Reactions of cp_3UCl ($cp = \eta\text{-}C_5H_5$) with Various Reducing Agents: Synthesis and Crystal Structure of the Uranium(III) Hydride $[(cp_3U)_2(\mu\text{-}H)][Na(THF)_2]$ (THF = tetrahydrofuran)

Jean-François Le Maréchal, Claude Villiers, Pierrette Charpin, Monique Lance, Martine Nierlich, Julien Vigner, and Michel Ephritikhine*

Service de Chimie Moléculaire, DLPC, CEA-CEN Saclay, IRDI/DESICP, CNRS UA 331, 91191 Gif sur Yvette Cédex, France

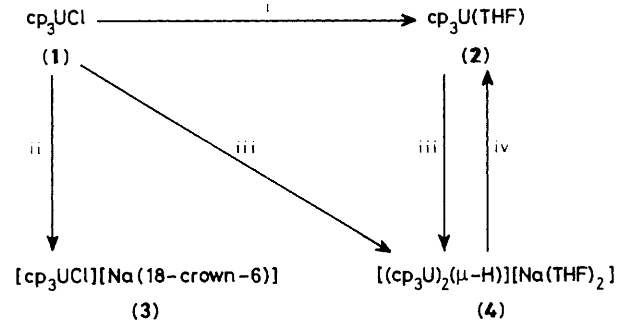
The compounds $cp_3U(THF)$ (**2**), $[cp_3UCl][Na(18\text{-crown-}6)]$ (**3**), and $[(cp_3U)_2(\mu\text{-}H)][Na(THF)_2]$ (**4**) ($cp = \eta\text{-}C_5H_5$, THF = tetrahydrofuran) were respectively prepared from cp_3UCl (**1**) by treatment with sodium amalgam, Na/Hg in the presence of 18-crown-6 ether, and NaH; the crystal structure of (**4**) has been determined.

Much attention should be paid to the reduction of U^{IV} compounds which represents the most attractive route to organouranium(III) complexes.[1] We found that the uranium(IV) chloride cp_3UCl (**1**) reacted with various reducing agents to give, not only the known neutral compound $cp_3U(THF)$ (**2**), but also the anionic derivatives $[cp_3UCl][Na(18\text{-crown-}6)]$ (**3**) and $[(cp_3U)_2(\mu\text{-}H)][Na(THF)_2]$ (**4**). Here we report the convenient and selective syntheses of these complexes and the *X*-ray crystal structure of (**4**).

Compound (**2**) was obtained in 70% yield from the reaction of (**1**)[2] (0.47 g) with a slight excess of 2% sodium amalgam (1.31 g) in THF (30 ml) (Scheme 1); the mixture was stirred for 24 h at 20 °C and the solution, after filtration and evaporation under vacuum, deposited air-sensitive brown crystals. The complex† was found to be identical to that prepared by treating UCl_3 with Kcp[4] or by reducing (**1**) with sodium naphthalide.[5] Similar Na/Hg reduction of (**1**) in the presence of 1 equiv. of 18-crown-6 ether led to the formation of the anionic U^{III} chloride (**3**), which was isolated as red crystals† from THF–pentane (55% yield). The cp_3UCl^- anion was previously observed after electrolysis of (**1**) but was not extracted from the supporting electrolyte.[6] It is noteworthy that the other tris(cyclopentadienyl)U^{III} anion, $(cp_3UBu^n)^-$, was formed by reduction of (**1**) with an excess of butyllithium.[7]

Another reduction of (**1**) (1.0 g) in THF (25 ml) was performed with sodium hydride (0.14 g);‡ after stirring for 48 h at 20 °C, the suspension was filtered and evaporated, leaving a red powder of (**4**) (0.81 g, 73%) which was recrystallized from THF–pentane.† A THF solution of (**4**) in the presence of 18-crown-6 ether deposited red crystals of $[(cp_3U)_2(\mu\text{-}H)][Na(18\text{-crown-}6)]$ (**5**).† The hydride (**4**) was alternatively prepared by the reaction of (**2**) with NaH; when treated with $(Et_3NH)(BPh_4)$ in $[^2H_8]$THF, (**4**) was quantitatively transformed into (**2**), with evolution of hydrogen (n.m.r. experiment).

Uranium hydrides are very rare and $(C_5Me_5)_2U(Me_2PCH_2CH_2PMe_2)H$ was the unique example of such a complex in the +3 oxidation state;[10] it was therefore of interest to determine the crystal structure of (**4**).§ It consists of infinite puckered chains of $(cp_3U)_2(\mu\text{-}H)$ and $Na(THF)_2$ fragments linked by Nacp bonds (Figure 1). The U–Na axis is perpendicular to the bridging cp plane at its centroid. The sodium atom, which is located on the mirror plane, has a tetrahedral environment: two cp ligands and two THF molecules partially disordered from the mirror plane. The geometry of the cp_3U moiety is unexceptional; the averaged U–C(ring) distance is equal to 2.82 Å and the three ring centroid–U–ring centroid angles are between 117 and 119°. The final difference map showed a peak (0, −0.0156, 0.0176; intensity 1 e $Å^{-3}$) which would correspond to the bridging hydride ligand. The latter would then occupy statistically two positions symmetrical with respect to the inversion centre, the



Scheme 1. *Reagents and conditions*: i, Na/Hg; ii, Na/Hg 18-crown-6; iii, NaH; iv, $(Et_3NH)(BPh_4)$. All reactions in THF.

