Pentadienyl, Cyclohexadienyl, and Arene Uranium Borohydride Complexes

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The compounds (η-2,4-dimethylpentadienyl)$U(BH_4)_3$ **(2)** and (η-6,6-dimethylcyclohexadienyl)$_2U(BH_4)_2$ **(5)** were obtained from the reactions of $U(BH_4)_4$ **(1)** with the corresponding potassium dienyl anions; treatment of (η-2,4-$Me_2C_5H_5)_3U$ with $TlBH_4$ gave (η-2,4-$Me_2C_5H_5)_2$ $U(BH_4)_2$ **(3)** and the equimolecular mixture of **(5)** and **(1)** was transformed into (η-6,6-dimethylcyclohexadienyl)$U(BH_4)_3$ **(4)**, whereas reduction of **(1)** in mesitylene afforded the arene complex (η-mesitylene)$U(BH_4)_3$ **(6)**.

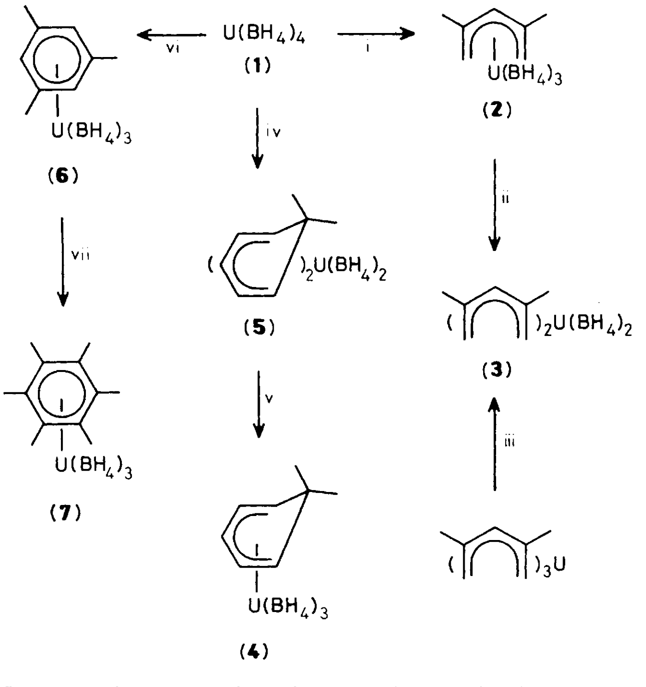
Although most of the organolanthanoid and actinoid complexes so far reported contain the ubiquitous cyclopentadienyl ligands (η-C_5H_5 and its modified analogues),[1] only the two open dimethylpentadienyl compounds (η-2,4-$Me_2C_5H_5)_3M$ (M = Nd,U)[2,3] have been described, and a cyclohexadienyl derivative of an f-element has not been reported. Here we present the synthesis of such dienyl complexes from uranium tetraborohydride $U(BH_4)_4$ (**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-$Me_2C_5H_5)K$[5] in toluene (5 ml) at 20 °C led to the immediate formation of a red precipitate of $U(BH_4)_3$[6] in a green solution. After filtration, evaporation below 20 °C and sublimation (40 °C, 10^{-2} mmHg), green crystals of (η-2,4-$Me_2C_5H_5)U(BH_4)_3$ (**2**) were obtained in 32% yield (Scheme 1). Similar reactions with $(C_5H_7)K$ and $(3\text{-}MeC_5H_6)K$ 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 (η-2,4-$Me_2C_5H_5)_3U$[3] (77 mg) with $TlBH_4$ (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-$Me_2C_5H_5)_2Mg$.

The borohydride (**1**) (125 mg) reacted in toluene (20 ml) with 2 equiv. of the potassium anion (dmch)K[7] (dmch = 6,6-dimethylcyclohexadienyl) to give, after the usual work-up and recrystallization from pentane at −78 °C, the brown compound (η-dmch)$_2U(BH_4)_2$ (**5**) in 30% yield. Treatment of (**5**) with the stoicheiometric 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 (cp)$U(BH_4)_3$[8] (cp = η-C_5H_5). All these air-sensitive complexes are stable in toluene up to 70—100 °C; however, in contrast to (cp)$U(BH_4)_3$, compounds (**2**)—(**5**) undergo immediate reduction into uranium(III) trisborohydrides[6] upon addition of polar ligands.

The derivatives of $U(BH_4)_3$ 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-$Me_2C_5H_5)K$; ii, (2,4-$Me_2C_5H_5)_2Mg$; iii, $TlBH_4$; iv, (dmch)K; v, (**1**); vi, 150 °C in mesitylene; vii, C_6Me_6. All reactions in toluene.

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† 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, [$^2H_8$]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); (η-$C_5H_7)U(BH_4)_3$: 107.04 (12H, q, *J* 85 Hz, BH_4), 18.53 (2H, br, $W_{\frac{1}{2}}$ 30 Hz, 2,4-H), −9.88 (1H, br.t, $W_{\frac{1}{2}}$ 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); (η-3-$MeC_5H_6)U(BH_4)_3$: 137 (12H, br., $W_{\frac{1}{2}}$ 340 Hz, BH_4), 48.90 (3H, s, CH_3), 16.43 (2H, br.t, $W_{\frac{1}{2}}$ 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 (12 H, q, *J* 85 Hz, BH_4), 69.63 (1H, br.t, $W_{\frac{1}{2}}$ 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, $W_{\frac{1}{2}}$ 16 Hz, 2,4-H), −8.99 (2H, br., $W_{\frac{1}{2}}$ 12 Hz, 3-H, −24.09 (4H, d, *J* 7 Hz, 1, 5-H); (**6**): 150 (12H, br., $W_{\frac{1}{2}}$ 480 Hz, BH_4), 7.2 and 2.3 (CH and CH_3 of free C_9H_{12}), −12.11 and −18.41 (CH and CH_3 of co-ordinated C_9H_{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., $W_{\frac{1}{2}}$ 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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