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

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The cationic organouranium(IV) compounds $[U(\eta\text{-}C_5H_5)_3(thf)]BPh_4$ (thf = tetrahydrofuran) **1**, $[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$ **2**, $[U(\eta\text{-}C_5R_5)_2(NEt_2)(thf)]BPh_4$ (R = H **3** or Me **4**), $[U(\eta\text{-}C_5Me_5)_2(NMe_2)(thf)]BPh_4$ **5**, $[U(\eta\text{-}C_8H_8)(NEt_2)(thf)_2]BPh_4$ **6**, $[U(\eta\text{-}C_5R_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$ (R = H **7** or Me **8**) have been synthesized from the neutral amide precursors by protonolysis of the $U\text{-}NR_2$ (R = Et or Me) bond with $NHEt_3BPh_4$; the crystal structures of **2** and **8** have been determined.

In the preceding paper,[1] we have presented the novel protonolysis reaction of a $U\text{-}NEt_2$ bond by means of $NHEt_3BPh_4$ [equation (1)], which served to prepare a number

$$[\{U\}\text{-}NEt_2] + NHEt_3BPh_4 \longrightarrow [\{U\}]BPh_4 + NHEt_2 + NEt_3 \quad (1)$$

of mono- and di-cations from the uranium tetramide $[U(NEt_2)_4]$ and chloroamides $[U(NEt_2)Cl_3(thf)]$ and $[U(NEt_2)_2Cl_2]$. It was obvious that reaction (1) would be useful for the synthesis of cationic organometallic compounds.[2] Organouranium cations are not numerous and with the exception of $[U(\eta\text{-}C_5H_4R)_3]^+$ (R = H,[3] Bu^t or SiMe$_3$[4]) and $[U(\eta\text{-}C_5H_5Me_2)_2]^+$,[5] which were synthesized by protonolysis of a U–H or a U–C bond, all have been prepared by heterolytic cleavage of a metal–halogen bond. A series of tris-cyclopentadienyl cations $[U(\eta\text{-}C_5H_5)_3L_2]^+$ [L = RCN (R = Me, Et, Pr^n or Ph) or $C_6H_{11}NC$],[6] two arene cations, $[U_2(\eta\text{-}C_6Me_6)_2Cl_7]^+$ and $[U_3(\eta\text{-}C_6Me_6)_3(AlCl_4)_3Cl_5]^+$,[7] and two indenyl cations, $[U(C_9H_7)Br_2(MeCN)_4]^+$ and $[\{U(C_9H_7)Br(MeCN)_4\}_2O]^{2+}$,[8] have been so far described. Here we report on some unique examples of cationic mono- and bis-cyclopentadienyl, cyclooctatetraene and mixed-ring complexes of uranium(IV) that have been obtained by protonolysis of their amide precursors; two of these have been characterized by their X-ray crystal structure, $[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$ and $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$ (thf = tetrahydrofuran).

Results and Discussion

Synthesis.—The protonolysis reaction (1) was first applied to the tris(cyclopentadienyl)diethylamidouranium $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$ in tetrahydrofuran and gave immediately the cationic compound $[U(\eta\text{-}C_5H_5)_3(thf)]BPh_4$ **1** which was isolated in 90% yield as a pale brown microcrystalline powder (Scheme 1). Not surprisingly, **1** was transformed into the chloride $[U(\eta\text{-}C_5H_5)_3Cl]$ by addition of NBu_4Cl and was reduced to $[U(\eta\text{-}C_5H_5)_3(thf)]$ by means of sodium amalgam (NMR experiments). Protonolysis of $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$ with $NHEt_3BPh_4$ in benzene afforded, after 1 h at 20 °C, the free amine NEt_3 and a brown precipitate which could be dissolved in thf by forming **1** and 1 equivalent of free $NHEt_2$; these facts suggested that the brown powder was $[U(\eta\text{-}C_5H_5)_3(NHEt_2)]BPh_4$. These adducts $[U(\eta\text{-}C_5H_5)_3L]BPh_4$ (L = thf or $NHEt_2$) could not be transformed, even upon prolonged heating under vacuum, into the base-free complex $[U(\eta\text{-}C_5H_5)_3]BPh_4$. This latter was however claimed to have been isolated by two methods; the first was by treatment of $[U(\eta\text{-}C_5H_5)_4]$ with NH_4BPh_4 in toluene[3] and the beige product was extracted in thf, whereas the second was by dehydration of the aqua cation $[U(\eta\text{-}C_5H_5)_3(H_2O)_2]BPh_4$ and the beige-brown product was found to decompose in tetrahydrofuran or toluene.[6,9] These unexpected and contradictory results cast some doubt on the formulation of these compounds as the genuine co-ordinatively unsaturated salt $[U(\eta\text{-}C_5H_5)_3]BPh_4$.

It was interesting to compare the protonolysis of a $U\text{-}NR_2$ bond with that of a U–R bond. A number of organothorium cations have been synthesized by treating the corresponding alkyl precursors with $NHEt_3BPh_4$[10] and **1** was similarly obtained in thf from $[U(\eta\text{-}C_5H_5)_3Bu^n]$. However, this transformation was much slower than reaction (1), requiring 10 h for completion; this difference is easily explained by the more facile attack of the proton onto the nitrogen atom.

