

Pentadienyluranium borohydride complexes and their cyclopentadienyl analogues; crystal structures of $(\eta\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$ and $(\eta\text{-C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$

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Abstract

Treatment of $\text{U}(\text{BH}_4)_4$ (I) with the potassium salt of the 2,4-dimethylpentadienyl anion (dmpd) afforded the pentadienyl complex $(\text{dmpd})\text{U}(\text{BH}_4)_3$ (II), whereas the reaction of $(\text{dmpd})_3\text{U}$ (VI) with TiBH_4 gave $(\text{dmpd})_2\text{U}(\text{BH}_4)_2$ (IV). Complex VI reacted with KBH_4 in the presence of 18-crown-6-ether to give the anionic uranium(III) compound $[(\text{dmpd})_2\text{U}(\text{BH}_4)_2][\text{K}(18\text{-crown-6})]$ (VII), and the corresponding cyclopentadienyl derivative $[\text{Cp}_2\text{U}(\text{BH}_4)_2][\text{Na}(18\text{-crown-6})]$ (VIII) was obtained from the Na/Hg reduction of $\text{Cp}_2\text{U}(\text{BH}_4)_2$ (V). The open pentadienyl ligand of these complexes was found to be less strongly bound to the metal centre than its cyclic counterpart in the corresponding cyclopentadienyl derivatives. The crystal structures of the pseudo-tetrahedral II and $\text{CpU}(\text{BH}_4)_3$ (III) complexes show that the U–C(pentadienyl) bonds are longer than the U–C(cyclopentadienyl) bonds, and that there is a large degree of ionic character in the metal–pentadienyl bonding.

Introduction

The chemistry of transition metal-pentadienyl complexes has received much attention during the last years, and an important contribution in this area has been made by Ernst and coworkers [1]. The open pentadienyl ligand was recently claimed, at least for titanium and vanadium, to be both more reactive and more strongly bound than its cyclic counterpart [2]. It seemed to us of interest to examine the behaviour of this ligand coordinated to uranium. Whereas most of the organo-lanthanide and actinide complexes are cyclopentadienyl derivatives [3], only the two dimethylpentadienyl compounds $(\text{dmpd})_3\text{M}$ ($\text{M} = \text{Nd}, \text{U}$; $\text{dmpd} = 2,4\text{-Me}_2\text{C}_5\text{H}_5$) have been described [4,5]. We have prepared a series of pentadienyl uranium

borohydride complexes and the following $(\text{dmpd})\text{U}(\text{BH}_4)_3$ (II), $(\text{dmpd})_2\text{U}(\text{BH}_4)_2$ (IV), and $[(\text{dmpd})_2\text{U}(\text{BH}_4)_2][\text{K}(18\text{-crown-6})]$ (VII), have been isolated in crystalline form. We consider here the stabilities of the complexes, and compare then with those of their cyclopentadienyl analogues. We also report the X-ray crystal structures of II and $\text{CpU}(\text{BH}_4)_3$ (III) [6*,7*].

