

Synthesis of Organouranium(v) Compounds by Oxidation of Neutral Tetravalent Precursors. Crystal Structures of $[U(\eta\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3(\text{OC}_4\text{H}_8)][\text{BPh}_4]$ and $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{NEt}_2)_2][\text{BPh}_4]$, the First Cationic Uranium(v) Complexes

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The cationic organouranium(v) compounds $[U(\eta\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3(\text{thf})][\text{BPh}_4]$ **1**, $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{NEt}_2)_2][\text{BPh}_4]$ **2** and $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2(\text{thf})][\text{BPh}_4]$ **3**, were synthesized by oxidation of the corresponding neutral U^{IV} precursors using AgBPh₄; the neutral complex $[U(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)(\text{NEt}_2)_2]$ **4** was isolated from the reaction of $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]$ with $\text{Ti}(\eta\text{-C}_5\text{H}_5)$.

The synthesis of high-valent organouranium compounds remains a challenging goal and it is at present unclear whether the difficulties in isolating these complexes are due to their method of preparation or their inherent instability. The only successful approach to U^V compounds consisted in oxidizing trivalent precursors by means of organic azides or pyridine N-oxide; thus were prepared the imide and oxo derivatives $[U(\eta\text{-C}_5\text{H}_4\text{Me})_3(\text{NR})]$ (R = SiMe₃, Ph),¹ $[U(\text{cp}'')_2\text{Cl}(\text{NSiMe}_3)]$ [$\text{cp}'' = \eta\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$]² and $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{O-C}_6\text{H}_3\text{Pr}^{2-2,6})(\text{O})]$.³ Recently we have described the first organometallic U^{IV} → U^V transformation, *i.e.* the synthesis of $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_3]$ by electron transfer from the parent anion.⁴ We found that some neutral tetravalent uranium amide complexes could also undergo such a facile oxidation, leading to the corresponding U^V cations. Here we present the synthesis and characterization of $[U(\eta\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3(\text{thf})][\text{BPh}_4]$ **1**, $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{NEt}_2)_2][\text{BPh}_4]$ **2** and $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2(\text{thf})][\text{BPh}_4]$ **3**, including the crystal structures of **1** and **2**: to our knowledge, these are the first cationic U^V complexes to have been isolated.⁵ We also describe the preparation of the neutral mixed-ring derivative $[U(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)(\text{NEt}_2)_2]$ **4**.

Oxidation of $[U(\eta\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]^+$ (245 mg) by AgBPh₄ (199 mg) in thf (20 cm³) gave immediately the cationic U^V compound $[U(\eta\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3(\text{thf})][\text{BPh}_4]$ **1** and a grey precipitate of metallic silver; after filtration, the solution was evaporated and black needles of **1** were crystallized from thf-pentane (186 mg, 43%). The biscyclopentadienyl complex $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{NEt}_2)_2]^+$ (179 mg) was similarly treated with AgBPh₄ (118 mg) in thf (20 cm³); the reaction mixture was stirred at 20 °C for 10 h, filtered, evaporated to dryness and $[U(\eta\text{-C}_5\text{Me}_5)_2(\text{NEt}_2)_2][\text{BPh}_4]$ **2** was isolated as dark red crystals after crystallization from thf-diethyl ether (198 mg, 74%). The $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]^+$ cation was obtained in almost quantitative yield by reacting $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]$ with 1 equiv. of AgBPh₄ in thf (NMR experiment); the dark brown compound $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2(\text{thf})][\text{BPh}_4]$ **3** was previously isolated from the protonolysis reaction of $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_3]$ with $[\text{NEt}_3\text{H}][\text{BPh}_4]$.⁴ It is noteworthy that these preparations of **1–3** represent a new synthetic route to organouranium cations, which are rather limited.^{4,7} The factors, steric and electronic, which determine the stability of the +5 oxidation state are not yet fully understood. If **1** and **2** are quite stable in the solid state and in solution, **3** slowly decomposes in thf into $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)(\text{thf})_2][\text{BPh}_4]$, by homolytic cleavage of a U–N bond. It was previously reported that electrochemical oxidation of $[U(\eta\text{-C}_5\text{H}_5)_3(\text{NEt}_2)]$ gave unidentified products, presumably *via* the unstable species $[U(\eta\text{-C}_5\text{H}_5)_3(\text{NEt}_2)]^+$;⁸ we found that in the presence of AgBPh₄, $[U(\eta\text{-C}_5\text{H}_5)_3(\text{NEt}_2)]$ was transformed into the U^V cation $[U(\eta\text{-C}_5\text{H}_5)_3(\text{thf})]^+$ (quantitative yield by NMR).⁴ Under the same conditions, $[U(\eta\text{-C}_5\text{H}_5)_2(\text{NEt}_2)_2]$ was converted into a complex mixture containing $[U(\eta\text{-C}_5\text{H}_5)_2(\text{NEt}_2)(\text{thf})]^+$ and $[U(\eta\text{-C}_5\text{H}_5)_3(\text{thf})]^+$.

