

Cyclohexadienyl uranium complexes

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Abstract

The potassium salt of the 6,6-dimethylcyclohexadienyl anion, (dmch)K, reacted with $\text{U}(\text{BH}_4)_4$ (I) to give $(\text{dmch})_2\text{U}(\text{BH}_4)_2$ (II), whereas $(\text{dmch})\text{U}(\text{BH}_4)_3$ (III) was obtained from an equimolecular mixture of II and I. The anionic compounds $[(\text{dmch})_2\text{UX}_2][\text{K}(18\text{-crown-6})]$ ($\text{X} = \text{Cl}$, IV; BH_4 , V) were synthesized by treatment of UCl_4 or (mesitylene) $\text{U}(\text{BH}_4)_3$ with (dmch)K. The neutral complex $(\text{dmch})_2\text{U}(\text{BH}_4)(\text{THF})$ (VI) was isolated by extracting the powder of $[(\text{dmch})_2\text{U}(\text{BH}_4)_2][\text{K}(\text{THF})_x]$ with pentane; VI reacted with OPPh_3 to give $(\text{dmch})_2\text{U}(\text{BH}_4)(\text{OPPh}_3)$ (VIII).

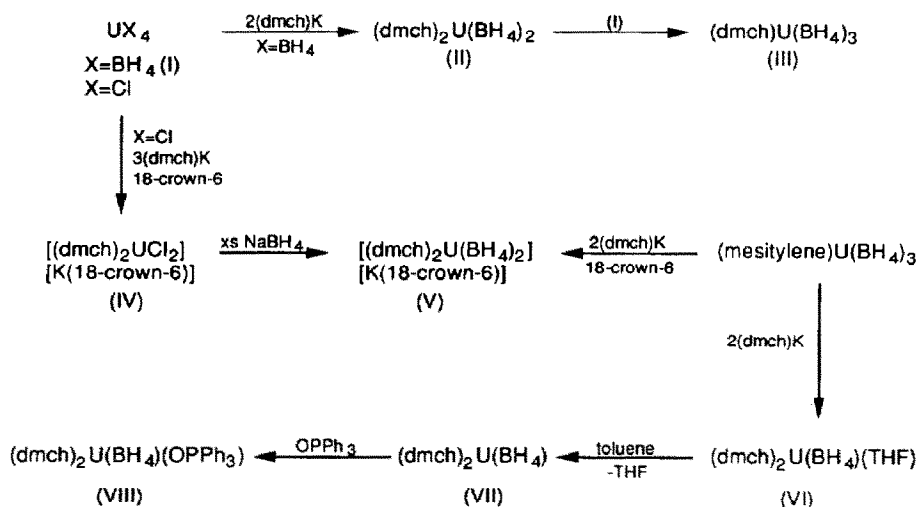
Introduction

Development of organouranium chemistry has been intimately connected with the use of the cyclopentadienyl ligand, and most of the known complexes are bis(pentamethylcyclopentadienyl) or tris(cyclopentadienyl) derivatives [1]. We recently described a unique series of open pentadienyl uranium compounds [2]. Here we describe the synthesis of cyclohexadienyl U(IV) and U(III) complexes [3]. Cyclohexadienyl compounds of the *d*-transition metals are generally prepared either by protonation of η -arene derivatives or by hydride abstraction from η -cyclohexadiene complexes [4]. However, because of the paucity and/or ligand lability of such precursors [5], these routes are not practicable in organoactinide chemistry. Therefore, as in the case of the preparation of the pentadienyl uranium compounds [2], we synthesized cyclohexadienyl complexes by substitution of borohydride or chloride ligands by a dienyl group; we used the 6,6-dimethylcyclohexadienyl anion (dmch), which is resistant to disproportionation [6].

