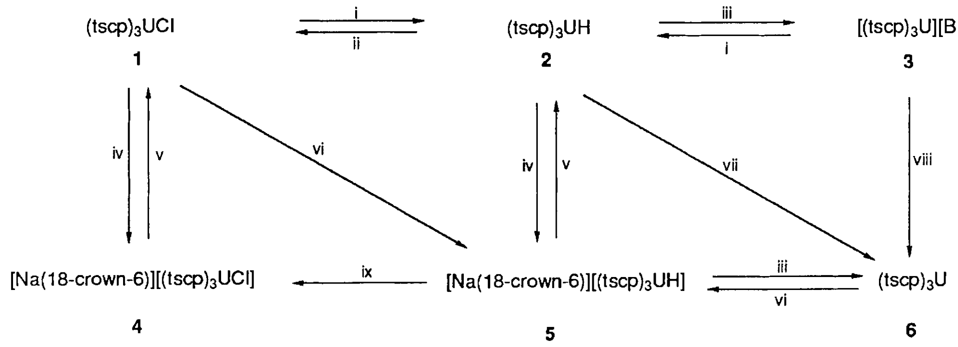
# $(\eta^5\text{-}C_5H_4SiMe_3)_3UH$: The First Stable Organouranium(IV) Hydride

**Jean-Claude Berthet, Jean-François Le Maréchal and Michel Ephritikhine***

*Service de Chimie Moléculaire, DSM, DPhG, CNRS URA 331, CEA CEN/Saclay, 91191 Gif sur Yvette Cédex, France*

The synthesis and reactions of $(tscp)_3UH$ and $[Na(18\text{-crown-}6)][(tscp)_3UH]$ (tscp = $\eta^5\text{-}C_5H_4SiMe_3$) are described.

Organoactinide hydrides in the +4 oxidation state are limited to the pair of bis(pentamethylcyclopentadienyl) complexes $[(C_5Me_5)_2MH_2]_2$ (M = Th, U);[1] however, the uranium derivative only exists under a dihydrogen atmosphere and is otherwise transformed, by easy and reversible elimination of $H_2$, into the $U^{III}$ hydride $(C_5Me_5)_2UH$.[2] This behaviour was interpreted in terms of the ready accessibility of the trivalent oxidation state for uranium. Here we report (*i*) a stable organouranium(IV) hydride $(tscp)_3UH$ **2** (tscp = $\eta^5\text{-}C_5H_4\text{-}SiMe_3$); (*ii*) its reversible reduction into [Na(18-crown-



**Scheme 1** *Reagents and conditions*: i, KBEt$_3$H; ii, CHCl$_3$; iii, NEt$_3$HBPh$_4$; iv, Na–Hg, 18-crown-6; v, TlBPh$_4$; vi, NaH, 18-crown-6; vii, UV radiation; viii, Na–Hg; ix, BuCl. All reactions in thf.

6)][(tscp)$_3$UH] **5**, the first anionic U$^{III}$ monohydride; and (*iii*) some reactions of these hydrides (Scheme 1).

The tris(trimethylsilylcyclopentadienyl)uranium(IV) hydride **2** was formed in tetrahydrofuran (thf) (20 ml) by treatment of the chloride **1**[3] (2.0 g) with an excess of KBEt$_3$H (3.5 ml of a 1 mol dm$^{-3}$ solution in thf); after 1 h at 60°C, the solution was evaporated *in vacuo* and the green product was extracted with pentane and crystallized from this solvent (1.88 g, 98%). The hydride **2** was found to be thermally stable in solution or in the solid state (no sign of decomposition after 20 h at 100°C) whereas it was quantitatively transformed into the trivalent metallocene (tscp)$_3$U **6**[3] by photolysis (450 W Hg lamp; 3 h); such activation of organotransition metal monohydrides by UV radiation is not common.[4] The hydridic character of **2** was evident from its reactions with chlorocarbons; reaction with chloroform gave the chloride **1** (quantitative yield by NMR spectroscopy). Protonation of **2** (150 mg) in thf (15 ml) by NEt$_3$HBPh$_4$ (97 mg) induced the immediate formation of [(tscp)$_3$U][BPh$_4$] **3**, with evolution of dihydrogen; this beige cationic compound was obtained pure in 86% yield after evaporation of the solvent and washing with pentane. Complex **3** was transformed back into **2** by treatment with KBEt$_3$H; similar reaction with LiBEt$_3$D gave the deuteride analogue of **2**. The cation **3** was converted into **6** by Na–Hg reduction (NMR experiments, quantitative yields).†