In the same way as for **1**, the series of compounds **2–8** were prepared in thf from the corresponding amide precursors (Schemes 1 and 2); the yields varied from 50 to 87%. These are unique examples of cationic monocyclopentadienyl (**2**), bis-cyclopentadienyl (**3**, **4** and **5**), cyclooctatetraene (**6**) and mixed-ring (**7** and **8**) complexes of uranium(IV). The convenient and efficient syntheses of compounds **1–8** emphasize the general applicability of the protonolysis reaction (1). This reaction was also useful for the transformation of $[U(\eta\text{-}C_8H_8)(NEt_2)_3]$ into $[U(\eta\text{-}C_8H_8)(NEt_2)_2(thf)]BPh_4$, the first cationic uranium(V) compound to have been isolated[2] and which was alternatively synthesized by oxidizing $[U(\eta\text{-}C_8H_8)(NEt_2)_2]$ with $AgBPh_4$.[11]

It is noteworthy that cationic amide complexes of the d and f elements are very rare, despite their potential interest in catalytic and stoichiometric organic processes.[12] Amide cations would also be quite useful in organometallic synthesis, taking

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

advantage of the high reactivity of the U–NR_2 bond and of the facile formation of neutral compounds by nucleophilic addition. Some examples are shown in Schemes 1 and 2: (*i*) **1** was obtained by treatment of $[U(NEt_2)_3]BPh_4$ with an excess of cyclopentadiene, (*ii*) $[U(\eta\text{-}C_8H_8)(NEt_2)_2]$, the precursor of **6**, was synthesized by treating $[U(NEt_2)_2(thf)_3][BPh_4]_2$ with $K_2(C_8H_8)$ whereas (*iii*) $[U(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)(NEt_2)]$ and $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(NEt_2)]$, the precursors of **7** and **8**, were isolated from the reactions of **6** and $K(C_5H_5)$ or $K(C_5Me_5)$ and (*iv*) **7** was prepared by treating **6** with cyclopentadiene. Other reactions of cationic uranium amide compounds, including insertion of small molecules into the U–NR_2 bond, will be presented in a forthcoming paper.

Compounds **1**–**8** have been characterized by their elemental analyses and their ^1H NMR spectra (Table 1) and, in the case of **2** and **8**, by their X-ray crystal structure.

Crystal Structures.—The crystals of $[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$ **2** and $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$ **8** are composed of discrete cation–anion pairs; two independent and identical pairs are present in the unit cell of **2**. The BPh_4 anions display the expected geometry; ORTEP drawings[13] of the cations are shown in Figs. 1 and 2, and selected bond distances and angles are listed in Table 2. The five co-ordination of the

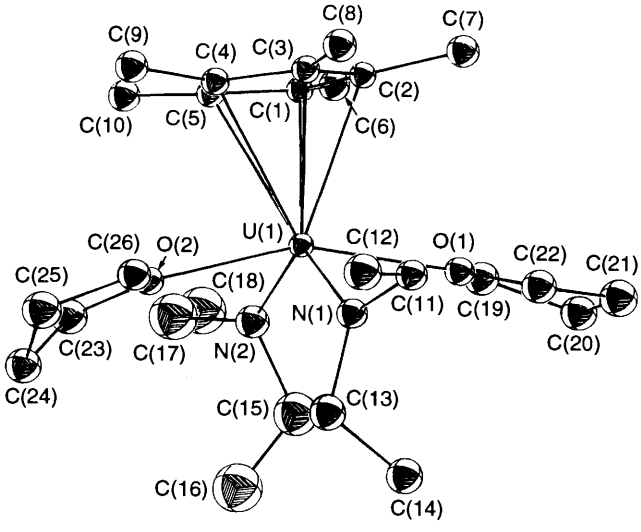


Fig. 1 Perspective view of one of the two independent cations $[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]^+$. Labels A have been omitted

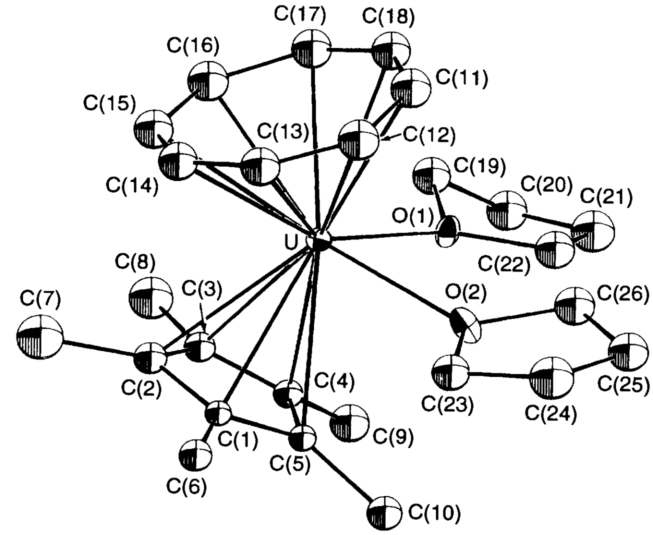
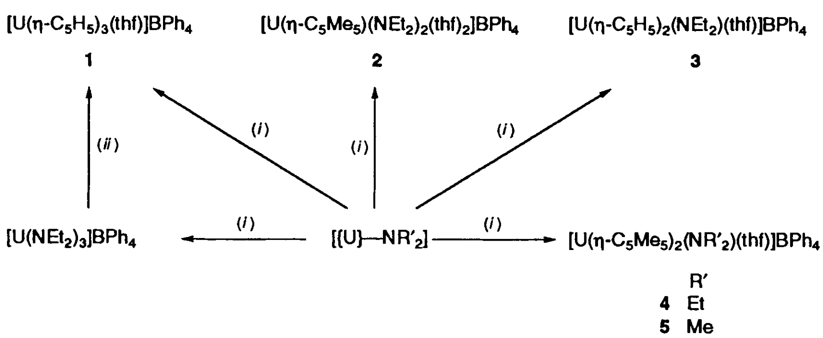
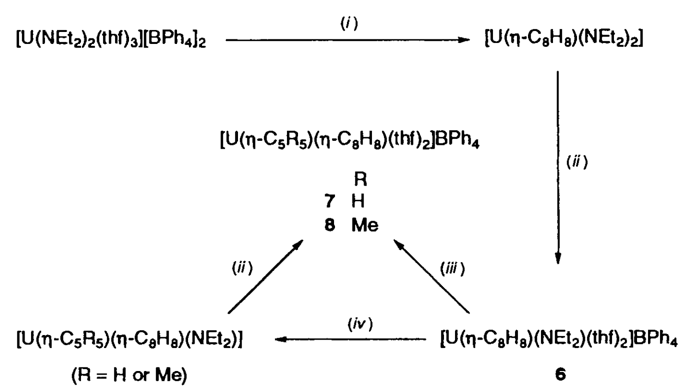