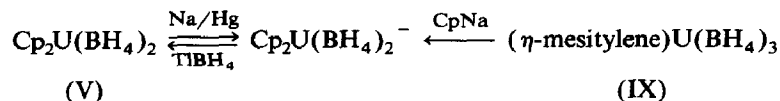
Results and discussion

Synthesis

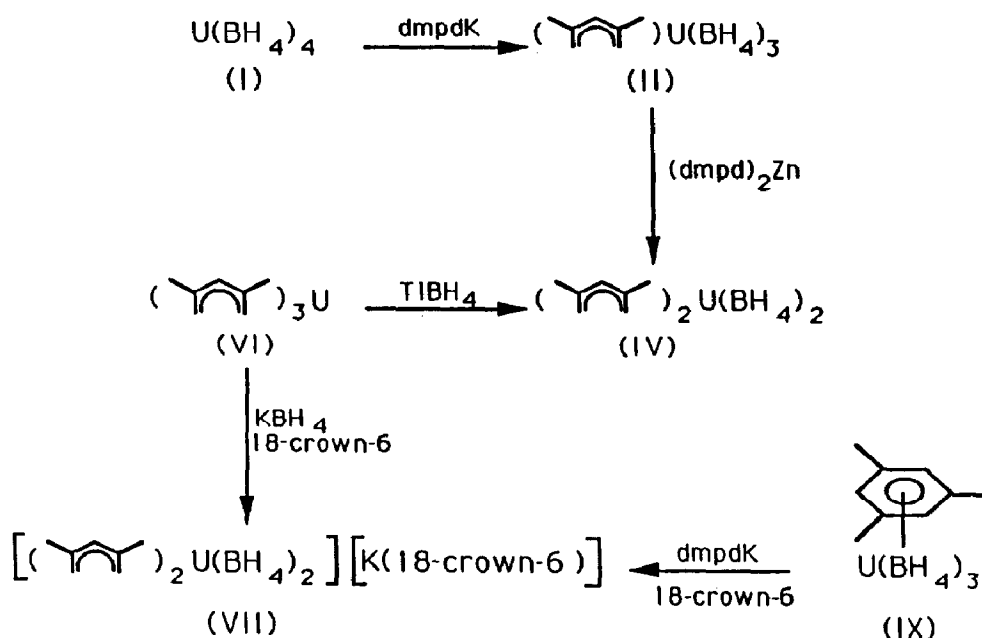
The monopentadienyluranium compound (II) was prepared in 33% yield from the reaction in toluene of $\text{U}(\text{BH}_4)_4$ (I) with a stoichiometric amount of the potassium salt of the dimethylpentadienyl anion (Scheme 1). The synthesis of II was slightly complicated by the concomitant reduction of the uranium tetraborohydride into $\text{U}(\text{BH}_4)_3$ [8], but the latter, which is not soluble in toluene, was removed by filtration. The green crystalline complex II which is soluble in pentane and aromatic solvents, was easily purified by sublimation ($40^\circ\text{C}/10^{-2}$ mmHg); this volatile uranium compound has a vapour pressure fairly similar to those of I and $\text{CpU}(\text{BH}_4)_3$ (III) [7*]. 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 pentadienyluranium compounds, which were identified only through their ^1H NMR spectra (see Experimental). It has been noted previously [1] that methylation of pentadienyl- or allyl-metal complexes bring about a substantial increase in stability.

Because of the interference by reduction, mentioned above, the bis(pentadienyl)-uranium complex IV could not be obtained from the reaction of I with 2 equivalents of the dimethylpentadienyl anion, but it was obtained in low yield by treating II with $(\text{dmpd})_2\text{Zn}$. The most straightforward route to complex IV involved the reaction of UCl_4 with 2 equivalents of NaBH_4 , followed by addition of 2 equivalents of dmpdK ; the product was isolated as red crystals in 35% yield. Compound IV was also made, in 63% yield, by TlBH_4 oxidation of the known tris(pentadienyl)uranium(III) complex (VI) in toluene.

Treatment of VI with the non oxidizing potassium borohydride in the presence of 18-crown-6 ether gave the anionic uranium(III) compound $[(\text{dmpd})_2\text{U}(\text{BH}_4)_2][\text{K}(18\text{-crown-6})]$ (VII). This brown crystalline product was also isolated in 90% yield from the reaction in tetrahydrofuran (THF) of the arene complex $(\eta\text{-mesitylene})\text{U}(\text{BH}_4)_3$ (IX) with 2 equivalents of the dimethylpentadienyl anion. The $(\text{dmpd})_2\text{U}(\text{BH}_4)_2^-$ anion was stable in solution only when the accompanying cation was solvated by the crown ether (see Experimental). The corresponding cyclopentadienyl anion $\text{Cp}_2\text{U}(\text{BH}_4)_2^-$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) was prepared in THF in almost quantitative yield either by the reaction of $\text{Cp}_2\text{U}(\text{BH}_4)_2$ (V) with a slight excess of sodium amalgam or by treatment of IX with 2 equivalents of CpNa ; after addition of 18-crown-6 ether, $[\text{Cp}_2\text{U}(\text{BH}_4)_2][\text{Na}(18\text{-crown-6})]$ (VIII) was isolated as red crystals. The $\text{Cp}_2\text{U}(\text{BH}_4)_2^-$ anion was readily reoxidized to V by thallium borohydride in THF.



* Reference numbers with asterisks indicate notes in the list of references.



Scheme 1.

