

Synthesis of Cationic Uranium Compounds by Protonolysis of Amide Precursors: Amide and Chloroamide Complexes †

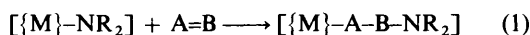
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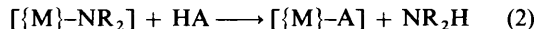
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The chloroamide compounds $[\text{U}(\text{NEt}_2)\text{Cl}_3(\text{thf})]$ and $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ were isolated from the comproportionation reactions of $[\text{U}(\text{NEt}_2)_4]$ and UCl_4 in tetrahydrofuran (thf) and were converted respectively into the cationic derivatives $[\text{UCl}_3(\text{thf})_2]\text{BPh}_4$ and $[\text{U}(\text{NEt}_2)\text{Cl}_2(\text{thf})_2]\text{BPh}_4$ by treatment with $\text{NHEt}_3\text{BPh}_4$. Protonolysis of $[\text{U}(\text{NEt}_2)_4]$ afforded the monocation $[\text{U}(\text{NEt}_2)_3]^+$ which was itself transformed into the dication $[\text{U}(\text{NEt}_2)_2(\text{thf})_3]^{2+}$; the crystal structures of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ (py = pyridine) have been determined.

Transition-metal amides have been widely employed as useful intermediates in the synthesis of a great variety of inorganic and organometallic complexes.¹ Two main reactions have been exploited: (a) insertion of a dipolar double bond into the metal–nitrogen bond [equation (1)] and (b) substitution of the amide

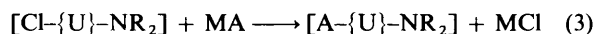


ligand by means of a protic molecule [equation (2)]. Thus were

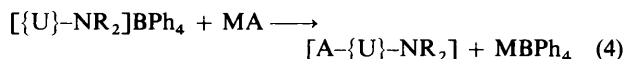


prepared from $[\text{U}(\text{NEt}_2)_4]$ a series of uranium(IV) carbamate, alkoxide, thiolate and cyclopentadienyl compounds.²

As we planned to prepare some new uranium amide complexes by using the metathesis reaction (3), we wished to



have at our disposal the chloroamides $[\text{U}(\text{NEt}_2)_{4-n}\text{Cl}_n]$ ($n = 1-3$). Here we describe the synthesis of these compounds that have been obtained by comproportionation of $[\text{U}(\text{NEt}_2)_4]$ and UCl_4 . However, it appeared that the synthetic route depicted by equation (3) was often impeded by the easy formation of the anionic product resulting from addition of A^- to the chloroamide precursor; moreover, elimination of the MCl salt from the reaction mixture was not always straightforward. In order to circumvent these difficulties, which are quite common in actinide chemistry, we considered the addition of A^- to a cationic amide species [equation (4)].



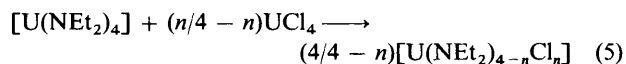
Such cations could not be prepared by chloride abstraction from the above chloroamide complexes and we had to devise another route. We found that protonolysis of a $\text{U}-\text{NR}_2$ bond by means of $\text{NHEt}_3\text{BPh}_4$ constitutes a new efficient synthesis of cationic uranium derivatives.³ Here we present some of those

which have been obtained from $[\text{U}(\text{NEt}_2)_4]$, $[\text{U}(\text{NEt}_2)\text{Cl}_3(\text{thf})]$ (thf = tetrahydrofuran) and $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$; we also describe the X-ray crystal structures of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ (py = pyridine).

Results and Discussion

Synthesis of the Chloroamide Complexes $[\text{U}(\text{NEt}_2)_{4-n}\text{Cl}_n]$ ($n = 1-3$).—Halogenoamide compounds of the transition metals, which contain two distinctly reactive functionalities, are of major interest in inorganic and organometallic syntheses. However, such complexes of the f elements are very rare, being limited to the disilylamide derivatives $[\text{M}\{\text{N}(\text{SiMe}_2)_2\}_3\text{Cl}]$ ($\text{M} = \text{Th}$ or U),⁴ the uranium(V) diphosphinoamide complex $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{PPr}^i)_2\}_3\text{Cl}_2]$ and some other diphosphinoamide compounds of the form $[\text{M}\{\text{N}(\text{CH}_2\text{CH}_2\text{PR}_2)_2\}_4-n\text{Cl}_n]$ ($\text{M} = \text{Th}$ or U , $\text{R} = \text{Et}$ or Pr^i).⁵ The mono- and bis-diethylamide compounds $[\text{U}(\text{NEt}_2)\text{Cl}_3(\text{thf})]$ and $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ could be obtained by treating $[\text{U}(\text{NEt}_2)_4]$ with the stoichiometric amount of NHEt_3Cl in tetrahydrofuran (NMR experiments). It seemed more straightforward to synthesize the chloroamide derivatives by stepwise chloride replacement from UCl_4 , rather than substituting NEt_2 groups from $[\text{U}(\text{NEt}_2)_4]$, which is itself prepared from the uranium tetrachloride. However, treatment of UCl_4 with LiNEt_2 did not afford the desired compounds but gave some anionic species; in particular, the reaction with 2 equivalents of LiNEt_2 in diethyl ether led to the formation of $\text{Li}[\text{U}(\text{NEt}_2)_2\text{Cl}_3]$, isolated in 91% yield as an ochre microcrystalline powder. This retention of the alkali metal and formation of 'ate' complexes is a pervasive problem in the chemistry of the f elements.⁶

The metathetical exchange reaction between halides and amides represents another classical route to mixed-ligand derivatives [equation (5)]. The titanium compounds