Results and discussion

Uranium(IV) complexes

The uranium tetraborohydride $\text{U}(\text{BH}_4)_4$ (I) reacted in toluene with 2 equiv. of the potassium salt of the dimethylcyclohexadienyl anion to give the bis(cyclohexa-



Scheme 1

dienyl) compound (II), which was isolated as brown crystals in 30% yield (Scheme 1). As in the case of the preparation of the corresponding dimethylpentadienyl derivative [2], this synthesis was complicated by the concomitant reduction of I to the insoluble uranium trisborohydride, but the latter was easily removed by filtration. Treatment of I with 1 equiv. of (dmch)K afforded, in addition to $\text{U(BH}_4\text{)}_3$, a 1:2 mixture of the desired product (dmch)U(BH₄)₃ (III) and II. Complex III was obtained in quantitative yield from the reaction of II with the stoichiometric amount of I, and was purified by sublimation (20 °C, 10⁻² mmHg). The red oily compound III exhibits a vapour pressure of the same order of magnitude as that of I, (C₅H₅)U(BH₄)₃ and (Me₂C₅H₅)U(BH₄)₃ [2]. Like their open pentadienyl analogues, complexes II and III are thermally stable up to 80 °C in toluene, but are readily reduced by polar ligands; in THF, III gave unidentified products, whereas II was transformed into a complex mixture containing (dmch)₂U(BH₄)₂(THF) (VI) (see below) as the major compound.

Uranium(III) complexes

Reaction of UCl₄ with 1 equiv. of (dmch)K in tetrahydrofuran (THF) immediately gave UCl₃(THF)_x [7], with dimerisation of the cyclohexadienyl radical. The (dmch)₂UCl₂⁻ anion was prepared in THF in almost quantitative yield by treatment of UCl₄ with 3 equiv. of (dmch)K; after addition of 18-crown-6 ether, [(dmch)₂UCl₂][K(18-crown-6)] (IV) was isolated as red-brown microcrystals from THF-pentane. The corresponding borohydride anion (dmch)₂U(BH₄)₂⁻ was formed by reaction of IV with NaBH₄ or by the sodium amalgam reduction of II, but a more efficient synthesis of this anion involved treating (mesitylene)U(BH₄)₃ [5] with 2 equiv. of (dmch)K; in the presence of 18-crown-6 ether, bronze crystals of [(dmch)₂U(BH₄)₂][K(18-crown-6)] (V) were isolated in 90% yield from THF-diethylether. Both IV and V reacted with PhCH₂Li to give the bis(benzyl) anion (dmch)₂U(CH₂Ph)₂⁻, which was characterized only by its NMR spectrum.

In contrast to the pentadienyl anion (2,4-Me₂C₅H₅)₂U(BH₄)₂⁻, but like Cp₂U(BH₄)₂⁻, the (dmch)₂UX₂⁻ anions (X = Cl, BH₄) are stable in THF even if

Table 1
Elemental analyses

Compound	Analyses (found (calcd.) (%))			
	C	H	B or Cl	K or P
(dmch) ₂ U(BH ₄) ₂ (II)	39.50 (39.87)	6.03 (6.27)	4.31 (4.48)	
(dmch)U(BH ₄) ₃ (III)	23.84 (24.66)	5.77 (5.95)	8.37 (8.32)	
[(dmch) ₂ UCl ₂][K(18-crown-6)] (IV)	40.44 (40.68)	5.49 (5.61)	8.36 (8.58)	4.66 (4.73)
[(dmch) ₂ U(BH ₄) ₂][K(18-crown-6)] (V)	42.56 (42.82)	6.75 (6.93)	2.94 (2.75)	5.04 (4.98)
(dmch) ₂ U(BH ₄)(THF) (VI)	44.28 (44.54)	6.17 (6.35)	1.89 (2.00)	
(dmch) ₂ U(BH ₄) (VII)	40.34 (41.13)	5.32 (5.61)	2.67 (2.31)	
(dmch) ₂ U(BH ₄)(OPPh ₃) (VIII)	54.54 (54.78)	5.38 (5.54)	1.41 (1.45)	3.99 (4.15)

the cation is not complexed by crown ether. However, extraction of the powder of [(dmch)₂U(BH₄)₂][K(THF)_x] with pentane afforded a brown solution which, on cooling at -78°C , deposited bronze crystals of the neutral complex (dmch)₂U(BH₄)(THF) (VI), whereas brown crystals of (dmch)₂U(BH₄) (VII) were obtained by evaporating a toluene solution of VI. Compounds VI and VII reacted with the stoichiometric amount of triphenylphosphine oxide to give brown-green crystals of (dmch)₂U(BH₄)(OPPh₃) (VIII) in almost quantitative yield.