When treated with only 1 equivalent of dmpdK or CpM (M = Na, K), the uranium(III) trisborohydride IX was transformed into the anion $(\text{dmpd})\text{U(BH}_4)_3^-$ or $\text{CpU(BH}_4)_3^-$. These could not be isolated pure (see Experimental); in solution in the presence of 18-crown-6 ether they progressively decomposed to give ultimately a pale orange precipitate of $[\text{U(BH}_4)_4][\text{M(18-crown-6)}]$ (M = Na, X K) and other unidentified products. Complex X was prepared in quantitative yield by treatment of the arene compound IX with NaBH_4 in the presence of 18-crown-6 ether.

Pentadienyl, a ligand less strongly bound to uranium than cyclopentadienyl

No great difference was noted between the thermal stabilities of most of the open pentadienyl transition metal complexes and those of their cyclic analogues, especially in the metallocene series [1]. However, preparation of the stable "open titanocene" [9] and determination of the X-ray crystal structures of the "half open titano- and vanado-cenes" [2], which revealed that in these complexes, the M–C(pentadienyl) bonds are shorter than the M–C(cyclopentadienyl) bonds, indicated that the pentadienyl ligand, although more reactive, is more strongly bound than its cyclic analogue.

We found (Table 3) that the pentadienyluranium complexes II, IV, VII and their cyclopentadienyl analogues III, V and VIII behave quite differently in tetrahydrofuran solution. Disproportionation of the monocyclopentadienyl compound III to the uranium(IV) derivatives V and $\text{U(BH}_4)_4\text{L}_2$ occurred upon addition of various oxygen L ligands, including THF [10], whereas II was immediately reduced into uranium(III) borohydrides under the same conditions. In the case of the reaction of II with triphenylphosphine oxide, dimerisation of the pentadienyl ligand was observed. The bis(cyclopentadienyl) complexes V and VIII are quite stable in THF; in contrast, compound IV was readily transformed into a complex mixture in

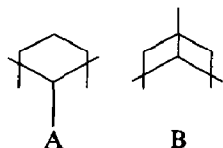
which the uranium(III) derivatives VI and $\text{U}(\text{BH}_4)_3$ were detected, while VII slowly decomposed in tetrahydrofuran (see Experimental). In comparison with the other pentadienyluranium borohydrides, the anionic complex VII was found to be rather stable in THF, since it was isolated pure after its preparation in this solvent. It is, however, noteworthy that, in contrast to $\text{Cp}_2\text{U}(\text{BH}_4)_2^-$, this pentadienyl anion could be observed only when the cation was complexed by crown-ether, suggesting the facile dissociation of a BH_4 group, which is consistent with the better electron donating ability of the pentadienyl ligand [1]. The neutral pentadienyl compounds II, IV and VI were found to be less thermally stable in toluene than the corresponding cyclopentadienyl derivatives.

It could be argued that the greater stability of the cyclopentadienyl complexes reflects the lower reactivity of the cyclic ligand rather than its stronger binding to the metal centre. In fact, organouranium complexes usually have labile ligands (this phenomenon is illustrated by the disproportionation of III), and during these ligand exchange reactions the aromatic Cp group certainly exhibits a greater resistance to modification through, for example, dimerisation. Taking advantage of this lability, a better measure of the relative strengths of the pentadienyl and cyclopentadienyl bonding would be provided by competition reactions during which the ligands remain intact. Such reactions were observed by treating the tris(cyclopentadienyl)- and tris(pentadienyl)-uranium(III) complexes at 20°C with 3 equivalents of dmpdK or CpK in tetrahydrofuran. In each case the same equilibrating mixture was obtained containing 90% of the tris(cyclopentadienyl)uranium compound and the free Cp and dmpd ligands in the ratio 15/85; the other, unidentified compounds, are almost certainly mixed cyclopentadienyluranium(III)-pentadienyluranium(III) derivatives. Thus, the pentadienyl ligand appears to be much less strongly bound to uranium than its cyclic analogue.

Crystal structures of $(\text{dmpd})\text{U}(\text{BH}_4)_3$ and $\text{CpU}(\text{BH}_4)_3$

The molecules II and III are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 4. The structures of II and III are very similar, and consist of discrete neutral molecules in which the dienyl ligand and the three borohydride ligands form a distorted tetrahedron around the uranium atom. In both compounds, the short U–B distances (ca $2.5\text{ \AA}$) are characteristic of tridentate BH_4^- ligands [12].

