

Pentadienyl, Cyclohexadienyl, and Arene Uranium Borohydride Complexes

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The compounds $(\eta\text{-}2,4\text{-dimethylpentadienyl})\text{U}(\text{BH}_4)_3$ (**2**) and $(\eta\text{-}6,6\text{-dimethylcyclohexadienyl})_2\text{U}(\text{BH}_4)_2$ (**5**) were obtained from the reactions of $\text{U}(\text{BH}_4)_4$ (**1**) with the corresponding potassium dienyl anions; treatment of $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_3\text{U}$ with TiBH_4 gave $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2$ (**3**) and the equimolecular mixture of (**5**) and (**1**) was transformed into $(\eta\text{-}6,6\text{-dimethylcyclohexadienyl})\text{U}(\text{BH}_4)_3$ (**4**), whereas reduction of (**1**) in mesitylene afforded the arene complex $(\eta\text{-mesitylene})\text{U}(\text{BH}_4)_3$ (**6**).

Although most of the organolanthanoid and actinoid complexes so far reported contain the ubiquitous cyclopentadienyl ligands ($\eta\text{-C}_5\text{H}_5$ and its modified analogues),¹ only the two open dimethylpentadienyl compounds $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_3\text{M}$ ($\text{M} = \text{Nd}, \text{U}$)^{2,3} have been described, and a cyclohexadienyl derivative of an f-element has not been reported. Here we present the synthesis of such dienyl complexes from uranium tetraborohydride $\text{U}(\text{BH}_4)_4$ (**1**);⁴ the latter was found to be also a precursor for the preparation of U^{III} arene compounds.

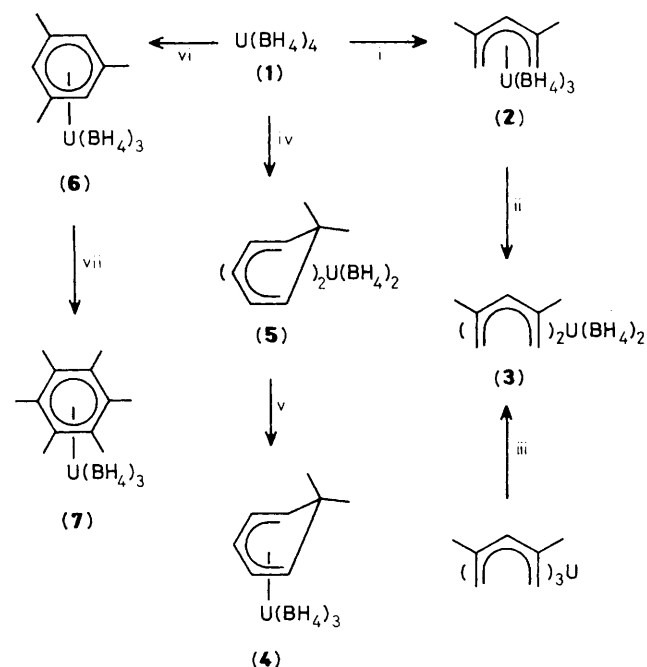
The reaction of (**1**) (76 mg) with 1 equiv. of the potassium salt of the dimethylpentadienyl anion $(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{K}$ ⁵ in toluene (5 ml) at 20 °C led to the immediate formation of a red precipitate of $\text{U}(\text{BH}_4)_3$ ⁶ in a green solution. After filtration, evaporation below 20 °C and sublimation (40 °C, 10^{-2} mmHg), green crystals of $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$ (**2**) were obtained in 32% yield (Scheme 1). Similar reactions with $(\text{C}_5\text{H}_7)\text{K}$ and $(3\text{-MeC}_5\text{H}_6)\text{K}$ gave small quantities (<5%) of the corresponding pentadienyl uranium compounds which were identified only by their ^1H n.m.r. spectra.[†] The synthesis of these derivatives, which is impeded by the concomitant reduction of (**1**), was not significantly improved by using the less reactive zinc or magnesium dienyl reagents. The bis-(dimethylpentadienyl) complex (**3**) was prepared in 50% yield from the reaction of $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)_3\text{U}^3$ (77 mg) with TiBH_4 (65 mg) in toluene (10 ml); the mixture was stirred at 20 °C for 2 h, filtered, and evaporated *in vacuo*, and the product was isolated as red crystals from toluene-pentane at -30 °C. Complex (**3**) was also formed in lower yield by the reaction of (**2**) with $(2,4\text{-Me}_2\text{C}_5\text{H}_5)_2\text{Mg}$.

The borohydride (**1**) (125 mg) reacted in toluene (20 ml) with 2 equiv. of the potassium anion $(\text{dmch})\text{K}$ ⁷ ($\text{dmch} = 6,6\text{-dimethylcyclohexadienyl}$) to give, after the usual work-up

and recrystallization from pentane at -78 °C, the brown compound $(\eta\text{-dmch})_2\text{U}(\text{BH}_4)_2$ (**5**) in 30% yield. Treatment of (**5**) with the stoichiometric amount of (**1**) in toluene led to the quantitative formation of the red mono(cyclohexadienyl) complex (**4**), which was purified by sublimation (20 °C; 10^{-2} mmHg).