The sodium amalgam reduction of **2** in the presence of 1 equiv. of 18-crown-6 ether led to the rapid formation of the corresponding anionic compound [Na(18-crown-6)][(tscp)$_3$UH] **5**. This latter was alternatively prepared in almost quantitative yield by addition of sodium hydride (55 mg) to **6** (200 mg) in the presence of the crown ether (81 mg); after stirring for 3 days at 20°C in thf (15 ml), the solution was filtered and evaporated, leaving the product as a red powder. Similar treatment of **1** also gave **5** (quantitative yield by NMR spectroscopy). Reoxidation of **5** to **2** was easily performed by using TlBPh$_4$.† Protonation of **5** gave **6** with evolution of H$_2$ and its reaction with Bu$^n$Cl afforded the anionic uranium(III) chloride **4** (quantitative yield by NMR spectroscopy). Complex **4** was also obtained in 80% yield by reaction of **1** with sodium amalgam in the presence of 18-crown-6 ether; after the usual work up, **4** was isolated as red microcrystals from thf–pentane. Treatment of **4** with TlBPh$_4$ gave back the U$^{IV}$ chloride **1**.†

It is noteworthy that all attempts to isolate the monohydrides (RC$_5$H$_4$)$_3$UH (R = H, Me) have been unsuccessful[5] and that reactions of (RC$_5$H$_4$)$_3$UCl or (RC$_5$H$_4$)$_3$U with NaH gave the hydrido bridged anions [{(RC$_5$H$_4$)$_3$U}$_2$(μ-H)]$^-$;[6] the anionic species [{(tscp)$_3$U}$_2$(μ-H)]$^-$ was only detected (NMR) as an intermediate in the similar reactions of **1** and **6**. The surprising distinct reactivity which has been observed in the trimethylsilylcyclopentadienyl series can be tentatively accounted for by the weak electron attracting property of the SiMe$_3$ substituent.[7] Formation of the anion (tscp)$_3$UH$^-$ is clearly favoured by a decreasing electron density which, on the other hand, should be sufficient to stabilize the U$^{IV}$ oxidation state of (tscp)$_3$UH, avoiding its spontaneous reduction into (tscp)$_3$U.

The new complexes have been characterized by their elemental analyses (C, H, B, Si, Na, Cl) and their $^1$H NMR spectra.‡

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† The $^1$H NMR spectra of mixtures of **1** and **4**, **2** and **5**, or **3** and **6** in [$^2$H$_8$]thf exhibited single averaged resonances corresponding to the tscp and H ligands of the U$^{IV}$ and U$^{III}$ complexes which undergo a rapid and reversible electron transfer reaction.

‡ *Spectral data*. NMR spectra of the complexes in [$^2$H$_8$]thf: δ(60 MHz; 30°C): **2** 290.50 (1H, s, $w_{1/2}$ 10 Hz, UH), 26.71 and −12.57 (6H + 6H, s, CH) and −12.74 (27H, s, CH$_3$); **3** 6.52 (20H, s, Ph), 0.71 and −2.71 (6H + 6H, s, CH) and −3.52 (27H, s, CH$_3$); **4** 3.21 (24H, s, 18-crown-6), −3.05 and −19.34 (6H + 6H, s, CH) and −3.60 (27H, s, CH$_3$); **5** 547.1 (1H, br, $w_{1/2}$ 220 Hz, UH), 3.70 (24H, s, 18-crown-6), 0.45 and −19.68 (6H + 6H, s, CH) and −7.42 (27H, s, CH$_3$). IR, ν(U–H) cm$^{-1}$ (Nujol): **2**, 1395; **5**, 1405; these frequencies are shifted respectively to 1015 and 1020 cm$^{-1}$ in the spectra of the deuteride analogues.