The plane of the boron atoms and that of the cyclopentadienyl ligand of III are parallel (the dihedral angle between these two planes being $3(6)^\circ$), and orthogonal to the plane of symmetry in which lie the U, C(1) and B(1) atoms. Though there is no crystallographic symmetry imposed on the molecule of II, the plane defined by U, C(3) and B(1) is a pseudo plane of symmetry. The angle between the planar pentadienyl ligand and the associated boron atoms in II is $9(2)^\circ$, B(1) being closer to the dienyl plane than B(2) and B(3). Such a geometry has invariably been encountered with other similar non cyclic (dienyl) ML_3 systems [13]; the latter always adopt configuration A, configuration B being much higher in energy [14].



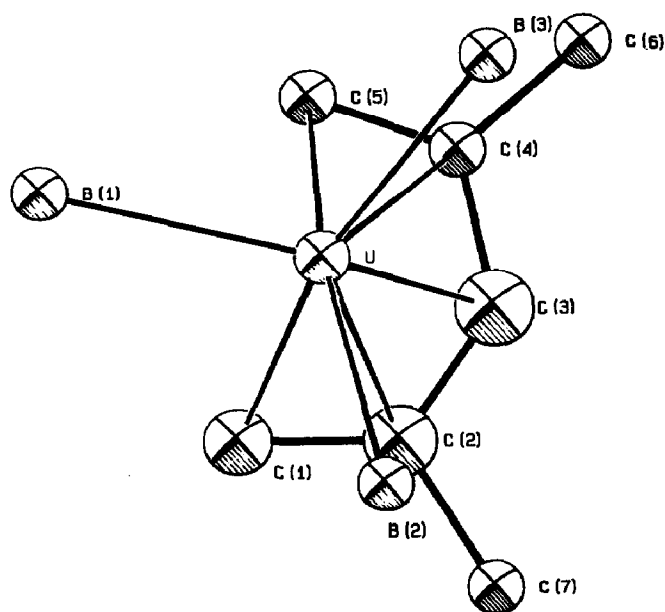


Fig. 1. View of molecule II along perpendicular axis of the dienyl ligand plane.

Quite unlike all the pentadienyl complexes so far reported [1], the U–C bonds in II are significantly longer than those in the corresponding cyclopentadienyl compound III (averaging 2.75(3) and 2.67(3) Å respectively), with the U–C(3) distance shorter (2.63(2) Å) than those for the 4 other uranium–carbon bonds (2.77(3)–2.80(2) Å). The distances between the U atom and the dienyl plane are respectively 2.29(1) and 2.42(1) Å in II and III. These observations reflect the larger size of the pentadienyl ligand [1].

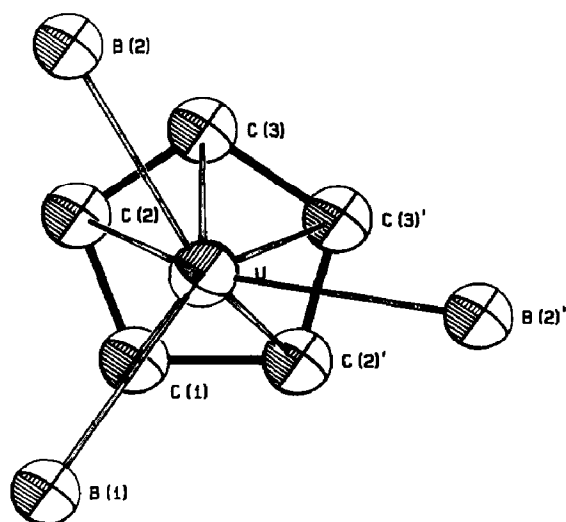


Fig. 2. View of molecule III along perpendicular axis of the dienyl ligand plane. Primed atoms are related by the plane of symmetry.

It is also of interest to consider the C–C bonds lengths within the pentadienyl group, which fall essentially in two sets; the lengths of the external C–C bonds, C(1)–C(2) and C(4)–C(5), average 1.35(3) Å, and are significantly shorter than those of the internal C(2)–C(3) and C(3)–C(4) bonds (1.44(4) Å), indicating the great contribution of the resonance hydrid $(\text{CH}_2=\text{CH})_2\text{CH}^-$ [4,15]. The shorter U–C(3) distance is also indicative of an important degree of ionic character in the uranium–pentadienyl bond.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (FRG). The infrared spectra were recorded on a Perkin–Elmer 782 instrument and the ^1H NMR spectra 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 ($\delta = 0$). The ^1H NMR spectral data and analytical data are given in Tables 1 and 2.

