

## New Reactions of Uranium Amide Complexes leading to Pentavalent and Cationic Derivatives

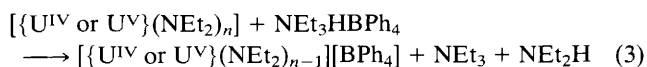
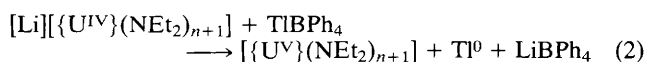
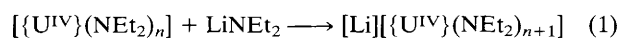
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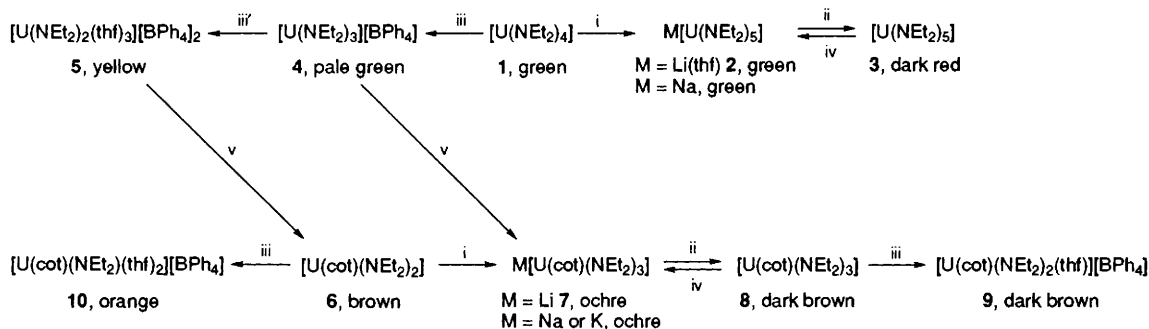
Protonolysis of U–N bonds in a series of uranium amide complexes by means of  $\text{NEt}_3\text{HBPh}_4$  gives the corresponding cationic compounds, whereas oxidation of anionic  $\text{U}^{\text{IV}}$  amide complexes by  $\text{TIBPh}_4$  affords the related pentavalent derivatives; thus the  $\text{U}^{\text{V}}$  compounds  $[\text{U}(\text{NEt}_2)_5]$ ,  $[\text{U}(\text{cot})(\text{NEt}_2)_3]$  and  $[\text{U}(\text{cot})(\text{NEt}_2)_2(\text{thf})][\text{BPh}_4]$  have been prepared (cot =  $\eta\text{-C}_8\text{H}_8$ , thf = tetrahydrofuran).

We report novel reactions of uranium amide complexes, depicted by eqns. (1), (2) and (3). These reactions are interesting as they constitute efficient and convenient syntheses of pentavalent and cationic uranium compounds. The only organouranium complexes in the +5 oxidation state are, at the present time, the imide derivatives  $[\text{U}(\text{C}_5\text{H}_4\text{-Me})_3(\text{NR})]$  (R =  $\text{SiMe}_3$ , Ph)<sup>1</sup> and  $[\text{U}(\text{cp}'')_2\text{Cl}(\text{NSiMe}_3)]^2$  [ $\text{cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$ ], which were synthesized by oxidation of the trivalent compounds  $[\text{U}(\text{C}_5\text{H}_4\text{Me})_3(\text{thf})]$  and  $[\text{U}(\text{cp}'')_2\text{Cl}(\text{thf})]$  (thf = tetrahydrofuran) with the organic azide  $\text{RN}_3$ . On the other hand, the number of organoactinide cations is rather limited and these have been prepared so far either by heterolytic cleavage of a metal halogen bond<sup>3</sup> or by protonolysis of a metal carbon bond.<sup>4</sup> While reaction (3) is unprecedented, it must be recalled that treatment of amide complexes with acidic proton substrates has been used

commonly to prepare a series of neutral derivatives, in particular with cyclopentadienyl or alkoxide ligands.<sup>5</sup> Reactions (1), (2) and (3) have been designed on the complexes  $[\text{U}(\text{NEt}_2)_4]^6$  and  $[\text{U}(\text{cot})(\text{NEt}_2)_2]$  (cot =  $\eta\text{-C}_8\text{H}_8$ ) (Scheme 1).