The new compounds II–VIII were characterized by their elemental analyses (Table 1) and ¹H NMR spectra (Table 2); the spectra of VI and VIII also revealed the dynamic behaviour of the complexes in solution.

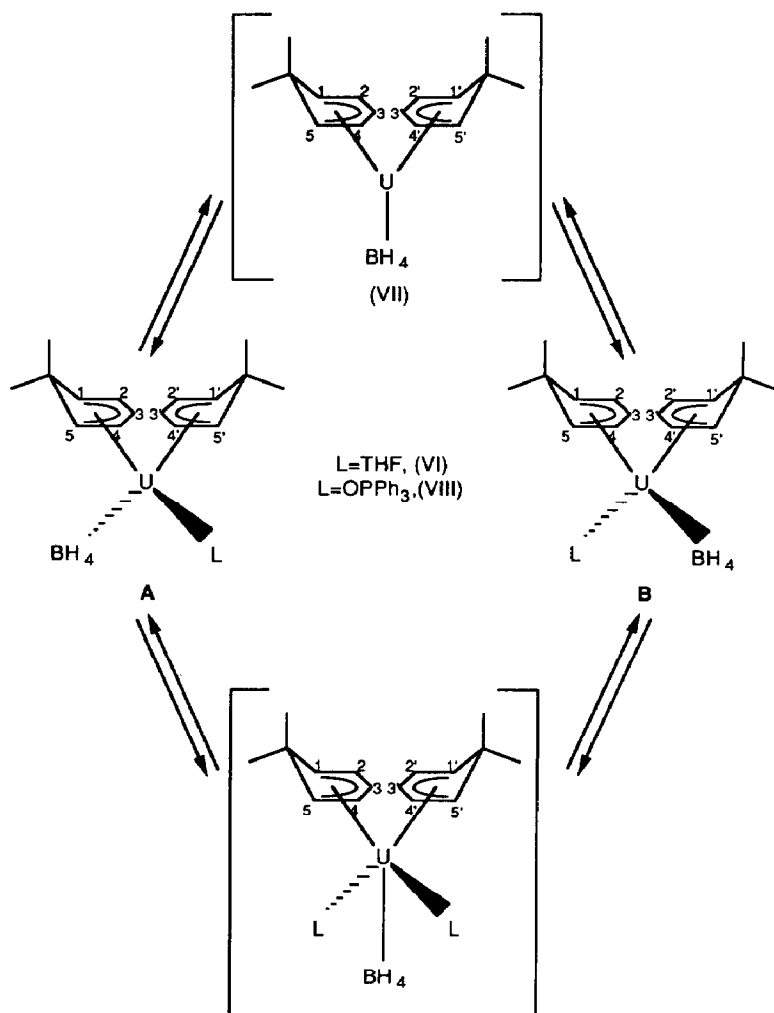
Dynamic behaviour of (dmch)₂U(BH₄)L (L = THF, OPPh₃) in solution

The ¹H NMR spectrum of VI in toluene-*d*₈ at 30°C (Table 2) exhibited the usual pattern of five signals (relative intensities 6:6:4:4:2) corresponding to the two cyclohexadienyl ligands. In contrast, the dmch groups of VIII gave rise, in addition to the two peaks of intensity 6H, to five signals, each one integrating for 2H. This spectrum can be easily interpreted by assuming that VIII adopts the tetrahedral configuration A (Scheme 2), in which the 1- and 5-positions, as well as the 2- and 4-positions, are non-equivalent (each hydrogen atom being equivalent to the related primed atom). Compound VI also adopts configuration A, but, as we have seen, the THF ligand of this complex is very labile, and its reversible dissociation, via the intermediate VII, leads to the permutation of the BH₄ and THF ligands. Thus, the 1- and 5-positions, (and the 2- and 4-positions) become equivalent because of the rapid equilibrium between forms A and B. This equilibration could be slowed down, and coalescence of the signals corresponding to the 1,5,2,4 protons occurred at -80°C , but the slow limit spectrum could not be reached. For complex VIII, the OPPh₃ ligand of which is much less easily dissociated, coalescence of the 1 and 5 protons signals was observed at 80°C , and even at 30°C in the presence of a small quantity (ca 10%) of triphenylphosphine oxide. The fast limit spectrum of VIII,