The neutral organouranium(IV) complexes considered above were all inert towards the thallium reagent TIBPh₄ which proved to be efficient in the oxidation of some U^{IV} anions.⁴ However, $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]$ (494 mg) was oxidized by $\text{Ti}(\eta\text{-C}_5\text{H}_5)$ (275 mg) in thf (50 cm³), leading to the formation of the mixed-ring derivative $[U(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)(\text{NEt}_2)_2]$ **4** and metallic thallium; after 1 h at 20 °C, the solution was filtered and evaporated to dryness and the dark red product was extracted in pentane and crystallized from this solvent (50% yield). It is then likely that this reaction, which represents a unique example of oxidation with $\text{Ti}(\eta\text{-C}_5\text{H}_5)$, does not involve the U^V cation $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]^+$ but proceeds by the intermediacy of the anion $[U(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{H}_5)(\text{NEt}_2)_2]^-$; the latter was made by addition of $\text{Na}(\eta\text{-C}_5\text{H}_5)$ to $[U(\eta\text{-C}_8\text{H}_8)(\text{NEt}_2)_2]$ and was oxidized into the U^V compound by TIBPh₄.[‡]

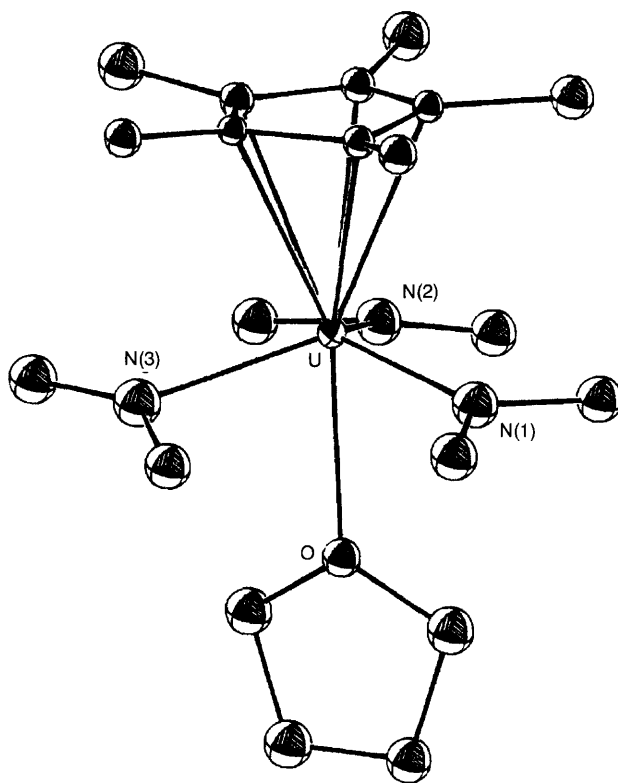


Fig. 1 The X-ray crystal structure of the cation in **1**. Carbon atoms labels have been omitted for clarity. Selected bond distances (Å) and angles (°): U–N(1) 2.25(2), U–N(2) 2.31(3), U–N(3) 2.35(5), U–O 2.55(2), <U–C> 2.76(1), U–1 2.47(4); N(1)–U–N(2) 117(1), N(1)–U–N(3) 111(2), N(2)–U–N(3) 119(1), O–U–1 179(2), O–U–N(1) 77.9(7), O–U–N(2) 78.4(9), O–U–N(3) 78(1). 1 denotes the centroid of the $\eta\text{-C}_5\text{Me}_5$ ligand.