$[\text{Ti}(\text{NR}_2)_{4-n}\text{X}_n]$ ($\text{R} = \text{Me}$ or Et , $\text{X} = \text{F}$ or Cl) were thus prepared from $[\text{Ti}(\text{NR}_2)_4]$ and TiX_4 .⁷ The two complexes $[\text{U}(\text{NEt}_2)\text{Cl}_3(\text{thf})]$ **1** and $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ **2** were easily synthesized from 1:3 and 1:1 mixtures of $[\text{U}(\text{NEt}_2)_4]$ and UCl_4 in tetrahydrofuran (Scheme 1); after evaporation of the solvent, they were isolated as green and yellow microcrystals, in

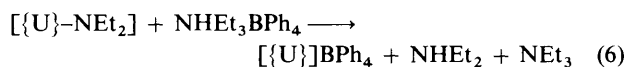
† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

92 and 83% yield respectively. The tris-diethylamide compound $[\text{U}(\text{NEt}_2)_3\text{Cl}]$ was found to be in equilibrium with $[\text{U}(\text{NEt}_2)_4]$ and $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$, the three complexes being obtained in the same proportions (60:20:20 in thf) when $[\text{U}(\text{NEt}_2)_4]$ was mixed with UCl_4 (0.33 equivalents) or $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ (1 equivalent) or when it was treated with NHEt_3Cl (1 equivalent).

The exact structure of these chloroamide compounds is difficult to determine but it is likely that they are poly- or oligomerized in the solid state and in solution. The tetramide $[\text{U}(\text{NEt}_2)_4]$, which is a dimer in its crystalline form, is partially dissociated in toluene⁸ whereas the titanium complexes $[\text{Ti}(\text{NR}_2)_4-n\text{X}_n]$ exist as halogen-bridged oligomers.⁷

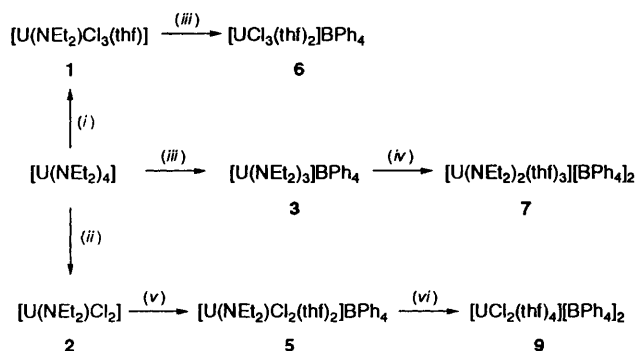
Synthesis of the Cationic Complexes.—Cationic metal complexes are generally prepared either by protonolysis of a metal-carbon bond or by heterolytic cleavage of a metal-halogen bond. The compounds $[\text{UCl}_3(\text{EtCONEt}_2)_4]$, $[\text{UCl}_5(\text{EtCONEt}_2)_2]$,⁹ $[\text{UCl}_3(\text{dcc})_2\text{UCl}_6]$ (dcc = dicyclohexano-18-crown-6, hexadecahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecine)¹⁰ and $[\text{UCl}_2(\text{Me}_2\text{SO})_6]\text{UCl}_6$ ¹¹ were thus synthesized from UCl_4 and were crystallographically characterized. However, all attempts to abstract chloride ions from the above chloroamide complexes in thf or MeCN were unsuccessful. Unexpectedly, treatment of $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ with AgBPh_4 led to the formation of the cation $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]^+$; such reactions, which are likely to proceed *via* the oxidation of the uranium(IV) precursor into the corresponding U^{V} cation, followed by homolytic cleavage of a $\text{U}-\text{NEt}_2$ bond, will be discussed elsewhere.

We found that protonation of a NEt_2 ligand by means of $\text{NHEt}_3\text{BPh}_4$ in thf constitutes an efficient alternative route to cationic metal complexes [equation (6)]; the liberated amines



NHEt_2 and NEt_3 are easily eliminated from the reaction mixture.

While the reactivity of the $\text{M}-\text{NR}_2$ bond towards acidic proton substrates is well established [equation (2)], the protonolysis reaction (6) is unprecedented. Treatment of $[\text{U}(\text{NEt}_2)_4]$, $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ or $[\text{U}(\text{NEt}_2)\text{Cl}_3(\text{thf})]$ with 1 equivalent of $\text{NHEt}_3\text{BPh}_4$ in thf gave, after evaporation of the solvent, analytically pure microcrystalline powders of $[\text{U}(\text{NEt}_2)_3]\text{BPh}_4$ **3** (pale green, 97%), $[\text{U}(\text{NEt}_2)\text{Cl}_2(\text{thf})_2]\text{BPh}_4$ **5** (yellow, 93%) and $[\text{UCl}_3(\text{thf})_2]\text{BPh}_4$ **6** (green, 69%). Dark green crystals of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ **4** were obtained by crystallization from thf-pentane of the pale green powder of **3** and were transformed back into the thf-free compound **3** by drying *in vacuo*. The ^1H NMR spectrum of **3** in $[\text{D}_2\text{H}_8]$ -tetrahydrofuran exhibits a single signal at δ 6.44, corresponding



Scheme 1 Reagents and conditions: (i) UCl_4 (3 equivalents), 20 min, 20 °C; (ii) UCl_4 (1 equivalent), 90 min, 20 °C; (iii) $\text{NHEt}_3\text{BPh}_4$, 30 min, 20 °C; (iv) $\text{NHEt}_3\text{BPh}_4$, 30 min, 65 °C; (v) $\text{NHEt}_3\text{BPh}_4$, 30 min, 0 °C; (vi) $\text{NHEt}_3\text{BPh}_4$, 60 h, 20 °C. All reactions in thf

to the BPh_4 anion, but the spectrum in $[\text{D}_2\text{H}_8]$ toluene shows two distinct phenyl resonances of equal intensity at δ 9.23 and 0.38. These facts strongly suggest that **3** adopts a zwitterionic structure in the solid state or in non-co-ordinating solvents, with two phenyl groups of BPh_4 co-ordinated to the uranium atom. Such π co-ordination of tetraphenylborate and related anions to metal centres is now well documented;¹² for example, the lanthanum complex $[\text{R}(\eta\text{-C}_5\text{Me}_5)\text{La}(\eta\text{-Ph})_2\text{BPh}_4]$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] was synthesized by protonation in toluene of $[\text{La}(\eta\text{-C}_5\text{Me}_5)\text{R}_2]$ by means of $\text{NHEt}_3\text{BPh}_4$ and was irreversibly transformed in tetrahydrofuran into $[\text{La}(\eta\text{-C}_5\text{Me}_5)\text{R}(\text{thf})_3]\text{BPh}_4$.¹³