The anionic compound  $[\text{Li}(\text{thf})][\text{U}(\text{NEt}_2)_5]$  **2** was isolated in 73% yield from the reaction of  $\text{UCl}_4$  (800 mg) and  $\text{LiNEt}_2$  (833 mg) in thf (20  $\text{cm}^3$ ); after 2 h at 20 °C, the solution was



**Scheme 1** Reagents and conditions: i,  $\text{LiNEt}_2$ , 30 min; ii,  $\text{TIBPh}_4$ , immediate; iii and iii',  $\text{NEt}_3\text{HBPh}_4$ , 30 min; iv,  $\text{Na}(\text{Hg})$ , 15 min; v,  $\text{K}_2\text{cot}$ , 30 min. All reactions in  $\text{thf}$  at  $20^\circ\text{C}$ , except iii' at  $65^\circ\text{C}$ .

evaporated to dryness and the product was extracted in pentane and crystallized from this solvent. As expected, complex **2** was also formed by treating  $[\text{U}(\text{NEt}_2)_4]$  **1** with 1 equiv. of  $\text{LiNEt}_2$ , thus demonstrating that **1** is an electrophile, like the other  $\text{UX}_4$  compounds ( $\text{X} = \text{halogen, alkoxide, thiolate}$ )<sup>7</sup> which can be transformed into anions by addition of  $\text{X}^-$ . Oxidation of **2** (720 mg) by  $\text{TIBPh}_4$  (590 mg) in  $\text{thf}$  ( $20\text{ cm}^3$ ) gave immediately the pentavalent neutral compound  $[\text{U}(\text{NEt}_2)_5]$  **3**; the solution was filtered, evaporated and **3** was isolated as a pasty material from pentane (90% yield). Reduction of **3** by sodium amalgam gave back the anion  $[\text{U}(\text{NEt}_2)_5]^-$  (NMR experiment). Osmometric measurements showed that **3** is monomeric in benzene, like the other known pentamide complexes  $\text{Nb}(\text{NR}_2)_5$  and  $\text{Ta}(\text{NR}_2)_5$ .<sup>8</sup> Treatment of **1** (2770 mg) with  $\text{NEt}_3\text{HBPh}_4$  (2210 mg) in  $\text{thf}$  ( $50\text{ cm}^3$ ) afforded the cationic compound  $[\text{U}(\text{NEt}_2)_3][\text{BPh}_4]$  **4** in quantitative yield; the reaction mixture was stirred for 30 min at  $20^\circ\text{C}$ , and the product crystallized from  $\text{thf}$ -pentane. A refluxing  $\text{thf}$  solution of **4** and  $\text{NEt}_3\text{HBPh}_4$  (1 equiv.) deposited, within 30 min, a microcrystalline powder of  $[\text{U}(\text{NEt}_2)_2(\text{thf})_3][\text{BPh}_4]_2$  **5** in 88% yield.

Reaction (3) was also useful to prepare the cyclopentadienyl compounds  $[\text{U}(\text{cp})_3(\text{thf})][\text{BPh}_4]$  (beige, 90%) and  $[\text{U}(\text{cp})_2(\text{NEt}_2)(\text{thf})][\text{BPh}_4]$  (orange, 70%) from  $[\text{U}(\text{cp})_3(\text{NEt}_2)]$  and  $[\text{U}(\text{cp})_2(\text{NEt}_2)]$ <sup>5</sup> respectively ( $\text{cp} = \eta\text{-C}_5\text{H}_5$ ); formation of these cations was achieved after 15 min at  $20^\circ\text{C}$ , in contrast to the protonation of  $[\text{U}(\text{cp})_3\text{Me}]$  which required 10 h for completion.

The monocyclooctatetraenyl compound  $[\text{U}(\text{cot})(\text{NEt}_2)_2]$  **6** was synthesized in diethyl ether ( $25\text{ cm}^3$ ) by treatment of  $\text{UCl}_4$  (1000 mg) with  $\text{LiNEt}_2$  (416 mg) followed, after 12 h, by addition of  $\text{K}_2\text{cot}$  (480 mg); this second step was immediate and the solution was filtered, evaporated, leaving a powder which was washed with pentane (42% yield). By using the same procedures as above, the crystalline derivatives  $\text{Li}[\text{U}(\text{cot})(\text{NEt}_2)_3]$  **7**,  $[\text{U}(\text{cot})(\text{NEt}_2)_3]$  **8**,  $[\text{U}(\text{cot})(\text{NEt}_2)_2(\text{thf})][\text{BPh}_4]$  **9** and  $[\text{U}(\text{cot})(\text{NEt}_2)(\text{thf})_2][\text{BPh}_4]$  **10** were isolated in high yields (75–95%). The anion  $[\text{U}(\text{cot})(\text{NEt}_2)_3]^-$  and complex **6** were also prepared in almost quantitative yield by addition of  $\text{K}_2\text{cot}$  to the cations **4** and **5** respectively, or by sodium amalgam reduction of **8** and **9** respectively. Of particular interest are the compounds **8**, the first pentavalent organouranium complex to have been prepared from a  $\text{U}^{\text{IV}}$  precursor, and **9**, the unique example of a  $\text{U}^{\text{V}}$  organometallic cation.