Table 2. ^1H NMR spectral data for the complexes ^a

Compound	dmch signals	BH ₄ signal	Other signals
(dmch) ₂ U(BH ₄) ₂ (II)	4.97 and -6.80 (s, 6H+6H, Me) 3.84 (br.t., 16, 4H, 2,4-H) -8.99 (br., 12, 2H, 3-H) -24.09 (d, 7, 4H, 1,5-H)	69.86 (q, 85, 8H)	
(dmch) ₂ U(BH ₄) ₃ (III)	69.63 (br.t., 11, 1H, 3-H) 28.17 (d.d., 7 and 5, 2H, 2,4-H) 12.57 and -22.32 (s, 3H+3H, Me) -55.74 (d, 7, 2H, 1,5-H)	76.92 (q, 85, 12H)	
[(dmch) ₂ UCl ₂]- [K(18-crown-6)] (IV)	1.59 and -6.91 (s, 6H+6H, Me) -4.54 and -21.04 (br., 40 and 27, 4H +4H, 1,5- and/or 2,4-H) -24.55 (br., 40, 2H, 3-H)		2.81 (s, 24H, 18-crown-6)
[(dmch) ₂ U(BH ₄) ₂]- [K(18-crown-6)] (V)	1.18 and -4.17 (s, 6H+6H, Me) -10.18 and -17.98 (br., 23 and 16, 4H+4H, 1,5- and/or 2,4-H) -30.48 (br., 23, 2H, 3-H)	72.72 (q, 82, 8H)	3.05 (s, 24H, 18-crown-6)
(dmch) ₂ U(BH ₄)(THF) (VI)	6.19 and 9.88 (s, 6H+6H, Me) -4.28 and -22.36 (br., 60 and 40, 4H +4H, 1,5- and/or 2,4-H) ^b -37.90 (br., 90, 2H, 3-H)	90 (br., 900, 4H)	-7.20 (br., 20, 4H, β -THF) -17.51 (br., 45, 4H, α -THF)
(dmch) ₂ U(BH ₄) (VII)	10.74 and -12.24 (s, 6H+6H, Me) -2.66 and -20.11 (br., 100, 4H+4H, 1,5- and/or 2,4-H) -47.32 (br., 100, 2H, 3-H)	30 (br., >1000, 4H)	
(dmch) ₂ U(BH ₄)(OPPh ₃) (VIII)	1.77 and -6.27 (s, 6H+6H, Me) -2.39 and -12.36 (br., 30, 2H+2H, 1- and 5- or 2- and 4-H) ^c -13.76 and -32.84 (br., 25, 2H+2H, 1- and 5- or 2- and 4-H) ^c -27.20 (br., 30, 2H, 3-H)	122.56 (br., 380, 4H)	6.50 (t, 7, 3H, <i>p</i> -Ph) 6.09 (br.t., 7, 6H, <i>m</i> -Ph) 2.27 (br., 20, 6H, <i>o</i> -Ph)

^a In toluene-*d*₈ except IV and V, in THF-*d*₆. δ relative to TMS (multiplicity, *J* or half height width in Hz, intensity, assignment). ^b Coalescence at -80 °C.^c Coalescence at +80 °C.



Scheme 2

which exhibited the normal pattern of signals from the dienyl ligand (in the ratio 6:6:4:4:2) was observed at 30°C after addition of 1 equiv. of OPPh_3 . These results indicated that two dynamic processes involving ligand dissociation or association (Scheme 2) are involved in the molecular rearrangement of VI and VIII.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (F.R.G.). The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The chemical shifts are given as δ values relative to tetramethylsilane. The analytical data and ^1H NMR spectra are given in Table 1 and 2.