Fig. 2 Perspective view of the cation $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(thf)_2]^+$



Scheme 1 Synthesis of the cationic cyclopentadienyl complexes of uranium(IV) **1**–**5**. (*i*) $NHEt_3BPh_4$; (*ii*) cyclopentadiene. All reactions in thf



Scheme 2 Synthesis of the cationic cyclooctatetraene and mixed-ring uranium(IV) complexes **6**, **7** and **8**. (*i*) $K_2(C_8H_8)$; (*ii*) $NHEt_3BPh_4$; (*iii*) cyclopentadiene; (*iv*) $K(C_5H_5)$ or $K(C_5Me_5)$. All reactions in thf

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

Compound	Analyses [a] (%)	NMR data [b]
1 $[U(\eta\text{-}C_5H_5)_3(thf)]BPh_4$	C 60.9 (60.65) H 4.9 (4.7) B 1.35 (1.4)	6.15 (20 H, Ph), −3.77 (15 H, C_5H_5)
2 $[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$	C 60.95 (61.2) H 7.15 (7.3) N 2.7 (2.85)	38.42 (8 H, s, $w_{\frac{1}{2}}$ 55, CH_2), 9.28 (12 H, Me), 6.16 (20 H, Ph), 0.45 (15 H, C_5Me_5)
3 $[U(\eta\text{-}C_5H_5)_2(NEt_2)(thf)]BPh_4$	C 60.4 (60.65) H 5.8 (5.8) N 1.6 (1.7)	102.40 (4 H, q, *J* 6, CH_2), 35.90 (6 H, *J* 6, Me), 6.26 (20 H, Ph), −18.38 (10 H, C_5H_5)
4 $[U(\eta\text{-}C_5Me_5)_2(NEt_2)(thf)]BPh_4$	C 63.95 (64.25) H 6.9 (7.05) N 1.45 (1.45)	22.14 (4 H, s, $w_{\frac{1}{2}}$ 45, CH_2), 8.17 (30 H, C_5Me_5), 6.24 (6 H, Me), 5.90 (20 H, Ph)
5 $[U(\eta\text{-}C_5Me_5)_2(NMe_2)(thf)]BPh_4$	C 63.35 (63.60) H 6.8 (6.85) N 1.5 (1.5)	27.85 (6 H, Me), 8.38 (30 H, C_5Me_5), 6.1 (m, 20 H, Ph)
6 $[U(\eta\text{-}C_8H_8)(NEt_2)(thf)_2]BPh_4$	C 59.90 (60.2) H 6.05 (6.2) N 1.6 (1.6)	[c]122.02 (4 H, CH_2), 44.24 (6 H, Me), 6.9 (20 H, Ph), −27.13 (8 H, C_8H_8), 3.58 and 1.61 (2 × 8 H, thf)
7 $[U(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$	C 61.85 (62.05) H 5.4 (5.65) B 1.1 (1.25)	[d]24.66 (5 H, C_5H_5), 6.61 (20 H, Ph), −34.87 (8 H, C_8H_8), 3.50 and 1.79 (2 × 8 H, thf)
8 $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$	C 63.55 (63.85) H 6.2 (6.3) B 1.15 (1.15)	[c]15.41 (15 H, C_5Me_5), 6.9 (20 H, Ph), 3.74 and 1.73 (2 × 8 H, thf), −32.88 (8 H, C_8H_8)
$[U(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_8)(NEt_2)]$	C 42.5 (42.6) H 4.7 (4.85) N 2.75 (2.9)	[e]111.31 (4 H, s, $w_{\frac{1}{2}}$ 50, CH_2), 18.99 (6 H, Me), −31.95 (5 H, C_5H_5), −36.20 (8 H, C_8H_8)
$[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(NEt_2)]$	C 47.75 (48.1) H 5.9 (6.05) N 2.45 (2.55)	[e]93.43 and 70.93 (2 H + 2 H, CH_2), 13.11 (6 H, Me), −4.01 (15 H, C_5Me_5), −35.78 (8 H, C_8H_8)

[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 $w_{\frac{1}{2}}$ = 10–30 Hz. Solvent is $[^2H_8]$tetrahydrofuran unless otherwise specified. [c] In $[^2H_5]$pyridine. [d] In $[^2H_3]$acetonitrile. [e] In $[^2H_6]$benzene.

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

$[U(\eta\text{-}C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$ **2** [a]			
U–N(1)	2.17(1)	U–C(2)	2.72(1)
U–N(2)	2.18(1)	U–C(3)	2.75(1)
U–O(1)	2.475(9)	U–C(4)	2.76(1)
U–O(2)	2.462(9)	U–C(5)	2.82(1)
U–C(1)	2.80(1)	U–Cent(1) [b]	2.50(1)
O(1)–U–O(2)	157.5(3)	Cent(1)–U–N(2)	113.1(4)
N(1)–U–N(2)	114.8(5)	Cent(1)–U–O(1)	103.1(4)
Cent(1)–U–N(1)	131.8(4)	Cent(1)–U–O(2)	99.3(3)
$[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(thf)_2]BPh_4$ **8**			
U–C(1)	2.73(1)	U–C(15)	2.63(2)
U–C(2)	2.75(2)	U–C(16)	2.62(2)
U–C(3)	2.74(2)	U–C(17)	2.64(2)
U–C(4)	2.75(2)	U–C(18)	2.68(2)
U–C(5)	2.73(1)	U–Cent(1) [b]	2.48(2)
U–C(11)	2.68(2)	U–Cent(2) [b]	1.96(2)
U–C(12)	2.65(2)	U–O(1)	2.56(1)
U–C(13)	2.64(2)	U–O(2)	2.57(1)
U–C(14)	2.65(2)		
Cent(1)–U–Cent(2)	139.6(5)	Cent(2)–U–O(1)	113.8(4)
Cent(1)–U–O(1)	96.1(5)	Cent(2)–U–O(2)	111.8(5)
Cent(1)–U–O(2)	97.2(4)	O(1)–U–O(2)	84.1(3)