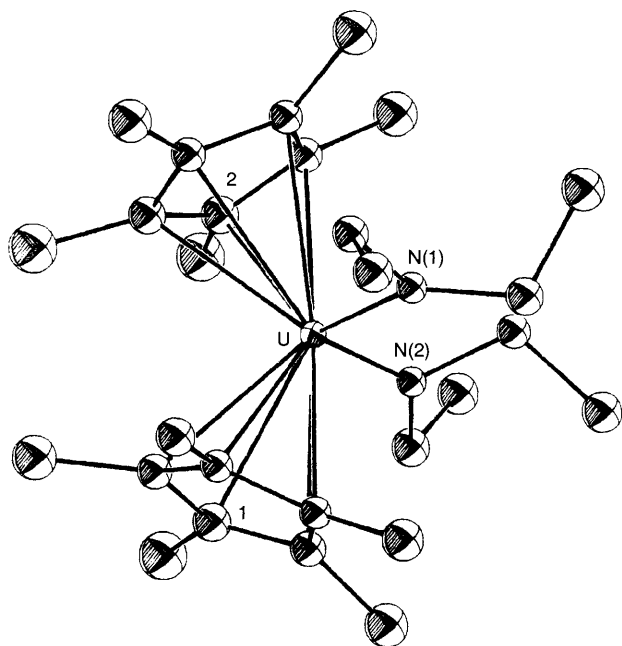


Fig. 2 The X-ray crystal structure of the cation in **2**. Carbon atoms labels have been omitted for clarity. Selected bond distances (Å) and angles (°): U–N(1) 2.167(9), U–N(2) 2.162(9), <U–C> 2.76(2), U–1 2.484(8), U–2 2.501(8); N(1)–U–N(2) 108.2(3), N(1)–U–1 103.1(5), N(1)–U–2 107.8(5), N(2)–U–1 101.9(5), N(2)–U–2 101.5(5), 1–U–2 132.6(5). 1 and 2 are the centroids of the η -C₅Me₅ ligands.

The new complexes gave satisfactory elemental analyses (C, H, N); their ¹H NMR spectra[‡] exhibit very broad resonances, consistent with a 5f¹ U^V metal centre. The crystal structures of **1** and **2** consist of discrete cation–anion pairs.[§] The BPh₄ anions display the expected geometry; ORTEP drawings of the cations are shown in Fig. 1 and 2 together with selected data. In the cation of **1**, the uranium atom is found in a pseudo trigonal bipyramidal environment; such five coordination is very rare for actinide complexes.⁹ The pyramid axis, which passes through the metal centre and the apical positions occupied by the ring centroid and the oxygen atom of the thf ligand, is essentially linear [179(2)°] and perpendicular to the equatorial base consisting of the three nitrogen atoms of the amide groups. The uranium atom is out of this trigonal base by 0.47(1) Å towards the η -C₅Me₅ ligand. The cation of **2** adopts the *pseudo* tetrahedral structure which is typical of the [M(η -C₅Me₅)₂X₂] fragment. The U–N bond lengths are different in compounds **1** and **2**, averaging respectively 2.30(5) and 2.164(3) Å; these values may be compared to those measured in the other two structurally characterized amide complexes of uranium(v), 2.295(10) Å in [(Me₃Si)₂N]₃U(NSiMe₃)¹⁰ and 2.156(4) Å in [UCl₂{N(CH₂CH₂PPri₂)₂}]₃.¹¹

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Footnotes

[†] [U(η -C₅Me₅)(NMe₂)₃] was prepared in 80% yield by treatment of UCl₄ (547 mg) with LiNMe₂ (221 mg) in thf (20 cm³) followed, after 5 h at 20 °C, by addition of K(η -C₅Me₅) (251 mg); the reaction mixture was stirred for 1.5 h, evaporated to dryness and the yellow product was extracted in pentane and crystallized from this solvent. Satisfactory elemental analyses. ¹H NMR

δ (60 MHz, 30 °C, in [²H₆] benzene): –0.43 (15 H, s, η -C₅Me₅) and –15.01 (18 H, s, Me).