The monocation $[\text{U}(\text{NEt}_2)_3]^+$ could be further protonated in refluxing thf and the yellow microcrystalline powder of the dicationic compound $[\text{U}(\text{NEt}_2)_2(\text{thf})_3][\text{BPh}_4]_2$ **7** which precipitated in this solvent (88% yield) was recrystallized from pyridine-thf, giving green crystals of $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ **8**. Treatment of $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$ with 2 equivalents of $\text{NHEt}_3\text{BPh}_4$ afforded the dicationic derivative $[\text{UCl}_2(\text{thf})_4][\text{BPh}_4]_2$ **9**, isolated as a pale green powder in 60% yield.

The new complexes have been characterized by elemental analyses and ^1H NMR spectroscopy (Table 1); the crystal structures of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ have been determined.

Crystal Structures.—The crystals of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ **4** and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ **8** are composed of discrete cations and anions. The BPh_4 anions display the expected structural parameters; ORTEP drawings¹⁴ of the cations of **4** and **8** are shown in Fig. 1 and 2 respectively, and selected bond distances and angles are listed in Table 2. In the monocation of **4**, the uranium atom is in a distorted facial octahedral environment, each amide group being *trans* to a thf ligand. The angles $\text{N}(1)-\text{U}-\text{O}(1)$, $\text{N}(2)-\text{U}-\text{O}(2)$ and $\text{N}(3)-\text{U}-\text{O}(3)$ deviate from linearity by 14.4, 13.0 and 16.8°; the $\text{N}-\text{U}-\text{N}$ angles, which average 99(3)°, are $>90^\circ$, the ideal value in the octahedron, whereas the $\text{O}-\text{U}-\text{O}$ angles are smaller, with a mean value of 79.2(5)°. Similar distortions were observed in the uranium(III) compound $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$.¹⁵ However, it is noteworthy that the oxygen and nitrogen atoms are at the corners of a regular octahedron. The two equilateral triangles defined by $\text{O}(1)$, $\text{O}(2)$, $\text{O}(3)$ and $\text{N}(1)$, $\text{N}(2)$, $\text{N}(3)$ are equal and parallel in a quite perfectly staggered conformation. The ratio of the side of the

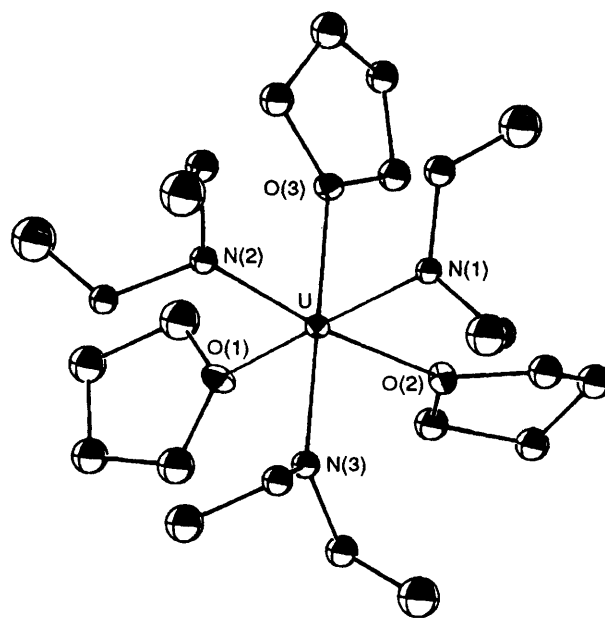
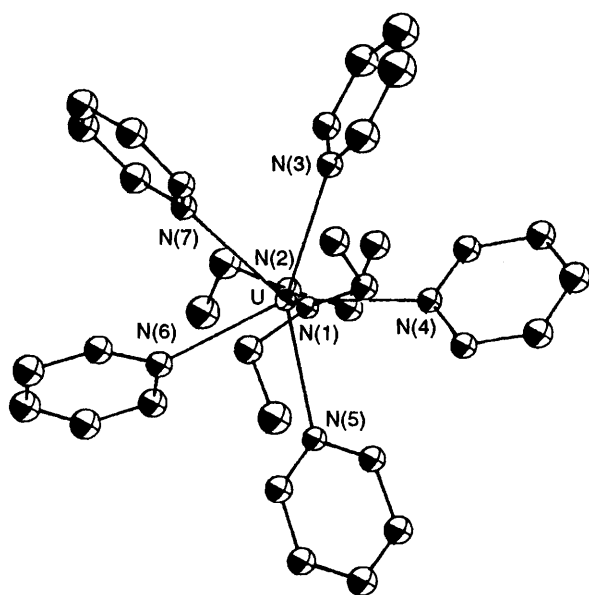


Fig. 1 Perspective view of the monocation $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]^+$