[a] Only the data corresponding to the independent cation shown in Fig. 1 are given. [b] Cent(1) and Cent(2) are the centroids of the η-C_5Me_5 and η-C_8H_8 rings respectively.

uranium atom in the cation of **2** (Fig. 1) is rather unusual in 5f element chemistry;[14] in particular, the other rare monocyclopentadienyl actinide complexes which have been so far described are either tetrahedral $\{[U(\eta\text{-}C_5H_5)(BH_4)_3]\}$[15] or octahedral $\{[U(\eta\text{-}C_5H_5)Cl_3L_2]$ (L = oxygen or nitrogen ligand)$\}$.[16] The geometry of the cation is best described as a distorted trigonal bipyramid with the O(1)–U–O(2) axis deviating from linearity by 22.6(4)°. The equatorial base contains U, N(1), N(2) and the ring centroid (within ±0.02 Å) and is orthogonal to the plane passing through U, O(1) and O(2). The U–N bond distances, which average 2.17(1) Å, are similar to those determined in the cations $[U(NEt_2)_3(thf)_3]^+$ and $[U(NEt_2)_2(py)_5]^{2+}$.[1] The co-ordination of the η-C_5Me_5 and thf ligands is unexceptional.

We have attempted to determine the crystal structure of $[U(\eta\text{-}C_5H_5)_2(NEt_2)(thf)_2]BPh_4$, obtained by crystallization of **3** from tetrahydrofuran. The crystals were found to be monoclinic, belonging to space group $P2_1/n$, with a = 11.265(2), b = 25.909(6), c = 14.158(10) Å, β = 92.91(4)° and Z = 4. The structure could not be solved with a good accuracy because of the poor quality of the crystals giving insufficient data. However, the model clearly indicated that the amide and two thf ligands were lying in the equatorial girdle of the bent-sandwich complex, with a symmetrical arrangement, in contrast to that found in the thorium alkyl compound $[Th(\eta\text{-}C_5Me_5)_2(Me)(thf)_2]BPh_4$.[10]

Complex **8** is, after $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(dmbipy)]$ (dmbipy = 4,4′-dimethyl-2,2′-bipyridine),[17] the second mixed-ring uranium derivative to have been crystallographically characterized. In both compounds, the uranium centre is found in a pseudo-tetrahedral environment (Fig. 2); the η-C_5Me_5 centroid–U–η-C_8H_8 centroid angles are quite similar [139.6(5) and 138.2°] whereas the O–U–O and N–U–N angles are 84.1(3) and 64.6(4)° respectively. In **8**, the U–C(η-C_8H_8) and U–C(η-C_5Me_5) bond distances, which average 2.65(2) and 2.74(1) Å, are slightly shorter than those found in the trivalent compound $[U(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(dmbipy)]$ (2.703 and 2.752 Å), and compare well with those determined in other cyclooctatetraene[18] and pentamethylcyclopentadienyl uranium(IV) compounds.[19]

Experimental

The general methods and procedures were identical to those described in the preceding paper.[1] [U(η-C_5H_5)$_3$(NEt_2)],[20] [U(η-C_5H_5)$_3$$Bu^n$],[21] [U(η-$C_5Me_5$)($NEt_2$)$_3$],[22] [U(η-$C_5H_5$)$_2$($NEt_2$)$_2$],[23] [U(η-$C_5Me_5$)$_2$($NEt_2$)$_2$],[24] [U(η-$C_5Me_5$)$_2$($NMe_2$)$_2$],[24] [U($NEt_2$)$_3$]$BPh_4$[1] and [U($NEt_2$)$_2(thf)_3$][$BPh_4$]$_2$[1] were prepared by published methods.

[U(η-C_5H_5)$_3$(thf)]BPh_4 **1**.—(*a*) A round-bottom flask (50 cm^3) was charged with [U(η-C_5H_5)$_3$(NEt_2)] (310 mg, 0.61 mmol) and $NHEt_3BPh_4$ (240 mg, 0.57 mmol) and thf (20 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 15 min at 20 °C and a brown powder precipitated; after evaporation to dryness, the beige product was washed with toluene (3 × 20 cm^3) and dried under vacuum (421 mg, 90%).

(*b*) An NMR tube was charged with [U(NEt_2)$_3$]BPh_4 (10 mg, 13 μmol) in [$^2H_8$]tetrahydrofuran (0.3 cm^3) and an excess of freshly distilled cyclopentadiene (8 mm^3) was introduced *via* a microsyringe. After 1.5 h, the spectrum showed that **1** was formed in almost quantitative yield.

(*c*) An NMR tube was charged with [U(η-C_5H_5)$_3$$Bu^n$] (10 mg, 20 μmol) and $NHEt_3BPh_4$ (8.4 mg, 20 μmol) in [$^2H_8$]tetrahydrofuran (0.3 cm^3). After 10 h at 20 °C, the spectrum showed that the alkyl complex was completely transformed into **1**.

Reactions of **1** *with* $NBu^n{}_4Cl$ *and Sodium Amalgam.*—(*a*) An NMR tube was charged with **1** (10 mg, 12 μmol) and $NBu^n{}_4Cl$ (3.4 mg, 12 μmol) in [$^2H_8$]tetrahydrofuran (0.4 cm^3). After 10 min at 20 °C, the spectrum showed the complete transformation of **1** into [U(η-C_5H_5)$_3$Cl].[25]

(*b*) An NMR tube was charged with **1** (10 mg, 12 μmol) and 2% sodium amalgam (40 mg, 35 μmol Na) in [$^2H_6$]benzene (0.3 cm^3) and was immersed in an ultrasound bath (60 W, 40 kHz). After 90 min at 20 °C, the spectrum showed that **1** was completely reduced to [U(η-C_5H_5)$_3$(thf)].[26]

Reaction of [U(η-C_5H_5)$_3$(NEt_2)] *with* $NHEt_3BPh_4$ *in Benzene.*—An NMR tube was charged with [U(η-C_5H_5)$_3$(NEt_2)] (10 mg, 19.8 μmol), $NHEt_3BPh_4$ (8.3 mg, 19.8 μmol) and [U(η-C_5H_5)$_3$Cl] (1 mg) as internal standard in [$^2H_6$]benzene (0.3 cm^3). The tube was immersed in an ultrasound bath (60 W, 40 kHz) for 1 h at 20 °C. A brown powder precipitated and the spectrum showed the disappearance of [U(η-C_5H_5)$_3$(NEt_2)] and the formation of 1 equivalent of free NEt_3. The solution was evaporated to dryness and the residue, after being heated (50 °C) under vacuum for 3 h, was dissolved in [$^2H_8$]tetrahydrofuran (0.6 cm^3); the spectrum showed the presence of **1** and free $NHEt_2$ (1 equivalent).

