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Cyclohexadienyl uranium complexes

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Abstract

The potassium salt of the 6,6-dimethylcyclohexadienyl anion, (dmch)K, reacted with $U(BH_4)_4$ (**I**) to give $(dmch)_2U(BH_4)_2$ (**II**), whereas $(dmch)U(BH_4)_3$ (**III**) was obtained from an equimolecular mixture of **II** and **I**. The anionic compounds $[(dmch)_2UX_2][K(18\text{-crown-}6)]$ (X = Cl, **IV**; BH_4, **V**) were synthesized by treatment of UCl_4 or (mesitylene)$U(BH_4)_3$ with (dmch)K. The neutral complex $(dmch)_2U(BH_4)(THF)$ (**VI**) was isolated by extracting the powder of $[(dmch)_2U(BH_4)_2][K(THF)_x]$ with pentane; **VI** reacted with $OPPh_3$ to give $(dmch)_2U(BH_4)(OPPh_3)$ (**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 $U(BH_4)_4$ (**I**) reacted in toluene with 2 equiv. of the potassium salt of the dimethylcyclohexadienyl anion to give the bis(cyclohexa-

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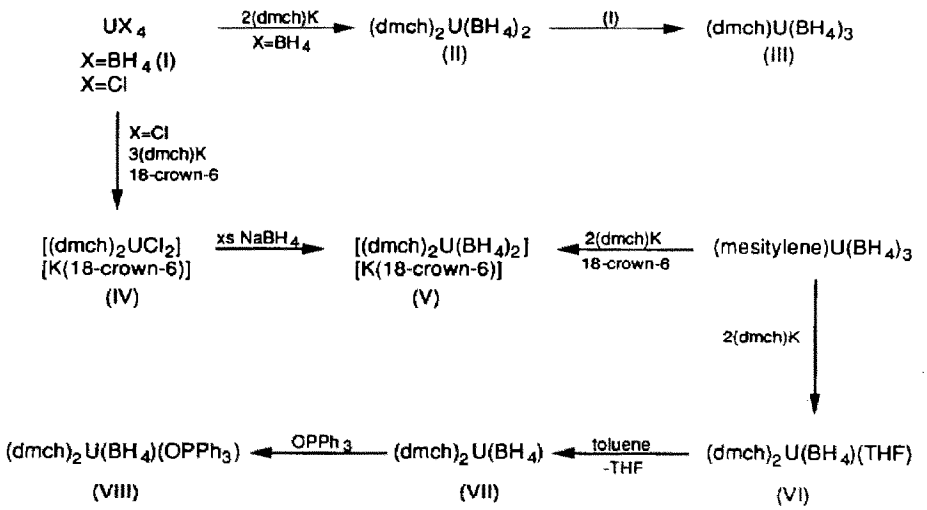


Scheme 1

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 $U(BH_4)_3$, a 1 : 2 mixture of the desired product $(dmch)U(BH_4)_3$ (**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**, $(C_5H_5)U(BH_4)_3$ and $(Me_2C_5H_5)U(BH_4)_3$ [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 $(dmch)_2U(BH_4)(THF)$ (**VI**) (see below) as the major compound.

Uranium(III) complexes

Reaction of UCl_4 with 1 equiv. of (dmch)K in tetrahydrofuran (THF) immediately gave $UCl_3(THF)_x$ [7], with dimerisation of the cyclohexadienyl radical. The $(dmch)_2UCl_2^-$ anion was prepared in THF in almost quantitative yield by treatment of UCl_4 with 3 equiv. of (dmch)K; after addition of 18-crown-6 ether, $[(dmch)_2UCl_2][K(18\text{-crown-}6)]$ (**IV**) was isolated as red-brown microcrystals from THF–pentane. The corresponding borohydride anion $(dmch)_2U(BH_4)_2^-$ was formed by reaction of **IV** with $NaBH_4$ or by the sodium amalgam reduction of **II**, but a more efficient synthesis of this anion involved treating $(mesitylene)U(BH_4)_3$ [5] with 2 equiv. of (dmch)K; in the presence of 18-crown-6 ether, bronze crystals of $[(dmch)_2U(BH_4)_2][K(18\text{-crown-}6)]$ (**V**) were isolated in 90% yield from THF–diethylether. Both **IV** and **V** reacted with $PhCH_2Li$ to give the bis(benzyl) anion $(dmch)_2U(CH_2Ph)_2^-$, which was characterized only by its NMR spectrum.