All experiments were carried out under argon in Schlenk-type glassware on a high vacuum line or in a glove box. Solvents were thoroughly dried and de-

oxygenated by standard methods and distilled immediately prior to use. 18-Crown-6 ether (Fluka) was dried under vacuum after evaporation of a solution of it in toluene. dmchH [6], UCl_4 [8], $\text{U}(\text{BH}_4)_4$ [9] and $(\text{mesitylene})\text{U}(\text{BH}_4)_3$ [5] were prepared by published methods. The synthesis of $(\text{dmch})\text{K}$ was similar to that of $(\text{Me}_2\text{C}_5\text{H}_5)\text{K}$ [10], with dmchH used in place of dimethylpentadiene; the product was obtained in 45% yield and characterized by comparison of its NMR spectrum with that previously described [6].

Syntheses

$(\text{dmch})_2\text{U}(\text{BH}_4)_2$ (**II**). A 50 ml round bottom flask was charged with $\text{U}(\text{BH}_4)_4$ (125 mg) and $(\text{dmch})\text{K}$ (124 mg) and toluene (20 ml) was condensed into it at -78°C under vacuum. The mixture was stirred for 30 min at 20°C , the red powder of $\text{U}(\text{BH}_4)_3$ then filtered off, and the red solution evaporated to dryness. Crystallisation of the residue from toluene-pentane gave microcrystals of **II**, which were filtered off and dried under vacuum (61 mg, 30%). The NMR spectrum of the red powder of $\text{U}(\text{BH}_4)_3$ in $\text{THF}-d_8$ showed the broad quartet (J 73 Hz) at -83 ppm corresponding to the BH_4 groups [5]. Compound **II** was immediately reduced to **VI** in $\text{THF}-d_8$, giving a mixture which contained **VI** as the major component (ca 50%).

$(\text{dmch})\text{U}(\text{BH}_4)_3$ (**III**). A 50 ml round bottom flask was charged with **I** (31 mg) and **II** (50 mg) and toluene (20 ml) was condensed into it at -78°C under vacuum. After evaporation of the solvent, sublimation of the residue (10^{-2} mmHg, 20°C) gave a red oil of **III** (50 mg, 62%).

$[(\text{dmch})_2\text{UCl}_2][\text{K}(18\text{-crown-6})]$ (**IV**). A 100 ml round bottom flask was charged with UCl_4 (650 mg), $(\text{dmch})\text{K}$ (750 mg) and 18-crown-6 ether (500 mg), and THF (40 ml) was condensed into it at -78°C under vacuum. The mixture was stirred for 40 min at 20°C then filtered, the volume of the filtrate was reduced to 15 ml and pentane (30 ml) was added; a brown-green oil was formed within a few minutes. After decantation of the solution the oil was dried under vacuum and was transformed into a bronze powder by trituration with toluene (10 ml). The product was filtered off and dried under vacuum (820 mg, 60%).

An NMR tube was charged with UCl_4 (5 mg) and $(\text{dmch})\text{K}$ (5 mg) in $\text{THF}-d_8$ (0.4 ml). The NMR spectrum showed the immediate formation of the $(\text{dmch})_2\text{U}-\text{Cl}_2^-$ anion. $\delta(30^\circ\text{C})$: -24.55 (s, 2H, 3-H); -21.02 and -0.48 (s, 4H + 4H, 1,5- and/or 2,4-H); -9.82 and 2.69 (s, 6H + 6H, CH_3).

Reaction of UCl_4 (100 mg) with 1 equiv. of $(\text{dmch})\text{K}$ (39 mg) in THF (10 ml) gave a purple solution of UCl_3 [7]. After evaporation of the solvent, the residue was extracted with pentane (10 ml). The pentane was evaporated off to leave a colourless oil (ca 20 mg), the NMR spectrum of which was identical to that described for $(\text{dmch})_2$ [6].