Their spectroscopic data,[†] and their remarkable volatility and solubility in non-polar solvents indicate that complexes (**2**)–(**5**) have a covalent and monomeric structure, as does the cyclopentadienyl compound $(\text{cp})\text{U}(\text{BH}_4)_3$ ⁸ ($\text{cp} = \eta\text{-C}_5\text{H}_5$). All these air-sensitive complexes are stable in toluene up to 70–100 °C; however, in contrast to $(\text{cp})\text{U}(\text{BH}_4)_3$, compounds (**2**)–(**5**) undergo immediate reduction into uranium(III) tris-borohydrides⁶ upon addition of polar ligands.

The derivatives of $\text{U}(\text{BH}_4)_3$ are limited to some adducts with heteroatom ligands (O,P,N).⁶ We found that a solution of (**1**) (500 mg) in mesitylene (10 ml) deposited, after heating at 150 °C for 10 min, bright red crystals (80%) of the arene complex (**6**). The ^1H n.m.r. spectrum in toluene showed that the mesitylene ligand of (**6**) was reversibly dissociating in competition with the aromatic solvent. These labile ligands could be readily displaced by hexamethylbenzene to give compound (**7**) which was more resistant to arene ligand dissociation (<5% by n.m.r. in benzene). A few examples of



Scheme 1. Reagents and conditions: i, $(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{K}$; ii, $(2,4\text{-Me}_2\text{C}_5\text{H}_5)_2\text{Mg}$; iii, TiBH_4 ; iv, $(\text{dmch})\text{K}$; v, (**1**); vi, 150 °C in mesitylene; vii, C_6Me_6 . All reactions in toluene.

[†] Compounds (**2**)–(**7**) were characterized by their elemental analyses (C,H,B) and their i.r. and ^1H n.m.r. spectra. N.m.r. δ (60 MHz; 30 °C, $[\text{C}_6\text{H}_6]$ toluene) (**2**): 110.38 (12H, q, J 85 Hz, BH_4), -8.34 (6H, s, CH_3), -28.80 (1H, s, CH), -34.81 and -75.49 (2H and 2H, s, CH_2); (**3**): 65.99 (2H, s, CH), 4.03 (12H, s, CH_3), 0.53 (8H, q, J 85 Hz, BH_4), -55.24 and -86.35 (4H and 4H, s, CH_2); $(\eta\text{-C}_5\text{H}_7)\text{U}(\text{BH}_4)_3$: 107.04 (12H, q, J 85 Hz, BH_4), 18.53 (2H, br, W_1 30 Hz, 2,4-H), -9.88 (1H, br, t, W_1 18 Hz, 3-H), -37.49 (2H, d, J 10 Hz, 1,5-syn H), -68.51 (2H, d, J 15 Hz, 1,5-anti H); $(\eta\text{-}3\text{-MeC}_5\text{H}_6)\text{U}(\text{BH}_4)_3$: 137 (12H, br., W_1 340 Hz, BH_4), 48.90 (3H, s, CH_3), 16.43 (2H, br, t, W_1 29 Hz, 2,4-H), -41.55 (2H, d, J 10 Hz, 1,5-syn H), -62.58 (2H, d, J 15 Hz, 1,5-anti H); (**4**): 76.92 (12H, q, J 85 Hz, BH_4), 69.63 (1H, br, t, W_1 11 Hz, 3-H), 28.17 (2H, dd, J 7 and 5 Hz, 2,4-H), 12.57 and -22.32 (3H and 3H, s, CH_3), -55.74 (2H, d, J 7 Hz, 1,5-H); (**5**): 69.86 (8H, q, J 85 Hz, BH_4), 4.97 and -6.80 (6H and 6H, s, CH_3), 3.84 (4H, br, t, W_1 16 Hz, 2,4-H), -8.99 (2H, br., W_1 12 Hz, 3-H), -24.09 (4H, d, J 7 Hz, 1,5-H); (**6**): 150 (12H, br., W_1 480 Hz, BH_4), 7.2 and 2.3 (CH and CH_3 of free C_6H_{12}), -12.11 and -18.41 (CH and CH_3 of co-ordinated C_6H_{12}) (spin saturation transfer was observed between the signals of free and co-ordinated mesitylene which are in the ratio 90 : 10 at 30 °C and 60 : 40 at -50 °C); (**7**) (in C_6D_6): 150 (12H, br., W_1 530 Hz, BH_4), -13.90 (18H, s, CH_3). The i.r. spectra of the complexes (**2**)–(**7**) all exhibit the bands characteristic of tridentate BH_4 ligands.⁸

arene-uranium compounds with Cl and/or AlCl_4 ligands have previously been obtained from UCl_4 under reductive Friedel-Crafts conditions.⁹

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