[U(η-C_5Me_5)(NEt_2)$_2$(thf)$_2$]BPh_4 **2**.—A round-bottom flask (50 cm^3) was charged with [U(η-C_5Me_5)(NEt_2)$_3$] (237 mg, 0.4 mmol) and $NHEt_3BPh_4$ (147 mg, 0.35 mmol) and thf (20 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C. The volume of the red solution was reduced to 10 cm^3 and addition of pentane (30 cm^3) gave a brown oily material which was filtered off and was expanded into a brown powder under vacuum. The product was washed with pentane (30 cm^3) and dried under vacuum (235 mg, 69%). Crystals suitable for an X-ray diffraction study were obtained from thf–pentane.

[U(η-C_5H_5)$_2$(NEt_2)(thf)]BPh_4 **3**.—A round-bottom flask (50 cm^3) was charged with [U(η-C_5H_5)$_2$(NEt_2)$_2$] (410 mg, 0.8 mmol) and $NHEt_3BPh_4$ (329 mg, 0.78 mmol) and thf (20 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was slowly (1.5 h) heated to −10 °C and the volume of the solution was reduced to 10 cm^3. Pentane (5 cm^3) was condensed into the solution at −20 °C and the orange powder which precipitated was rapidly filtered off. A second recrystallization from thf–pentane afforded an orange powder of **3** which was filtered off and dried under vacuum (451 mg, 69%). The product was found to be contaminated by **1** (2% by NMR); this contamination was more extensive when the synthesis of **3** was carried out at room temperature.

[U(η-C_5Me_5)$_2$(NEt_2)(thf)]BPh_4 **4**.—A round-bottom flask

Table 3 Crystallographic data and experimental details for [U(η-C_5Me_5)(NEt_2)$_2$(thf)$_2$]BPh_4 **2** and [U(η-C_5Me_5)(η-C_8H_8)(thf)$_2$]BPh_4 **8**

Compound	2	8
Formula	$C_{50}H_{71}BN_2O_2U$	$C_{50}H_{59}BO_2U$
M	980.98	940.87
Crystal size/mm	0.60 × 0.40 × 0.30	0.40 × 0.30 × 0.20
Colour	Brown	Dark red
a/Å	16.832(10)	9.834(3)
b/Å	16.947(7)	14.172(3)
c/Å	17.752(10)	15.812(4)
α/°	101.64(4)	93.46(2)
β/°	98.96(5)	104.70(2)
γ/°	102.21(4)	91.91(2)
U/Å^3	4742(5)	2125(1)
Z	4	2
D_c/g cm^{-3}	1.374	1.470
μ(Mo-Kα)/cm^{-1}	32.815	36.571
F(000)	1992	944
Range of absolute transmission	0.778–0.999	0.732–0.999
Range *h*,*k*,*l*	0–16, −16 to 16, −17 to 17	0–9, −13 to 13, −15 to 15
Reflections collected		
Total	9229	4275
Unique	8825	3960
with $I > 3\sigma(I)$	5614	2673
No. of parameters	479	232
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.045	0.049
$R' = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w(\|F_o\|)^2]^{\frac{1}{2}}$	0.056	0.052
Maximum residual electron density/e Å^{-3}	0.831	0.752

Details in common: Triclinic, space group $P\bar{1}$, T = 294 K, $1 < \theta < 20°$, ω–2θ scan type, scan width $0.8 + 0.35 \tan\theta$, $w^{-1} = \sigma(F)^2 = [4F^2/\sigma(I)^2 + (0.04F^2)^2]^{\frac{1}{2}}$.

($50\ cm^3$) was charged with $[U(\eta-C_5Me_5)_2(NEt_2)_2]$ (203 mg, 0.31 mmol) and $NHEt_3BPh_4$ (129 mg, 0.30 mmol) and thf ($25\ cm^3$) was condensed into it at $-78\ °C$ under vacuum. The orange solution immediately turned red and the reaction mixture was stirred for 35 min at 20 °C; after evaporation to dryness, the red microcrystalline powder was washed with diethyl ether ($3 \times 10\ cm^3$) and dried under vacuum (252 mg, 85%).

$[U(\eta-C_5Me_5)_2(NMe_2)(thf)]BPh_4$ **5**.—A round-bottom flask ($100\ cm^3$) was charged with $[U(\eta-C_5Me_5)_2(NMe_2)_2]$ (1080 mg, 1.80 mmol) and $NHEt_3BPh_4$ (730 mg, 1.73 mmol) and thf ($50\ cm^3$) was condensed into it at $-78\ °C$ under vacuum. The reaction mixture was stirred for 20 min at 20 °C; after evaporation to dryness, the residue was dissolved in thf ($20\ cm^3$) and upon addition of pentane ($40\ cm^3$), a red microcrystalline powder precipitated. After filtration, the product was washed with diethyl ether ($3 \times 10\ cm^3$) and dried under vacuum (1420 mg, 87%).