Table 1 Analytical and ^1H NMR data for the complexes

Compound	Analyses ^a (%)	NMR data ^b
$\text{Li}[\text{U}(\text{NEt}_2)_2\text{Cl}_3]$	C 18.85 (19.4) H 3.95 (4.05) N 5.45 (5.65)	53.90 (2 H, s, $w_{1/2}$ 580, CH_2), 15.44 (3 H, s, $w_{1/2}$ 120, Me) ^c 38.3 (2 H, s, $w_{1/2}$ 310, CH_2), 8.24 (3 H, s, $w_{1/2}$ 65, Me)
1 $[\text{U}(\text{NEt}_2)_2\text{Cl}_3(\text{thf})]$	C 19.4 (19.65) H 3.6 (3.7) N 2.85 (2.85)	117.71 (2 H, s, $w_{1/2}$ 34, CH_2), 42.52 (3 H, Me)
2 $[\text{U}(\text{NEt}_2)_2\text{Cl}_2]$	C 20.95 (21.2) H 4.3 (4.45) N 6.0 (6.2)	40.22 (2 H, CH_2), 9.86 (3 H, t, J 6, Me)
3 $[\text{U}(\text{NEt}_2)_3]\text{BPh}_4$	C 55.8 (55.9) H 6.45 (6.5) B 1.3 (1.4)	18.46 (12 H, q, J 7, CH_2), 2.11 (18 H, t, J 7, Me), 6.44 (20 H, Ph) ^c 24.65 (12 H, q, J 7, CH_2), 1.09 (18 H, t, J 7, Me), 9.23 and 0.38 (2 \times 10 H, Ph)
5 $[\text{U}(\text{NEt}_2)_2\text{Cl}_2(\text{thf})_2]\text{BPh}_4$	C 51.0 (51.2) H 5.35 (5.5) N 1.75 (1.65)	143.5 (4 H, s, $w_{1/2}$ 70, CH_2), 52.81 (6 H, Me), 6.3 and 6.8 (20 H, Ph)
6 $[\text{UCl}_3(\text{thf})_2]\text{BPh}_4$	C 47.45 (47.6) H 4.55 (4.5) Cl 12.9 (13.15)	8.52, 7.55 and 7.34 (m, Ph)
7 $[\text{U}(\text{NEt}_2)_2(\text{thf})_3][\text{BPh}_4]_2$	C 65.7 (66.0) H 6.65 (6.85) B 2.25 (2.25)	^d 182.9 (8 H, s, $w_{1/2}$ 200, CH_2), 68.1 (12 H, s, $w_{1/2}$ 55, Me), 6.64 (40 H, Ph), 3.55 and 1.65 (2 \times 12 H, thf)
9 $[\text{UCl}_2(\text{thf})_4][\text{BPh}_4]_2$	C 62.1 (62.2) H 6.0 (5.9) U 19.1 (19.25)	8.6 and 7.4 (m, Ph)

^a Analytical data given as: found (required) in %. ^b At 30 °C; data given as chemical shift (δ) (relative integral, multiplicity, coupling constant or half-height width in Hz, assignment); when not specified, the signal is a singlet with $w_{1/2} = 10\text{--}30$ Hz. Solvent is $[\text{H}_8]$ tetrahydrofuran unless otherwise specified. ^c In $[\text{H}_8]$ toluene ^d In $[\text{H}_5]$ pyridine.

**Fig. 2** Perspective view of the dication $[\text{U}(\text{NEt}_2)_2(\text{py})_5]^{2+}$

triangle [3.29(6) Å] to the distance between the triangles [2.76(2) Å] is equal to 1.19, *cf.* 1.22 in the ideal octahedron. The uranium atom lies on the pseudo- C_3 axis but is displaced from the central position by 0.38 Å towards the plane of the nitrogen atoms. The uranium–nitrogen bond lengths average 2.18(1) Å and are at the lower limit of the range of U–N bond distances for terminally co-ordinated amide groups, which vary from 2.162(5) Å in $[\text{U}(\text{OC}_6\text{H}_3\text{Bu}'_2\text{-2,6})_3(\text{NEt}_2)]^{16}$ to 2.35(2) Å in $[\text{U}(\text{NPh}_2)_4]$.¹⁷ As previously reported for transition-metal and uranium terminal amides, each nitrogen atom lies in the plane (within ± 0.02 Å) defined by the metal and the two α carbons; these structural parameters suggest the presence of a π interaction

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

$[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ 4			
U–N(1)	2.20(1)	U–O(2)	2.562(9)
U–O(1)	2.54(1)	U–N(3)	2.18(1)
U–N(2)	2.17(1)	U–O(3)	2.560(9)
O(1)–U–N(1)	165.6(4)	N(1)–U–N(3)	101.3(4)
O(2)–U–N(2)	167.0(4)	N(1)–U–O(2)	88.1(4)
O(3)–U–N(3)	163.2(4)	N(1)–U–O(3)	91.1(4)
O(1)–U–N(2)	94.4(4)	N(2)–U–N(3)	100.9(4)
O(1)–U–N(3)	86.4(4)	N(2)–U–O(3)	88.9(4)
O(1)–U–O(2)	79.7(3)	O(2)–U–N(3)	90.3(4)
O(1)–U–O(3)	79.2(3)	O(2)–U–O(3)	78.7(3)
N(1)–U–N(2)	96.0(4)		
$[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ 8			
U–N(1)	2.214(8)	U–N(5)	2.655(9)
U–N(2)	2.189(9)	U–N(6)	2.636(9)
U–N(3)	2.63(3)	U–N(7)	2.621(9)
U–N(4)	2.661(9)		
N(1)–U–N(2)	167.9(3)	N(2)–U–N(5)	89.3(3)
N(1)–U–N(3)	90.2(5)	N(2)–U–N(6)	87.4(3)
N(1)–U–N(4)	79.3(3)	N(2)–U–N(7)	102.0(3)
N(1)–U–N(5)	89.0(3)	N(3)–U–N(4)	71.9(5)
N(1)–U–N(6)	103.6(3)	N(3)–U–N(7)	66.6(5)
N(1)–U–N(7)	86.4(3)	N(4)–U–N(5)	78.2(3)
N(2)–U–N(3)	85.2(5)	N(5)–U–N(6)	74.0(3)
N(2)–U–N(4)	88.6(3)	N(6)–U–N(7)	72.0(3)

between the uranium and nitrogen atoms. The U–N–C angles vary from 120(1) to 133(1)° whereas the C–N–C angles range from 107(1) to 113(2)°; similar deviations from the idealized value of 120° for a trigonal-planar nitrogen atom have been encountered in many dialkyl and diaryl amides of the actinides and transition metals. The co-ordination of thf is unexceptional, with an average value of 2.55(1) Å for the U–O distances.