In contrast to the pentadienyl anion $(2,4\text{-}Me_2C_5H_5)_2U(BH_4)_2^-$, but like $Cp_2U(BH_4)_2^-$, the $(dmch)_2UX_2^-$ anions (X = Cl, BH_4) are stable in THF even if

Table 1

Elemental analyses

Compound	Analyses (found (calcd.) (%))			
	C	H	B or Cl	K or P
$(dmch)_2U(BH_4)_2$ (II)	39.50	6.03	4.31	
	(39.87)	(6.27)	(4.48)	
$(dmch)U(BH_4)_3$ (III)	23.84	5.77	8.37	
	(24.66)	(5.95)	(8.32)	
$[(dmch)_2UCl_2][K(18\text{-crown-}6)]$ (IV)	40.44	5.49	8.36	4.66
	(40.68)	(5.61)	(8.58)	(4.73)
$[(dmch)_2U(BH_4)_2][K(18\text{-crown-}6)]$	42.56	6.75	2.94	5.04
(V)	(42.82)	(6.93)	(2.75)	(4.98)
$(dmch)_2U(BH_4)(THF)$ (VI)	44.28	6.17	1.89	
	(44.54)	(6.35)	(2.00)	
$(dmch)_2U(BH_4)$ (VII)	40.34	5.32	2.67	
	(41.13)	(5.61)	(2.31)	
$(dmch)_2U(BH_4)(OPPh_3)$ (VIII)	54.54	5.38	1.41	3.99
	(54.78)	(5.54)	(1.45)	(4.15)

the cation is not complexed by crown ether. However, extraction of the powder of $[(dmch)_2U(BH_4)_2][K(THF)_x]$ with pentane afforded a brown solution which, on cooling at $-78\,^{\circ}C$, deposited bronze crystals of the neutral complex $(dmch)_2U(BH_4)(THF)$ (**VI**), whereas brown crystals of $(dmch)_2U(BH_4)$ (**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 $(dmch)_2U(BH_4)(OPPh_3)$ (**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.

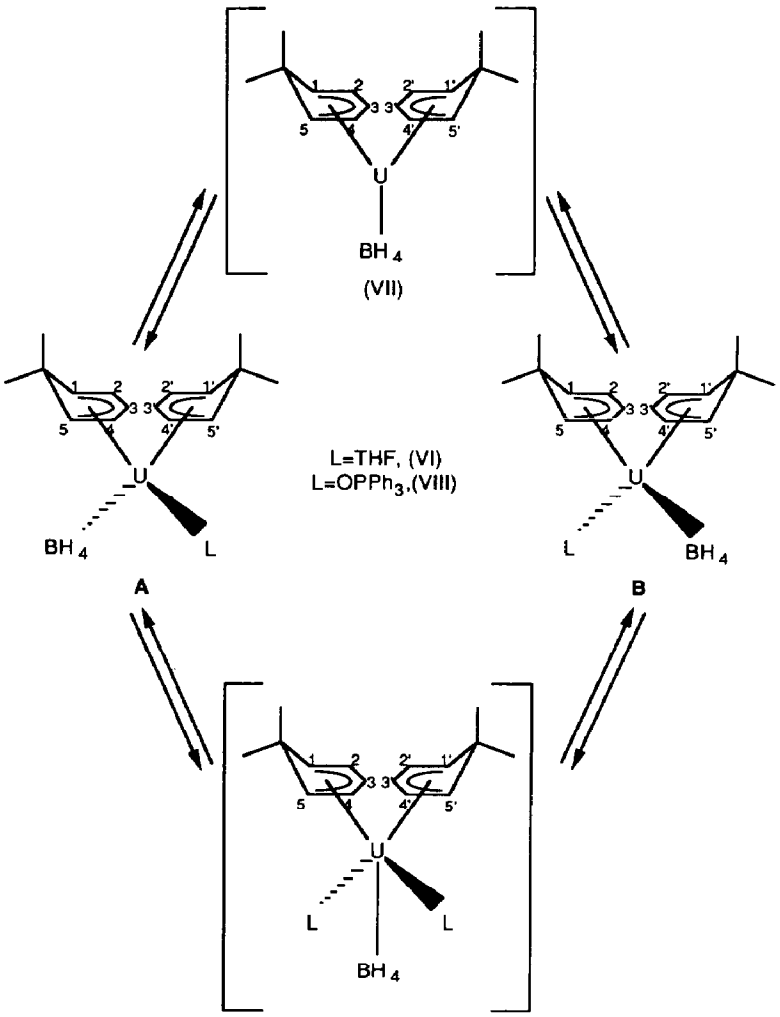
Dynamic behaviour of $(dmch)_2U(BH_4)L$ ($L = THF, OPPh_3$) in solution

