameters for organouranium complexes with trigonal bipyramidal configurations.

Compound	c.g. ^d	U–N(nitrile) distances(Å)	$\nu(\text{CN})$ (cm ⁻¹) (KBr)	Ref.
[Cp ₃ U(NCMe) ₂][BPh ₄]	tbp	2.576(9); 2.572(8)	2275, (2308)	this paper
[Cp ₃ U(NCMe) ₂] ₂ [UO ₂ Cl ₄] _{0.25} ^{a,b}	tbp	2.61(2) ^a , 2.58(2) ^a , 2.60(2) ^b , 2.58(2) ^b	2250	[1,23]
Cp ₃ U(NCS)(NCMe) ^c	tbp	2.68(2), 2.66(1)	2268 (2298)	[7] this paper
[(Ind)UBr ₂ (NCMe) ₄] ₂ [UBr ₆]	pbp	2.56(3), 2.53(3), 2.57(3), 2.57(3)	2278 (2305)	[10]
[{(Ind)UBr(NCMe) ₄] ₂ O][UBr ₆]	pbp	2.55(1), 2.56(1), 2.56(1), 2.60(1)	2278 (2306)	[10]
UCl ₄ (NCMe) ₄	dod	2.567(6), 2.599(6)	2283 (2316)	[10,25]
free NCMe (liquid)			2254 (2293)	[10]

^a Acetonitrile. ^b = Butadiene. ^c ref. [7]. ^d c.g. = coordination geometry, tbp = trigonal bipyramid, pbp = pentagonal bipyramid, dod = dodecahedral.

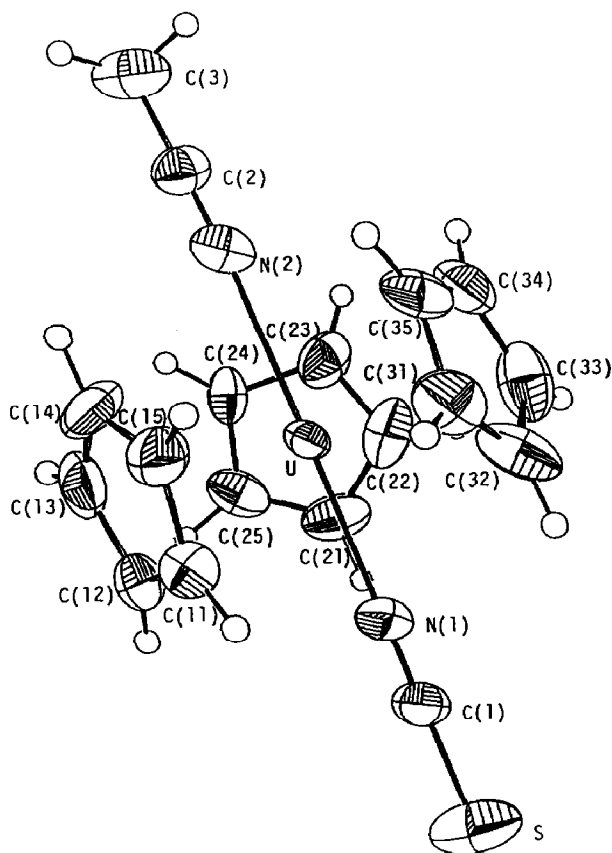


Fig. 3. ORTEP drawing for 4; (thermal ellipsoids are at 50% probability level).

Preliminary structural data on $\text{Cp}_3\text{U}(\text{NCCH}_3)(\text{NCBH}_3)$ shows cell parameters very close to that of the NCS derivative, and indicate an analogous structure (Refinement of the structure is in progress).

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