In conclusion, the results indicate that the amide group should be a useful ligand to stabilize uranium complexes in the +5 oxidation state<sup>†</sup> and that formation of cationic compounds by protonolysis of uranium amide bonds should be a general reaction; moreover, these products should themselves undergo further transformations since the  $\text{U}-\text{N}$  bond is very reactive towards unsaturated molecules and compounds with acidic hydrogen.<sup>5</sup>

<sup>†</sup> Oxidation of the anions  $[\text{U}(\text{cot})\text{X}_3]^-$  ( $\text{X} = \text{BH}_4, \text{alkyl}$ )<sup>9</sup> did not afford  $\text{U}^{\text{V}}$  complexes.

The new complexes have been characterized by their  $^1\text{H}$  NMR spectra<sup>‡</sup> and, except for **7**, by their elemental analyses (C, H, N, B).

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<sup>‡</sup>  $^1\text{H}$  NMR spectroscopic data:  $\delta$  (60 MHz,  $30^\circ\text{C}$ , in  $[\text{D}_2\text{H}_8]\text{thf}$ , except **1**, **2**, **3**, **8** in  $[\text{D}_2\text{H}_8]\text{toluene}$  and **5** in  $[\text{D}_2\text{H}_5]\text{pyridine}$ ) **1**: 13.64 (16 H,  $\text{CH}_2$ ) and  $-2.41$  (24 H, Me); **2**: 9.23 (4 H, thf), 4.11 (4 H, thf), 1.39 (20 H,  $w_1$  40 Hz,  $\text{CH}_2$ ) and  $-2.10$  (30 H,  $w_1$  30 Hz, Me); **3**: 14.9 (20 H,  $w_1$  300 Hz,  $\text{CH}_2$ ) and 0.9 (30 H,  $w_1$  70 Hz, Me); **4**: 18.46 (12 H, q,  $J$  7 Hz,  $\text{CH}_2$ ), 6.44 (20 H, Ph) and 2.11 (18 H, t,  $J$  7 Hz, Me); **5**: 182.9 (8 H,  $w_1$  200 Hz,  $\text{CH}_2$ ), 68.1 (12 H,  $w_1$  56 Hz, Me) and 6.64 (40 H, Ph); **6**: 22.70 (8 H, q,  $J$  7 Hz,  $\text{CH}_2$ ), 5.85 (12 H, t,  $J$  7 Hz, Me) and  $-27.76$  (8 H, s, cot); **7**: 0.22 (12 H, q,  $J$  7 Hz,  $\text{CH}_2$ ),  $-1.39$  (18 H, t,  $J$  7 Hz, Me) and  $-15.84$  (8 H, cot); **8**: 13.8 (12 H,  $w_1$  200 Hz,  $\text{CH}_2$ ), 0.17 (18 H,  $w_1$  40 Hz, Me) and  $-9.5$  (8 H,  $w_1$  110 Hz, cot); **9**: 31.2 (8 H,  $w_1$  360 Hz,  $\text{CH}_2$ ), 6.44 (20 H, Ph), 3.8 (12 H,  $w_1$  60 Hz, Me) and  $-15.3$  (8 H,  $w_1$  170 Hz, cot); **10**: 122.59 (4 H,  $w_1$  35 Hz,  $\text{CH}_2$ ), 42.29 (6 H, Me), 6.49 (20 H, Ph) and  $-29.71$  (8 H, cot);  $[\text{U}(\text{cp})_3(\text{thf})][\text{BPh}_4]$ : 6.15 (20 H, Ph) and  $-3.77$  (15 H, cp);  $[\text{U}(\text{cp})_2(\text{NEt}_2)(\text{thf})][\text{BPh}_4]$ : 102.40 (4 H, q,  $J$  6 Hz,  $\text{CH}_2$ ), 35.90 (6 H, t,  $J$  6 Hz, Me), 6.26 (20 H, Ph) and  $-18.38$  (10 H, cp). When not specified, the signals are singlets with  $w_1 = 5\text{--}20$  Hz.