$[U(\eta-C_8H_8)(NEt_2)_2]$.—(*a*) A round-bottom flask ($50\ cm^3$) was charged with UCl_4 (1000 mg, 2.63 mmol) and $LiNEt_2$ (416 mg, 5.2 mmol) and diethyl ether ($25\ cm^3$) was condensed into it at $-78\ °C$ under vacuum. The reaction mixture was stirred for 12 h at 20 °C and $K_2(C_8H_8)$ (480 mg, 2.6 mmol) was added to the green solution. After 15 min at 20 °C, the solution was

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for $[U(\eta-C_5Me_5)(NEt_2)_2(thf)_2]BPh_4$ **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	0.216 00(3)	0.469 91(3)	0.181 13(3)	U(2)	0.275 87(3)	0.949 16(3)	0.694 49(3)
O(1A)	0.180 9(5)	0.426 5(6)	0.299 5(5)	O(1B)	0.360 9(5)	0.862 3(5)	0.750 5(5)
O(2A)	0.304 6(5)	0.513 2(6)	0.091 2(5)	O(2B)	0.240 2(6)	1.046 7(5)	0.615 7(5)
N(1A)	0.288 9(6)	0.378 1(7)	0.179 0(6)	N(1B)	0.266 9(6)	0.862 7(6)	0.583 0(6)
N(2A)	0.278 3(8)	0.592 2(8)	0.258 5(7)	N(2B)	0.393 3(6)	1.042 1(7)	0.740 5(6)
C(1A)	0.060 6(7)	0.506 7(8)	0.158 0(7)	C(1B)	0.180 1(8)	0.881 2(8)	0.788 2(8)
C(2A)	0.047 5(8)	0.420 3(8)	0.140 7(8)	C(2B)	0.175 2(8)	0.962 9(9)	0.799 7(8)
C(3A)	0.072 7(8)	0.395 3(8)	0.069 1(8)	C(3B)	0.128 7(8)	0.972 8(8)	0.730 5(8)
C(4A)	0.107 1(8)	0.467 7(8)	0.046 6(8)	C(4B)	0.102 4(8)	0.893 9(8)	0.675 5(8)
C(5A)	0.099 9(8)	0.537 4(8)	0.099 2(8)	C(5B)	0.136 0(8)	0.837 0(8)	0.712 0(8)
C(6A)	0.029 6(9)	0.558 7(9)	0.222 8(8)	C(6B)	0.218(1)	0.840(1)	0.853(1)
C(7A)	−0.002 2(9)	0.360 4(9)	0.180 9(9)	C(7B)	0.203(1)	1.028(1)	0.881(1)
C(8A)	0.059 8(9)	0.305(1)	0.025 7(9)	C(8B)	0.096(1)	1.048(1)	0.722(1)
C(9A)	0.128 2(9)	0.469(1)	−0.033 8(9)	C(9B)	0.037(1)	0.873(1)	0.600(1)
C(10A)	0.115 1(9)	0.625 2(9)	0.089 0(9)	C(10B)	0.114(1)	0.740(1)	0.681 0(9)
C(11A)	0.248 5(9)	0.283(1)	0.150 2(9)	C(11B)	0.205 6(9)	0.800 0(9)	0.517 4(9)
C(12A)	0.276(1)	0.243(1)	0.076(1)	C(12B)	0.220(1)	0.710(1)	0.507(1)
C(13A)	0.377 8(9)	0.401(1)	0.206 0(9)	C(13B)	0.352(1)	0.875(1)	0.569(1)
C(14A)	0.406(1)	0.380(1)	0.283(1)	C(14B)	0.367(1)	0.911(1)	0.498(1)
C(15A)	0.344(1)	0.594(1)	0.323(1)	C(15B)	0.380 0(9)	1.111 5(9)	0.799 8(9)
C(16A)	0.423(2)	0.635(2)	0.326(2)	C(16B)	0.427(1)	1.117(1)	0.887(1)
C(17A)	0.282(2)	0.698(2)	0.258(2)	C(17B)	0.481(1)	1.055(1)	0.730(1)
C(18A)	0.252(2)	0.716(2)	0.307(2)	C(18B)	0.498(1)	1.118(1)	0.683(1)
C(19A)	0.158(1)	0.480(1)	0.364(1)	C(19B)	0.437(1)	0.888(1)	0.813 9(9)
C(20A)	0.165(1)	0.436(1)	0.432(1)	C(20B)	0.493(1)	0.836(1)	0.782(1)
C(21A)	0.157(1)	0.351(1)	0.399(1)	C(21B)	0.439 2(9)	0.763 0(9)	0.715 4(9)
C(22A)	0.184 4(9)	0.345(1)	0.315 2(9)	C(22B)	0.351 1(9)	0.771 3(9)	0.718 7(9)
C(23A)	0.351(1)	0.597(1)	0.093(1)	C(23B)	0.193(1)	1.020(1)	0.534(1)
C(24A)	0.425(1)	0.579(1)	0.056(1)	C(24B)	0.182(1)	1.093(1)	0.506(1)
C(25A)	0.388(1)	0.504(1)	−0.005(1)	C(25B)	0.217(1)	1.168(2)	0.571(1)
C(26A)	0.326(1)	0.453(1)	0.030(1)	C(26B)	0.267(1)	1.141(1)	0.639(1)
C(30A)	0.143 9(8)	0.923 9(8)	0.244 0(8)	C(30B)	0.171 3(7)	0.453 1(7)	0.667 9(7)
C(31A)	0.082 5(8)	0.863 3(9)	0.185 9(8)	C(31B)	0.121 0(9)	0.372 4(9)	0.629 6(9)
C(32A)	0.025 3(9)	0.800(1)	0.203 2(9)	C(32B)	0.040 3(8)	0.358 2(9)	0.580 2(8)
C(33A)	0.028 5(9)	0.797 6(9)	0.280 9(9)	C(33B)	0.011 8(9)	0.426 1(9)	0.569 7(9)
C(34A)	0.082 9(9)	0.857 9(9)	0.340 0(9)	C(34B)	0.060 4(8)	0.506 5(9)	0.605 8(8)
C(35A)	0.143 9(8)	0.922 3(9)	0.323 9(8)	C(35B)	0.138 8(8)	0.518 9(8)	0.654 6(8)
C(36A)	0.141 2(8)	1.049 3(8)	0.179 0(7)	C(36B)	0.297 5(7)	0.551 2(8)	0.786 8(7)
C(37A)	0.125 5(9)	1.046 2(9)	0.099 3(9)	C(37B)	0.382 0(8)	0.590 3(8)	0.810 9(8)
C(38A)	0.063(1)	1.084(1)	0.065(1)	C(38B)	0.415 0(9)	0.660 9(9)	0.874 0(9)
C(39A)	0.018(1)	1.125(1)	0.115(1)	C(39B)	0.356 8(9)	0.693(1)	0.914 6(9)
C(40A)	0.033(1)	1.127(1)	0.193(1)	C(40B)	0.273 3(9)	0.656 3(9)	0.893 7(9)
C(41A)	0.096 4(9)	1.092(1)	0.225 7(9)	C(41B)	0.242 5(8)	0.584 2(8)	0.829 3(8)
C(42A)	0.259 0(7)	0.965 7(8)	0.154 0(7)	C(42B)	0.272 2(8)	0.395 3(8)	0.762 7(8)
C(43A)	0.260 0(9)	0.879(1)	0.135 2(9)	C(43B)	0.207 8(8)	0.353 0(9)	0.793 0(8)
C(44A)	0.313(1)	0.852(1)	0.082(1)	C(44B)	0.217 3(9)	0.294(1)	0.840 3(9)
C(45A)	0.359(1)	0.911(1)	0.051 9(9)	C(45B)	0.296 4(9)	0.281(1)	0.861 2(9)
C(46A)	0.359 8(9)	0.994 6(9)	0.070 3(9)	C(46B)	0.358(1)	0.318(1)	0.833(1)
C(47A)	0.307 0(9)	1.019 9(9)	0.122 1(8)	C(47B)	0.354(1)	0.373(1)	0.782(1)
C(48A)	0.277 3(8)	1.061 6(8)	0.293 1(8)	C(48B)	0.321 7(8)	0.471 4(9)	0.646 5(8)
C(49A)	0.287(1)	1.148(1)	0.317 6(9)	C(49B)	0.342(1)	0.397(1)	0.609(1)
C(50A)	0.355(1)	1.195(1)	0.383(1)	C(50B)	0.388(1)	0.411(1)	0.538(1)
C(51A)	0.406(1)	1.161(1)	0.422 9(9)	C(51B)	0.400(1)	0.485(1)	0.523(1)
C(52A)	0.397 8(9)	1.076 1(9)	0.398 2(9)	C(52B)	0.381(1)	0.552(1)	0.556(1)
C(53A)	0.333 8(9)	1.025 1(9)	0.335 3(9)	C(53B)	0.341(1)	0.541(1)	0.621(1)
B(1)	0.203 3(9)	1.000(1)	0.217 0(9)	B(2)	0.265(1)	0.466(1)	0.716(1)