In the dication of **8**, the uranium atom is seven-coordinate in

a distorted pentagonal-bipyramidal arrangement. The metal and the five nitrogen atoms of the pyridine ligands are out of their mean plane by ± 0.33 Å; the N(py)–U–N(py) angles range from 66.6(5) to 78.2(3)° and their sum is equal to 362.7°. The N(1)–U–N(2) axis deviates from linearity by 12.1°; the N(amide)–U–N(py) angles vary from 79.3(3) to 103.6(3)° and average 90°. The U–N(1) and U–N(2) distances, 2.214(8) and 2.189(9) Å, are similar to those found in the monocation of **4** and the geometry of the UNC₂ fragment is planar. The U–N(py) distances range from 2.621(9) to 2.661(9) Å and average 2.64(2) Å; this value compares with those of 2.64(1) Å in [U(C₈H₈)Cl₂(py)₂]¹⁸ and 2.56(9) Å in [U(SPrⁱ)₂I₂(py)₃].¹⁹

Conclusion

The protonolysis reaction of a U–NR₂ bond by means of NHEt₃BPh₄ constitutes a novel and efficient synthesis of cationic uranium compounds. Thus the cations [U(NEt₂)₃]⁺ and [U(NEt₂)₂(thf)₃]²⁺ have been prepared from the uranium tetramide [U(NEt₂)₄] and [U(NEt₂)Cl₂(thf)₂]⁺, [UCl₃(thf)₂]⁺ and [UCl₂(thf)₄]²⁺ from the chloroamide complexes [U(NEt₂)₂Cl₂] and [U(NEt₂)Cl₃(thf)]. The protonolysis reaction (6) has also been useful for the preparation of organometallic cations.²⁰ These cations are themselves interesting precursors for the synthesis of various derivatives since they are likely to undergo the insertion, substitution and addition reactions depicted by equations (1), (2) and (4); some examples are given in the following paper.²⁰

Experimental

All preparations and reactions were carried out under argon (< 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. Deuteriated solvents were dried over Na–K alloy (thf, benzene and toluene) or molecular sieves (pyridine).

Elemental analyses were performed by Analytische Laboratorien at Gummersbach (Germany). The ¹H 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 salt NHEt₃BPh₄ precipitated by mixing NHEt₃Cl and NaBPh₄ in water, [U(NEt₂)₄]⁸ and UCl₄²¹ were prepared by published methods.

Reactions of [U(NEt₂)₄] with NHEt₃Cl.—An NMR tube was charged with [U(NEt₂)₄] (10 mg, 19 μ mol) and NHEt₃Cl (5.2 mg, 38 μ mol) in [²H₈]tetrahydrofuran (0.3 cm³). After 10 min, the spectrum of the yellow solution showed the quantitative formation of [U(NEt₂)₂Cl₂], with liberation of NHEt₂ and NEt₃ (2 equivalents each). The compound [U(NEt₂)₄] was similarly treated with 3 equivalents of NHEt₃Cl and was transformed into [U(NEt₂)Cl₃(thf)].

Li[U(NEt₂)₂Cl₂].—A round-bottom flask (50 cm³) was charged with UCl₄ (1000 mg, 2.63 mmol) and LiNEt₂ (417 mg, 5.27 mmol) and diethyl ether (20 cm³) was condensed into it under vacuum at –78 °C. The dark red solution became green after stirring for 48 h at 20 °C; it was then filtered and evaporated to dryness, leaving an ochre microcrystalline powder which was washed with pentane (2 × 20 cm³) and dried under vacuum (1190 mg, 91 %).

[U(NEt₂)Cl₃(thf)] 1.—A round-bottom flask (50 cm³) was charged with UCl₄ (433 mg, 1.14 mmol) and [U(NEt₂)₄] (200 mg, 0.38 mmol) and thf (15 cm³) was condensed into it under vacuum at –78 °C. The reaction mixture was stirred for 20 min at 20 °C and the orange solution was filtered and evaporated to

dryness, leaving a green microcrystalline powder which was washed with diethyl ether (2 × 20 cm³) and dried under vacuum (682 mg, 92%).

[U(NEt₂)₂Cl₂] 2.—A round-bottom flask (50 cm³) was charged with UCl₄ (1080 mg, 2.84 mmol) and [U(NEt₂)₄] (1500 mg, 2.85 mmol) and thf (25 cm³) was condensed into it under vacuum at –78 °C. After 90 min at 20 °C, the green solution was evaporated to dryness and the residue was extracted into diethyl ether (25 cm³). The yellow microcrystalline powder obtained after evaporation was washed with pentane (2 × 15 cm³) and dried under vacuum (2140 mg, 83%).

Equilibrium between [U(NEt₂)₃Cl], [U(NEt₂)₂Cl₂] and [U(NEt₂)₄].—An NMR tube was charged with [U(NEt₂)₄] (10 mg, 19 μ mol) and UCl₄ (2.4 mg, 6.3 μ mol) in [²H₈]tetrahydrofuran (0.3 cm³). After 10 min at 20 °C, the spectrum showed the signals corresponding to [U(NEt₂)₄], [U(NEt₂)₂Cl₂] and other resonances attributed to [U(NEt₂)₃Cl]. δ_{H} (30 °C): 12.32 (2 H) and 0.51 (3 H). The three compounds were in the relative proportions 20:20:60 (8:8:84 in pyridine). The same mixture was obtained from equimolar quantities of [U(NEt₂)₂Cl₂] and [U(NEt₂)₄] or by treating the uranium tetramide with 1 equivalent of NHEt₃Cl with, in this case, liberation of NEt₃ and NHEt₂ (1 equivalent of each).

[U(NEt₂)₃]BPh₄ 3.—A round-bottom flask (100 cm³) was charged with [U(NEt₂)₄] (2700 mg, 5.13 mmol) and NHEt₃BPh₄ (2100 mg, 5.0 mmol) and thf (50 cm³) was condensed into it under vacuum at –78 °C. After 30 min at 20 °C, a green precipitate in a green solution was obtained. The solution was filtered and the precipitate was extracted into thf (20 cm³); the combined solutions were evaporated to dryness, leaving a pale green microcrystalline powder which was washed with pentane (25 cm³) and dried under vacuum (3740 mg, 97%). Recrystallization from thf gave dark green crystals of [U(NEt₂)₃(thf)₃]BPh₄ **4** which were suitable for X-ray diffraction studies; under vacuum, these crystals were transformed back into the pale green powder of **3**.