$[(\text{dmch})_2\text{U}(\text{BH}_4)_2][\text{K}(18\text{-crown-6})]$ (**V**). (a) A 50 ml two necked round bottom flask was charged with $(\text{mesitylene})\text{U}(\text{BH}_4)_3$ (400 mg) and was attached to another 50 ml round bottom flask containing $(\text{dmch})\text{K}$ (320 mg) and 18-crown-6 ether (300 mg). THF was condensed into the flasks (20 ml in each one) under vacuum at -78°C . The solution of $(\text{dmch})\text{K}$ was slowly added to the solution of the uranium compound and the mixture was stirred for 1 h at 20°C . The solution was filtered and its volume was reduced to 10 ml and a brown-green oil was obtained after addition of pentane (20 ml). After decantation of the solution, the oil was dried under vacuum and then triturated with pentane (20 ml) for 1 h; the bronze powder

thus obtained was filtered off and dried under vacuum (647 mg, 83%). Similar reaction in the absence of crown ether gave, after evaporation of the THF, a bronze powder of $[(\text{dmch})_2\text{U}(\text{BH}_4)_2][\text{K}(\text{THF})_x]$, the NMR spectrum of which was similar to that of V, but without the peak at 3.05 ppm.

(b) An NMR tube was charged with IV (10 mg) and NaBH_4 (4 mg) in $\text{THF-}d_8$ (0.4 ml). The NMR spectrum showed, after 10 h at 20°C , the formation of the $(\text{dmch})_2\text{U}(\text{BH}_4)_2^-$ anion (ca 20%).

(c) An NMR tube was charged with I (5 mg) and 2% $\text{Na}(\text{Hg})$ (15 mg) in $\text{THF-}d_8$ (0.4 ml). The NMR spectrum after 5 min at 20°C revealed the formation of the corresponding bisborohydride anion (ca 50%) along with other, unidentified, products.

Reaction of IV and V with benzyl lithium. An NMR tube was charged with IV (10 mg) or V (9.5 mg) and PhCH_2Li (5 mg) in $\text{THF-}d_8$ (0.4 ml). The NMR spectrum revealed the immediate and almost quantitative formation of the $(\text{dmch})_2\text{U}(\text{CH}_2\text{Ph})_2^-$ anion. $\delta(30^\circ\text{C})$: -49.49 (br, 4H, CH_2); -30.59 (br, 2H, 3-H); -18.93 and -7.08 (br, 4H + 4H, 1,5- and/or 2,4-H); -5.80 and -3.93 (s, 6H + 6H, CH_3); 0.17 (br.d., 7, 4H, *o*-Ph); 2.44 (br.t., 7, 2H, *p*-Ph); 3.42 (s, 24H, 18-crown-6); 6.97 (br.t., 7, 4H, *m*-Ph).

$(\text{dmch})_2\text{U}(\text{BH}_4)(\text{THF})$ (VI). A 50 ml round bottom flask was charged with (mesitylene) $\text{U}(\text{BH}_4)_3$ (500 mg) and $(\text{dmch})\text{K}$ (425 mg), and THF (30 ml) was condensed into it at -78°C under vacuum. The mixture was stirred for 40 min at 20°C ; the THF was evaporated off and pentane (30 ml) was condensed into it under vacuum at -78°C . The solution was filtered and its volume was reduced to 10 ml; on cooling at -78°C , brown microcrystals of VI were deposited, and these were filtered off and dried under vacuum (460 mg, 69%).

$(\text{dmch})_2\text{U}(\text{BH}_4)$ (VII). A ca. 0.025 M toluene solution of VI was evaporated to dryness three times in succession, to give finally a brown powder of VII in quantitative yield.

$(\text{dmch})_2\text{U}(\text{BH}_4)(\text{OPPh}_3)$ (VIII). A 50 ml round bottom flask was charged with VI (355 mg) or VII (310 mg) and OPPh_3 (150 mg), and THF (20 ml) was condensed into it at -78°C under vacuum. The mixture was stirred for 10 h at 20°C and the solvent was evaporated off, to leave brown microcrystals of VIII, which were washed with pentane, filtered off, and dried under vacuum (400 mg, 82%).

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