[‡] ¹H NMR spectroscopic data: δ (60 MHz, 30 °C, in [²H₈] thf except **4** in [²H₆] benzene) **1**: 19.3 (15 H, w_{1/2} 160 Hz, η -C₅Me₅), 6.38 and 6.74 (20 H, s, Ph) and 6.5 (18 H, w_{1/2} 300 Hz, Me); **2**: 14.1 (38 H, w_{1/2} 85 Hz, CH₂ and η -C₅Me₅), 6.68 and 7.16 (20 H, Ph) and –4.7 (12 H, w_{1/2} 130 Hz, Me); **3**: 31.2 (8 H, w_{1/2} 360 Hz, CH₂), 6.44 (20 H, s, Ph), 3.8 (12 H, w_{1/2} 60 Hz, Me) and –15.3 (8 H, w_{1/2} 170 Hz, η -C₈H₈); **4**: 22.5 (8 H, w_{1/2} 370 Hz, CH₂), 0.35 (12 H, w_{1/2} 25 Hz, Me), –3.2 (5 H, w_{1/2} 95 Hz, η -C₅H₅) and –12.5 (8 H, w_{1/2} 120 Hz, η -C₈H₈); Na[U(η -C₈H₈)(η -C₅H₅)(NEt₂)₂] (at –23 °C): 22.19 and 12.97 (2 × 4 H, s, CH₂), 2.86 (12 H, s, CH₃), –28.29 (8 H, s, η -C₈H₈), –28.83 (5 H, s, η -C₅H₅).

[§] Crystal data for **1**: C₄₄H₆₁ON₃BU, *M* = 896.84, crystal dimensions (mm): 0.40 × 0.35 × 0.30; orthorhombic, space group *Pbca*, *a* = 19.003(5), *b* = 19.078(6), *c* = 22.659(7) Å, *V* = 8215(7) Å³, *Z* = 8, *D_c* = 1.450 g cm^{–3}, μ = 37.80 cm^{–1}, *F*(000) = 3608, *T*_{min} = 0.75, *T*_{max} = 1.20, *R* = 0.050 and *R_w* = 0.057 (*w* = 1) for 1704 observed reflections with *I* > 3σ(*I*) and 206 refined parameters, residual electron density: 0.791 e Å^{–3}; For **2**: C₅₂H₇₀N₂BU, *M* = 971.99, crystal dimensions (mm): 0.50 × 0.40 × 0.30, monoclinic, space group *P2₁/c*, *a* = 11.299(7), *b* = 21.324(6), *c* = 19.065(6) Å, β = 93.80(4)°, *V* = 4583(5) cm³, *Z* = 4, *D_c* = 1.409 g cm^{–3}, μ = 33.92 cm^{–1}, *F*(000) = 1972, *T*_{min} = 0.937, *T*_{max} = 1.184, *R* = 0.039 and *R_w* = 0.044 (*w* = 1) for 3147 observed reflections with *I* > 3σ(*I*) and 230 refined parameters, residual electron density = 0.660 e Å^{–3}. Data were collected at room temperature using an Enraf-Nonius CAD-4 diffractometer (Mo-K α radiation, λ = 0.71073 Å) in the range 2 < 2θ < 40°. Accurate unit cell parameters were obtained from least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. The intensities of three standard reflections were measured after each hour: a decay was observed (0.5% in 40 hrs for **1**, 0.6% in 60 hrs for **2**) and was linearly corrected. An empirical absorption correction was applied.¹² The structures were solved by the heavy-atom method and were refined by full-matrix least-squares (*F*) with *U* atoms refined anisotropically; H atoms were not introduced. Analytical scattering factors for neutral atoms were corrected for *f'* and *f''*. Crystallographic calculations were carried out on a VAX 4200 computer using the MolEN Enraf-Nonius package.¹³ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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