[U(NEt₂)Cl₂(thf)₂]BPh₄ 5.—A round-bottom flask (50 cm³) was charged with [U(NEt₂)₂Cl₂] **2** (192 mg, 0.42 mmol) and NHEt₃BPh₄ (144 mg, 0.34 mmol) and thf (20 cm³) was condensed into it under vacuum at –78 °C. After stirring for 30 min at 0 °C, the solution was filtered and evaporated to dryness, leaving a yellow microcrystalline powder which was washed with diethyl ether (30 cm³) and dried under vacuum (268 mg, 93%).

[UCl₃(thf)₂]BPh₄ 6.—A round-bottom flask (50 cm³) was charged with [U(NEt₂)Cl₃(thf)] **1** (120 mg, 0.245 mmol) and NHEt₃BPh₄ (100 mg, 0.24 mmol) and thf (20 cm³) was condensed into it under vacuum at –78 °C. The reaction mixture was stirred for 30 min at 20 °C and the volume of the solution was reduced to 5 cm³. The brown oily material obtained after addition of diethyl ether (10 cm³) was filtered off and became a green powder when dried under vacuum (132 mg, 69%).

[U(NEt₂)₂(thf)₃]BPh₄ 7.—A round-bottom flask (50 cm³) was charged with [U(NEt₂)₃]BPh₄ **3** (1000 mg, 1.29 mmol) and NHEt₃BPh₄ (545 mg, 1.29 mmol) and thf (30 cm³) was condensed into it under vacuum at –78 °C. The reaction mixture was heated at 65 °C for 30 min and the yellow microcrystalline powder was filtered off, washed with thf (2 × 20 cm³) and dried under vacuum (1400 mg, 88%). Recrystallization from pyridine gave green crystals of [U(NEt₂)₂(py)₅][BPh₄]₂·1.5py **8** which were suitable for X-ray diffraction studies.

[UCl₂(thf)₄]BPh₄ 9.—A round-bottom flask (50 cm³) was charged with [U(NEt₂)₂Cl₂] **2** (122 mg, 0.27 mmol) and

Table 3 Crystallographic data and experimental details for $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ **4** and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ **8***

	4	8
Formula	$\text{C}_{48}\text{H}_{74}\text{BN}_3\text{O}_3\text{U}$	$\text{C}_{88.5}\text{H}_{92.5}\text{B}_2\text{N}_{8.5}\text{U}$
<i>M</i>	989.98	1534.93
Crystal size/mm	$0.50 \times 0.35 \times 0.20$	$0.45 \times 0.45 \times 0.30$
Colour	Dark green	Green
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
<i>a</i> /Å	10.720(3)	14.519(2)
<i>b</i> /Å	15.020(5)	15.067(8)
<i>c</i> /Å	30.43(2)	17.869(3)
α /°	90	87.24(3)
β /°	98.46(3)	80.69(1)
γ /°	90	82.65(4)
<i>V</i> /Å ³	4847(7)	3824(4)
<i>Z</i>	4	2
<i>D_c</i> /g cm ⁻³	1.357	1.333
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	32.127	20.60
<i>F</i> (000)	2016	1570
Range of absolute transmission	0.800–0.998	0.871–0.999
Range <i>h, k, l</i>	0–10, 0–14, –28 to 28	0–14, –14 to 14, –17 to 17
Reflections collected		
Total	5089	8047
Unique	4513	6880
with <i>I</i> > 3σ(<i>I</i>)	2842	5203
No. of parameters	305	406
$R = \sum F_o - F_c / \sum F_o $	0.038	0.043
$R' = [\sum w F_o - F_c ^2 / \sum w(F_o)^2]^{1/2}$	0.044	0.051
Max. residual electron density/e Å ⁻³	0.775	0.682

* Details in common: *T* = 294 K, $1 < \theta < 20^\circ$, ω -2θ scan type, scan width $0.8 + 0.35 \tan \theta$; weighting scheme $w^{-1} = \sigma(F)^2$.

