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Preliminary communication

Anionic cyclopentadienyluranium(III) complexes

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Abstract

The Na/Hg reduction of Cp_3UX (X = Me, n-Bu, BH_4) and $Cp_2U(BH_4)_2$ in the presence of 18-crown-6 ether has given the anionic uranium(III) complexes $[Cp_3UX][Na(18\text{-crown-}6)]$ and $[Cp_2U(BH_4)_2][Na(18\text{-crown-}6)]$; in agreement with cyclic voltammetry experiments, the borohydride anions were found to be reoxidized by $TlBH_4$ into the corresponding uranium(IV) complexes.

In contrast to the variety of the anionic lanthanide(III) complexes [1], few organometallic anions of uranium(III) have been isolated. The bis(pentamethylcyclopentadienyl) anion $Cp'_2UCl_2Na \cdot 2THF$ was obtained by the sodium amalgam reduction of Cp'_2UCl_2 [2], and the alkyl derivatives Cp_3URLi ($Cp = \eta\text{-}C_5H_5$, R = Me, n-Bu) were synthesized from the Cp_3UR compounds by treatment with an excess of alkyllithium [3]. Electrochemical studies showed that tricyclopentadienyluranium(IV) complexes could be reversibly reduced, but the compounds were not extracted from the supporting electrolyte, or in some cases reacted with it [4,5]. Here we describe the convenient synthesis and separation of anionic cyclopentadienyluranium(III) products, obtained by the sodium amalgam reduction of the corresponding uranium(IV).

The uranium(III) borohydride anions $Cp_3U(BH_4)^-$ and $Cp_2U(BH_4)_2^-$ were prepared in almost quantitative yield by the reaction at 20 °C of $Cp_3U(BH_4)$ [6] and $Cp_2U(BH_4)_2$, respectively [7], with a slight excess of Na/Hg in tetrahydrofuran (THF). The mixture was stirred for 1 h, and the solution was then decanted, filtered, and evaporated. In the presence of 1 equiv. of 18-crown-6 the compounds $[Cp_3U(BH_4)][Na(18\text{-crown-}6)]$ (I) and $[Cp_2U(BH_4)_2][Na(18\text{-crown-}6)]$ (II) were iso-

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lated as air sensitive red crystals from THF/pentane or THF/diethyl ether *. The borohydride anions were also prepared by treatment of (η^6-mesitylene)U$(BH_4)_3$ [8] with 2 and 3 equiv. of NaCp in THF. Compounds I and II were characterized by their elemental analyses (C, H, B) and their ^{1}H NMR spectra: δ (60 MHz, THF-d_8, 30 °C) I: 14.50 (4H, q, J 78 Hz, BH_4), 3.40 (24 H, s, 18-crown-6), −13.27 (15H, s, Cp). II: 61.08 (8H, q, J 78 Hz, BH_4), 3.54 (24 H, s, 18-crown-6), −13.75 (10H, s, Cp).

When treated with $TlBH_4$ in THF, I and II were readily reoxidized to the corresponding uranium(IV) complexes; this behaviour is in keeping with the electrochemical behaviour of these compounds. It has previously been demonstrated that the tricyclopentadienyluranium borohydride undergoes a simple one-electron quasi reversible reduction at $E_{1/2} = -1.33$ V vs. Ag/AgCl [5]. The cyclic voltammograms of $Cp_2U(BH_4)_2$ in THF (supporting electrolyte 0.15 M Bu_4NPF_6) at either platinum or gold electrode also exhibit a single and reversible wave at $E_{1/2}$ −0.96 vs. Ag/AgCl (the iR drop was corrected, $\Delta E_p = 60$ mV and $i_{pa}/ip_c = 0.82$ at 50 mV/s). Some reaction of $Cp_2U(BH_4)_2$ with the electrolyte solution was evidenced by the progressive attenuation of the oxidation and reduction peaks and by NMR spectroscopy; the unidentified product(s) appeared to be not electroactive.

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* Sodium amalgam reduction of Cp_3UR (R = Me, n-Bu) in the presence of the crown ether similarly gave the crystalline [Cp_3UR][Na(18-crown-6)] compounds, the ^{1}H NMR spectra of which agree with those previously reported [3].