filtered, evaporated to dryness, leaving a brown powder which was washed with pentane (2 × 20 cm^3) and dried under vacuum (537 mg, 42%).

(*b*) An NMR tube was charged with [U(NEt$_2$)$_2$(thf)$_3$][BPh$_4$]$_2$ (11.5 mg, 9.3 μmol) and K$_2$(C$_8$H$_8$) (1.7 mg, 9.3 μmol) in [^{2}H$_8$]tetrahydrofuran (0.3 cm^3). The tube was immersed in the ultrasound bath for 5 min at 20 °C; a white precipitate of KBPh$_4$ appeared and the spectrum of the yellow-orange solution showed the formation of the unique product [U(η-C$_8$H$_8$)(NEt$_2$)$_2$].

[U(η-C$_8$H$_8$)(NEt$_2$)(thf)$_2$]BPh$_4$ **6**.—A round-bottom flask (50 cm^3) was charged with [U(η-C$_8$H$_8$)(NEt$_2$)$_2$] (335 mg, 0.69 mmol) and NHEt$_3$BPh$_4$ (282 mg, 0.67 mmol) and thf (25 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C and an orange powder precipitated; after evaporation to dryness, the orange microcrystalline product was washed with pentane (3 × 15 cm^3) and dried under vacuum (515 mg, 88%).

[U(η-C$_5$H$_5$)(η-C$_8$H$_8$)(NEt$_2$)].—A round-bottom flask (50 cm^3) was charged with [U(η-C$_8$H$_8$)(NEt$_2$)(thf)$_2$]BPh$_4$ **6** (500 mg, 0.57 mmol) and K(C$_5$H$_5$) (60 mg, 0.57 mmol) and thf (30 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 15 min at 20 °C and after evaporation to dryness, the residue was extracted with diethyl ether (20 cm^3); the solvent was evaporated off, leaving an orange powder. Another extraction with diethyl ether, followed by two similar extractions with toluene were necessary for complete elimination of KCl from the product which was isolated as an orange microcrystalline powder (179 mg, 65%). Molecular weight by osmometry in benzene = 531 (theoretical 479).

[U(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(NEt$_2$)].—A round-bottom flask (50 cm^3) was charged with [U(η-C$_8$H$_8$)(NEt$_2$)(thf)$_2$]BPh$_4$ (308 mg, 0.35 mmol) and K(C$_5$Me$_5$) (63 mg, 0.36 mmol) and thf (30 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C and after evaporation to dryness, the residue was extracted with pentane (20 cm^3); the solvent was evaporated off, leaving a red powder which was then extracted with diethyl ether (20 cm^3). A red microcrystalline powder of the product (95 mg, 49%) was obtained after evaporation to dryness. Molecular weight by osmometry in benzene = 589 (theoretical 549).

[U(η-C$_5$H$_5$)(η-C$_8$H$_8$)(thf)$_2$]BPh$_4$ **7**.—(*a*) A round-bottom flask (50 cm^3) was charged with [U(η-C$_8$H$_8$)(NEt$_2$)(thf)$_2$]BPh$_4$ **6** (204 mg, 0.23 mmol) in thf (30 cm^3) and freshly distilled cyclopentadiene (0.06 cm^3) was introduced *via* a microsyringe. The reaction mixture was stirred for 60 h at 20 °C and the brown powder which precipitated was filtered off, washed with pentane (3 × 20 cm^3) and toluene (2 × 15 cm^3) and dried under vacuum (154 mg, 76%).