The ^1H NMR spectrum of **VI** in toluene-d_8 at $30\,^{\circ}C$ (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 BH_4 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 $-80\,^{\circ}C$, but the slow limit spectrum could not be reached. For complex **VIII**, the $OPPh_3$ ligand of which is much less easily dissociated, coalescence of the 1 and 5 protons signals was observed at $80\,^{\circ}C$, and even at $30\,^{\circ}C$ in the presence of a small quantity (ca 10%) of triphenylphosphine oxide. The fast limit spectrum of **VIII**,

Table 2. ^{1}H NMR spectral data for the complexes [a]

Compound	dmch signals	BH_4 signal	Other signals
$(dmch)_2U(BH_4)_2$ (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)	
$(dmch)U(BH_4)_3$ (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)	
$[(dmch)_2UCl_2]$-[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)
$[(dmch)_2U(BH_4)_2]$-[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)
$(dmch)_2U(BH_4)(THF)$ (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)
$(dmch)_2U(BH_4)$ (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)	
$(dmch)_2U(BH_4)(OPPh_3)$ (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, *p*-Ph) 6.09 (br.t., 7, 6H, *m*-Ph) 2.27 (br., 20, 6H, *o*-Ph)

[a] In toluene-d_8 except IV and V, in THF-d_8. 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], $U(BH_4)_4$ [9] and (mesitylene)$U(BH_4)_3$ [5] were prepared by published methods. The synthesis of (dmch)K was similar to that of $(Me_2C_5H_5)K$ [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

$(dmch)_2U(BH_4)_2$ (II). A 50 ml round bottom flask was charged with $U(BH_4)_4$ (125 mg) and (dmch)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 $U(BH_4)_3$ 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 $U(BH_4)_3$ in 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 THF-d_8, giving a mixture which contained **VI** as the major component (ca 50%).

$(dmch)U(BH_4)_3$ (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%)

$[(dmch)_2UCl_2][K(18\text{-crown-}6)]$ (IV), A 100 ml round bottom flask was charged with UCl_4 (650 mg), (dmch)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 (dmch)K (5 mg) in THF-d_8 (0.4 ml). The NMR spectrum showed the immediate formation of the $(dmch)_2U\text{-}Cl_2^-$ anion. δ(30°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 (dmch)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 $(dmch)_2$ [6].

$[(dmch)_2U(BH_4)_2][K(18\text{-crown-}6)]$ (V). (a) A 50 ml two necked round bottom flask was charged with (mesitylene)$U(BH_4)_3$ (400 mg) and was attached to another 50 ml round bottom flask containing (dmch)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 (dmch)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 $[(dmch)_2U(BH_4)_2][K(THF)_x]$, 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 THF-d_8 (0.4 ml). The NMR spectrum showed, after 10 h at 20°C, the formation of the $(dmch)_2U(BH_4)_2^-$ anion (ca 20%).

(c) An NMR tube was charged with **I** (5 mg) and 2% Na(Hg) (15 mg) in 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 benzyllithium. An NMR tube was charged with **IV** (10 mg) or **V** (9.5 mg) and $PhCH_2Li$ (5 mg) in THF-d_8 (0.4 ml). The NMR spectrum revealed the immediate and almost quantitative formation of the $(dmch)_2U(Ch_2Ph)_2^-$ anion. δ(30°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).

$(dmch)_2U(BH_4)(THF)$ (VI). A 50 ml round bottom flask was charged with $(mesitylene)U(BH_4)_3$ (500 mg) and (dmch)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%).

$(dmch)_2U(BH_4)$ (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.

$(dmch)_2U(BH_4)(OPPh_3)$ (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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