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
U	0.204 06(5)	0.155 66(4)	0.385 10(2)	C(22)	0.767(2)	0.045(1)	0.708 9(7)
O(1)	–0.002 7(9)	0.200 8(7)	0.338 8(3)	C(23)	0.276(2)	0.168(2)	0.282 6(8)
O(2)	0.255 7(9)	0.316 2(6)	0.365 6(3)	C(24)	0.400(2)	0.185(2)	0.272 9(7)
O(3)	0.101 1(9)	0.243 2(6)	0.442 4(3)	C(25)	0.739(1)	0.013 7(9)	0.189 9(4)
N(1)	0.384 6(9)	0.152 0(8)	0.429 9(3)	C(26)	0.850(1)	–0.038(1)	0.204 2(5)
N(2)	0.129(1)	0.033 8(8)	0.409 5(4)	C(27)	0.859(2)	–0.091(1)	0.243 9(5)
N(3)	0.261(1)	0.109 0(8)	0.323 3(4)	C(28)	0.758(2)	–0.094(1)	0.267 9(5)
C(1)	–0.040(2)	0.186(2)	0.292 8(5)	C(29)	0.650(1)	–0.047(1)	0.253 3(5)
C(2)	–0.174(2)	0.175(1)	0.282 5(6)	C(30)	0.637(1)	0.008(1)	0.214 9(5)
C(3)	–0.226(1)	0.203(2)	0.323 0(6)	C(31)	0.825(1)	0.165(1)	0.15 22(4)
C(4)	–0.115(2)	0.233(2)	0.356 5(7)	C(32)	0.792(1)	0.244(1)	0.129 5(4)
C(5)	0.382(1)	0.358(1)	0.381 7(6)	C(33)	0.881(2)	0.315(1)	0.128 8(5)
C(6)	0.365(2)	0.453(1)	0.375 9(6)	C(34)	1.000(2)	0.306(1)	0.152 9(5)
C(7)	0.264(2)	0.462(1)	0.334 1(5)	C(35)	1.037(2)	0.231(1)	0.176 6(6)
C(8)	0.177(2)	0.380(1)	0.335 3(6)	C(36)	0.947(1)	0.156(1)	0.176 4(5)
C(9)	0.043(2)	0.201(1)	0.478 5(5)	C(37)	0.583(1)	0.109 4(9)	0.129 7(4)
C(10)	0.038(2)	0.270(1)	0.511 4(5)	C(38)	0.505(1)	0.069 9(9)	0.094 6(4)
C(11)	0.047(1)	0.359(1)	0.490 4(5)	C(39)	0.376(1)	0.096(1)	0.081 7(5)
C(12)	0.107(2)	0.339(1)	0.449 3(5)	C(40)	0.330(1)	0.165(1)	0.106 2(5)
C(13)	0.399(2)	0.153(2)	0.479 6(8)	C(41)	0.402(1)	0.206(1)	0.141 8(5)
C(14)	0.447(2)	0.221(2)	0.503 2(8)	C(42)	0.532(1)	0.178(1)	0.154 6(5)
C(15)	0.519(2)	0.135(2)	0.415 6(9)	C(43)	0.777(1)	0.020 5(9)	0.103 4(4)
C(16)	0.581(2)	0.064(2)	0.420 8(8)	C(44)	0.830(1)	0.061 3(9)	0.069 1(4)
C(17)	0.829(2)	0.027(2)	0.546 9(8)	C(45)	0.864(1)	0.012(1)	0.032 1(5)
C(18)	0.774(3)	0.099(2)	0.555 8(9)	C(46)	0.843(1)	–0.080(1)	0.030 2(5)
C(19)	0.985(2)	0.015(2)	0.618 9(8)	C(47)	0.794(1)	–0.122(1)	0.063 6(5)
C(20)	0.089(2)	0.030(2)	0.599 5(8)	C(48)	0.760(1)	–0.073(1)	0.100 4(5)
C(21)	0.313(2)	0.018(2)	0.320 3(9)	B	0.728(1)	0.076(1)	0.144 6(5)

$\text{NHtEt}_3\text{BPh}_4$ (214 mg, 0.51 mmol) and thf (20 cm³) was condensed into it under vacuum at –78 °C. The reaction mixture was stirred for 60 h at 20 °C, filtered, and the volume of the yellow solution was reduced to 10 cm³. The yellow oily material obtained after addition of diethyl ether (25 cm³) was filtered off and became a green powder when dried under vacuum. The product was recrystallized from thf–diethyl ether (187 mg, 60%).

Crystal Structure Determinations of $[\text{U}(\text{NEt}_2)_3(\text{thf})_3]\text{BPh}_4$ **4** and $[\text{U}(\text{NEt}_2)_2(\text{py})_5][\text{BPh}_4]_2 \cdot 1.5\text{py}$ **8**.—Selected single crystals were introduced into thin-walled Lindeman glass tubes in a glove-box. Data were collected on an Enraf-Nonius diffractometer equipped with a graphite-monochromator [$\lambda(\text{Mo-K}\alpha) = 0.700 73$ Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $8 < \theta < 12^\circ$. Three standard reflections were measured

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for $[U(NEt_2)_2(py)_5][BPh_4]_2 \cdot 1.5py$ **8**