(*b*) An NMR tube was charged with [U(η-C$_5$H$_5$)(η-C$_8$H$_8$)(NEt$_2$)] (10 mg, 20 μmol) and NHEt$_3$BPh$_4$ (8.8 mg, 20 μmol) in [^{2}H$_8$]tetrahydrofuran (0.3 cm^3). The tube was immersed in the ultrasound bath and after 5 min at 20 °C, the spectrum of the solution showed that [U(η-C$_5$H$_5$)(η-C$_8$H$_8$)(NEt$_2$)] was completely transformed into **7**.

[U(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(thf)$_2$]BPh$_4$ **8**.—A round-bottom flask (50 cm^3) was charged with [U(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(NEt$_2$)] (51 mg, 93 μmol) and NHEt$_3$BPh$_4$ (35 mg, 83 μmol) and thf (15 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 35 min at 20 °C, filtered, evaporated to dryness, giving an oil which was rapidly expanded under vacuum. The orange powder was washed with diethyl ether (15 cm^3), recrystallized from thf–diethyl ether and the product was dried under vacuum (39 mg, 50%).

Crystal Structure Determinations of [U(η-C$_5$Me$_5$)(NEt$_2$)$_2$(thf)$_2$]BPh$_4$ **2** *and* [U(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(thf)$_2$]BPh$_4$ **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 [λ(Mo-Kα) = 0.700 73 Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections 8 < θ < 12°. Three standard reflections were measured after every hour; a decay was observed (11% in 102 h

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for [U(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(thf)$_2$]BPh$_4$ **8**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	0.024 51(7)	0.334 64(4)	0.223 96(4)	C(25)	0.224(2)	0.065(1)	0.373(1)
O(1)	−0.172 0(9)	0.206 9(6)	0.163 2(6)	C(26)	0.129(2)	0.106(1)	0.306(1)
O(2)	0.135 3(9)	0.208 0(7)	0.326 1(6)	C(27)	0.462(1)	0.737 3(9)	0.320 1(8)
C(1)	0.015(1)	0.435 2(9)	0.374 9(9)	C(28)	0.395(2)	0.767(1)	0.385(1)
C(2)	−0.051(2)	0.492(1)	0.309(1)	C(29)	0.390(2)	0.711(1)	0.454(1)
C(3)	−0.179(1)	0.442(1)	0.266 8(9)	C(30)	0.456(2)	0.630(1)	0.460(1)
C(4)	−0.189(2)	0.362(1)	0.304 9(9)	C(31)	0.525(2)	0.598(1)	0.403(1)
C(5)	−0.067(1)	0.356(1)	0.372 8(9)	C(32)	0.524(1)	0.654(1)	0.330 3(9)
C(6)	0.147(2)	0.463(1)	0.448(1)	C(33)	0.520(1)	0.750 2(9)	0.162 1(8)
C(7)	−0.012(2)	0.593(1)	0.301(1)	C(34)	0.443(1)	0.669 8(9)	0.121 6(8)
C(8)	−0.290(2)	0.479(1)	0.197(1)	C(35)	0.471(1)	0.619(1)	0.050 8(9)
C(9)	−0.320(2)	0.300(1)	0.292(1)	C(36)	0.579(2)	0.650(1)	0.021(1)
C(10)	−0.054(2)	0.285(1)	0.441(1)	C(37)	0.662(2)	0.727(1)	0.057(1)
C(11)	0.192(2)	0.248(1)	0.137(1)	C(38)	0.633(1)	0.778(1)	0.128 8(9)
C(12)	0.280(2)	0.303(1)	0.206(1)	C(39)	0.608(1)	0.884 6(9)	0.299 1(8)
C(13)	0.282(2)	0.400(1)	0.231(1)	C(40)	0.743(2)	0.861(1)	0.326 5(9)
C(14)	0.203(2)	0.471(1)	0.205(1)	C(41)	0.854(2)	0.922(1)	0.378(1)
C(15)	0.081(2)	0.482(2)	0.144(1)	C(42)	0.820(2)	1.004(1)	0.407(1)
C(16)	−0.011(2)	0.422(1)	0.079(1)	C(43)	0.692(2)	1.033(1)	0.385(1)
C(17)	−0.009(2)	0.328(1)	0.053(1)	C(44)	0.582(2)	0.974(1)	0.331 4(9)
C(18)	0.075(2)	0.257(1)	0.077(1)	C(45)	0.334(1)	0.856(1)	0.199 3(9)
C(19)	−0.288(2)	0.216(1)	0.088(1)	C(46)	0.332(2)	0.932(1)	0.149 3(9)
C(20)	−0.394(2)	0.143(1)	0.085(1)	C(47)	0.202(2)	0.970(1)	0.102(1)
C(21)	−0.318(2)	0.067(1)	0.123(1)	C(48)	0.087(2)	0.930(1)	0.111(1)
C(22)	−0.185(2)	0.110(1)	0.177(1)	C(49)	0.078(2)	0.860(1)	0.157(1)
C(23)	0.257(2)	0.228(1)	0.401(1)	C(50)	0.202(2)	0.820(1)	0.204(1)
C(24)	0.316(2)	0.140(1)	0.418(2)	B	0.481(2)	0.809(1)	0.246(1)

for **2** and 55% in 48 h for **8**) and linearly corrected. The data were collected only up to $\theta < 20°$ owing to decomposition and poor diffraction of the crystals. The data were corrected for Lorentz polarization effects and absorption.[27] 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 oxygen atoms. The hydrogen atoms were not introduced for **2** and introduced at calculated positions and constrained to ride on their C atoms for **8**. Two independent and identical cation–anion pairs were found in the unit cell of **2**. All calculations were performed on a Vax 4000–200 computer with the Enraf-Nonius MolEN system.[28] Analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion.[29] Crystallographic data are given in Table 3, final positional parameters in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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