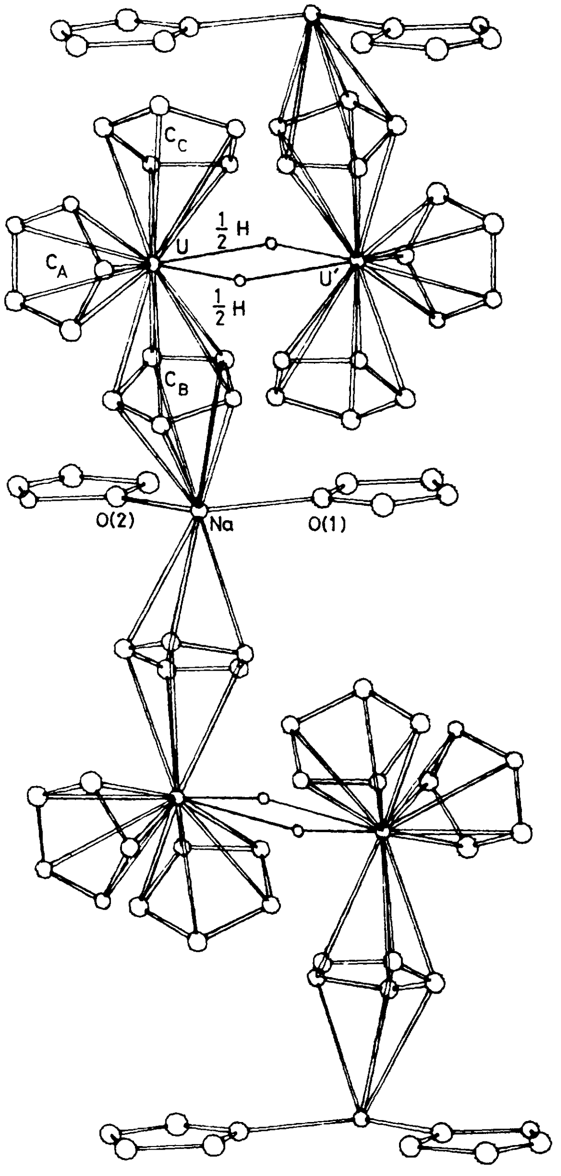


Figure 1. The *X*-ray crystal structure of (**4**). Some important distances and angles: U–C_A 2.49(2), U–C_B 2.57(2), U–C_C 2.55(2), U–U′ 4.403(2), Na–O(1) 2.33(4), Na–O(2) 2.30(4), Na–C_B 2.65(2) Å; <O(1)–Na–O(2) 109(2), O(1)–Na–C_B = O(2)–Na–C_B 104(2), C_B–Na–C_B 132°. C_A, C_B, and C_C are the ring centroids.

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† ^1H N.m.r. spectroscopic data; δ {60 MHz, 30 °C, in $[^2H_8]$ THF except (**2**) in $[^2H_8]$ toluene} (**2**): −13.52 (4H, s, β-THF), −15.24 (15H, s, cp), −30.55 (4H, s, α-THF); (**3**): 3.03 (24H, s, 18-crown-6), −13.95 (15H, s, cp); (**4**): 293 (1H, s, $w_{\frac{1}{2}}$ 55 Hz, U–H), −21.9 (30H, s, cp); (**5**): 293 (1H, s, $w_{\frac{1}{2}}$ 55 Hz, U–H), 3.55 (24H, s, 18-crown-6), −21.9 (30H, s, cp). The half height widths of the cp signals are in the range 12—18 Hz. The ^1H n.m.r. spectrum of (**2**) has not been previously reported; we also identified this compound obtained by the Na/Hg reduction of (**1**) by its *X*-ray crystal structure.[3] The new compounds gave satisfactory elemental analyses (C,H,U,Na).

‡ The product of this reaction has been misformulated as (**2**).[8] We previously synthesized the complexes cp_3URLi (R = Me, Bu^n) and $cp_3U(PhC{\equiv}CPh)$ from (**4**), thinking it was (**2**);[9] however, we found that these alkyl- and alkyne-U^{III} compounds could be effectively prepared from (**2**) by using the same experimental procedure.

§ *Crystal data for* (**4**): $C_{38}H_{47}O_2NaU_2$, orthorhombic, space group *Pnma*, $a = 10.595(4)$, $b = 18.866(4)$, $c = 16.866(3)$ Å, $U = 3550(3)$ $Å^3$, $Z = 4$, $D_c = 1.936$ g cm^{-3}, $\mu = 86.816$ cm^{-1}. Data were collected using an Enraf-Nonius CAD-4 diffractometer (Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.71073$ Å) in the range $2 < 2\theta < 50°$. 1423 reflections with $I > 2\sigma(I)$ were used after Lorentz–polarization, intensity decay (−5.3% after 27 h), and empirical absorption corrections. The structure was solved by the heavy-atom method and refined by full-matrix least squares (*F*). Only the U atom was refined anisotropically; the hydrogen atoms of the cp rings were introduced in idealized positions and constrained to ride on their parent carbon atoms. Analytical scattering factors for neutral atoms were corrected for f′ and f″. The final *R* values were $R = 0.066$ and $R_w = 0.082$ ($w = 1$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

U–H–U′ bridge being slightly bent (U–H–U′ = 160°) and asymmetric (U–H = 2 Å, U′-H = 2.4 Å).[11]

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