Atom	x	y	z	Atom	x	y	z
U	0.739 65(3)	0.283 34(3)	0.756 52(2)	C(42)	-0.034 1(9)	0.261 3(9)	1.077 7(7)
N(1)	0.683 4(5)	0.271 8(5)	0.878 9(4)	C(43)	-0.085 3(9)	0.202(1)	1.077 9(3)
N(2)	0.816 1(6)	0.311 3(6)	0.643 6(5)	C(44)	-0.043 8(9)	0.143 0(9)	1.023 0(8)
N(4)	0.861 0(6)	0.366 5(6)	0.815 6(5)	C(45)	0.054 0(8)	0.142 8(8)	0.992 2(7)
N(5)	0.872 7(6)	0.149 8(6)	0.775 4(5)	C(46)	0.251 3(7)	0.144 3(8)	0.910 6(6)
N(6)	0.690 3(6)	0.141 7(6)	0.699 5(5)	C(47)	0.270 9(8)	0.182 7(8)	0.836 1(7)
N(7)	0.564 2(6)	0.320 3(6)	0.735 4(5)	C(48)	0.301(1)	0.126(1)	0.771 7(8)
N(8)	0.238(1)	0.677(1)	0.708(1)	C(49)	0.313(1)	0.034(1)	0.780 7(8)
N(3)	0.680 2(6)	0.456 0(6)	0.756 9(5)	C(50)	0.290(1)	-0.006(1)	0.852 9(9)
C(1)	0.680 5(7)	0.320 0(8)	0.950 2(6)	C(51)	0.259 8(9)	0.050(1)	0.917 8(8)
C(2)	0.579 0(8)	0.343 2(8)	0.993 4(7)	C(52)	0.288 6(7)	0.160 4(7)	1.049 4(6)
C(3)	0.642 9(8)	0.187 4(8)	0.890 1(7)	C(53)	0.382 9(8)	0.131 1(9)	1.025 6(7)
C(4)	0.686(1)	0.122(1)	0.950 2(8)	C(54)	0.445 3(9)	0.095 1(9)	1.077 3(8)
C(5)	0.912 4(8)	0.334 4(8)	0.625 5(6)	C(55)	0.410 2(9)	0.088 0(9)	1.154 9(7)
C(6)	0.921 5(8)	0.424 3(8)	0.582 6(7)	C(56)	0.315 9(9)	0.117 5(9)	1.180 3(7)
C(7)	0.770 6(9)	0.309 1(9)	0.575 9(7)	C(57)	0.254 7(8)	0.154 1(8)	1.128 7(7)
C(8)	0.834(1)	0.253(1)	0.508 5(8)	C(58)	0.174 6(7)	0.123 0(7)	0.546 0(6)
C(9)	0.691 5(8)	0.504 9(8)	0.691 7(6)	C(59)	0.236 1(8)	0.061 2(8)	0.579 5(6)
C(10)	0.679 1(9)	0.599(1)	0.689 5(8)	C(60)	0.206 2(9)	-0.019 8(9)	0.614 1(7)
C(11)	0.652(1)	0.646(1)	0.755 7(9)	C(61)	0.115 5(9)	-0.039 8(9)	0.614 4(7)
C(12)	0.629(1)	0.593(1)	0.824 7(9)	C(62)	0.051 2(9)	0.025 2(9)	0.583 3(7)
C(13)	0.648(1)	0.498(1)	0.821 2(8)	C(63)	0.082 1(8)	0.103 5(8)	0.548 5(6)
C(14)	0.878 8(8)	0.448 5(8)	0.791 6(6)	C(64)	0.145 3(7)	0.246 1(7)	0.435 6(6)
C(15)	0.920 6(8)	0.504 6(8)	0.834 6(7)	C(65)	0.093 4(7)	0.329 1(8)	0.426 2(6)
C(16)	0.943 5(9)	0.470 5(9)	0.904 2(7)	C(66)	0.040 6(9)	0.348 6(9)	0.364 3(7)
C(17)	0.931 3(8)	0.384 1(9)	0.926 9(7)	C(67)	0.039 7(9)	0.283 1(9)	0.313 2(7)
C(18)	0.889 4(7)	0.330 2(8)	0.881 8(6)	C(68)	0.090 2(9)	0.198 2(9)	0.320 3(7)
C(19)	0.963 2(8)	0.167 3(8)	0.763 5(6)	C(69)	0.142 3(8)	0.180 5(8)	0.382 1(7)
C(20)	1.037 3(8)	0.104 1(8)	0.783 2(7)	C(70)	0.186 4(7)	0.297 6(7)	0.568 7(6)
C(21)	1.016 1(9)	0.021 4(9)	0.814 3(7)	C(71)	0.145 4(7)	0.281 6(7)	0.645 2(6)
C(22)	0.923 9(8)	0.002 3(8)	0.824 7(7)	C(72)	0.125 6(8)	0.351 9(8)	0.699 2(7)
C(23)	0.853 5(8)	0.068 4(8)	0.804 4(6)	C(73)	0.145 6(8)	0.437 1(8)	0.676 6(6)
C(24)	0.755 2(8)	0.104 0(8)	0.642 9(7)	C(74)	0.188 6(8)	0.455 4(8)	0.602 1(6)
C(25)	0.733 0(9)	0.045 8(9)	0.590 7(7)	C(75)	0.208 6(7)	0.384 4(8)	0.550 0(6)
C(26)	0.644 1(9)	0.025 0(9)	0.599 9(7)	C(76)	0.320 3(7)	0.206 8(7)	0.473 1(6)
C(27)	0.575 8(9)	0.057 2(9)	0.659 5(7)	C(77)	0.358 1(8)	0.195 9(8)	0.396 0(6)
C(28)	0.602 9(8)	0.116 7(8)	0.708 6(7)	C(78)	0.456 7(9)	0.181 3(9)	0.370 5(7)
C(29)	0.499 6(8)	0.333 6(8)	0.797 2(6)	C(79)	0.518(1)	0.179(1)	0.421 8(8)
C(30)	0.403 5(9)	0.357 9(9)	0.793 3(7)	C(80)	0.484(1)	0.191(1)	0.500 2(8)
C(31)	0.375 2(9)	0.367 4(9)	0.722 1(7)	C(81)	0.384 1(8)	0.204 7(8)	0.524 5(7)
C(32)	0.440 6(9)	0.353 7(9)	0.657 9(7)	C(82)	0.479(1)	0.437(1)	0.456(1)
C(33)	0.535 3(9)	0.330 0(9)	0.666 5(7)	C(83)	0.412(1)	0.503(1)	0.482 9(8)
C(34)	0.235 8(7)	0.309 1(7)	0.968 9(6)	C(84)	0.429(1)	0.566(1)	0.526(1)
C(35)	0.178 2(8)	0.363 7(8)	0.923 8(6)	C(85)	0.247(2)	0.768(2)	0.733(1)
C(36)	0.188 0(8)	0.454 9(8)	0.906 9(7)	C(86)	0.316(1)	0.773(1)	0.771(1)
C(37)	0.257 0(9)	0.495 1(9)	0.934 9(7)	C(87)	0.379(2)	0.708(2)	0.789(1)
C(38)	0.315 4(9)	0.441 5(9)	0.980 1(8)	C(88)	0.375(1)	0.628(2)	0.762(1)
C(39)	0.305 3(8)	0.350 3(8)	0.995 9(7)	C(89)	0.308(2)	0.609(2)	0.723(1)
C(40)	0.108 4(8)	0.201 6(8)	1.019 7(6)	B(1)	0.220 6(9)	0.204 0(9)	0.986 8(7)
C(41)	0.063 6(8)	0.260 0(8)	1.076 8(6)	B(2)	0.206 7(8)	0.219 0(9)	0.505 4(7)

after every hour; a decay was observed (23% in 63 h for **4** and 23% in 116 h for **8**) and linearly corrected. The data were collected only to $\theta < 20^\circ$ owing to decomposition and poor diffraction of the crystals. The data were corrected for Lorentz-polarization effects and absorption.²² The structure was solved by the heavy-atom method and refined by full-matrix least squares on F with anisotropic thermal parameters for the uranium and thf atoms in **4** and for the uranium atom in **8**. The hydrogen atoms were not introduced. There is a disordered pyridine molecule in the unit cell of **8** and the three peaks, close to an inversion centre, were assigned to C atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MoLEN system.²³ Analytical scattering factors were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion.²⁴ Crystallographic data are given in Table 3, final positional parameters in Tables 4 and 5.

Additional material available from the Cambridge Crystallo-

graphic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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