All experiments were carried out under argon in Schlenck type glassware on a high vacuum line or in a glove box. Solvents were thoroughly dried and de-oxygenated by the standard methods and distilled immediately prior to use. 18-crown-6 ether (Fluka) was dried under vacuum after evaporation of a toluene solution. $\text{Cp}_3\text{U}(\text{THF})$ [16*], $\text{U}(\text{BH}_4)_4$ [17*], $\text{CpU}(\text{BH}_4)_3$ [10], $\text{Cp}_2\text{U}(\text{BH}_4)_2$ [18], $(\eta\text{-mesitylene})\text{U}(\text{BH}_4)_3$ [19], TlBH_4 [20], dmpdK and the other pentadienyl reagents [21] were prepared by published methods.

Syntheses

$(\text{dmpd})\text{U}(\text{BH}_4)_3$ (II). A 50 ml round bottom flask was charged with $\text{U}(\text{BH}_4)_4$ (82 mg) and dmpdK (37 mg), and toluene (15 ml) was condensed into it under vacuum at -78°C . The mixture was stirred for 20 min at 20°C , the red precipitate was then filtered off, and the green filtrate evaporated to dryness below 20°C . Sublimation of the residue (10^{-2} mmHg, $40\text{--}90^\circ\text{C}$) gave green crystals of II (34 mg, 33%).

Table 1

^1H NMR spectra of the complexes ^a

Compound	BH_4 ligands	Dienyl ligands
$(\text{dmpd})\text{U}(\text{BH}_4)_3$ (II)	110.38(q, 85, 12H)	– 8.34(s, 6H, CH_3); – 28.80(s, 1H, CH); – 34.81 and – 75.49 (s, 2H + 2H, CH_2)
$(\text{dmpd})_2\text{U}(\text{BH}_4)_2$ (IV)	0.53(q, 85, 8H)	65.99(s, 2H, CH); 4.03(s, 12, CH_3); – 55.24 and – 86.35(s, 4H + 4H, CH_2)
$[(\text{dmpd})_2\text{U}(\text{BH}_4)_2]\text{-}$ [K(18-crown-6)] (VII)	72.52(br, 320, 8H)	– 12.01(s, 12H, CH_3); – 18.75 and – 46.12(s and br, 50, 4H + 4H, CH_2) – 26.46(br, 25, 2H, CH)
$[\text{Cp}_2\text{U}(\text{BH}_4)_2]\text{-}$ [K(18-crown-6)] (VIII)	61.08(q, 78, 8H)	– 13.75(s, 10H)

^a II and IV in toluene- d_8 , VII and VIII in THF- d_8 ; δ relative to TMS (multiplicity, J or half height width in Hz, intensity, assignment). The spectra of VII and VIII also exhibit a signal at 3.56 ppm (24 H) corresponding to the crown ether.

Table 2

Elemental analyses and IR ($\nu(\text{BH})$) frequencies of the complexes

Compound	Analyses (Found (calcd) (%))				$\nu(\text{BH})^a$ (cm^{-1})
	C	H	B	Na or K	
II	22.12 (22.22)	5.90 (6.08)	8.33 (8.73)		2090, 2156, 2518
IV	36.45 (36.68)	6.42 (6.55)	4.96 (4.80)		2145, 2198, 2486
VII	40.76 (40.99)	6.96 (7.09)	2.93 (2.89)	5.00 (5.12)	2218, 2283 2409
VIII	38.31 (38.54)	6.00 (6.13)	3.05 (3.21)	3.47 (3.36)	2119, 2140, 2181, 2215, 2406
X	24.41 (24.61)	6.73 (6.84)	7.23 (7.52)	4.10 (3.93)	2161, 2228 2298, 2439

^a In Nujol mull, except IV in toluene.

In THF, II was immediately reduced to $\text{U}(\text{BH}_4)_3(\text{THF})_n$. Addition of Ph_3PO to a solution of II in toluene led to the immediate formation of a red precipitate of uranium(III) borohydride. MS-GC analysis (Neimag R10-10 instrument) of the supernatant liquor revealed the presence of 6 isomers of $\text{C}_{14}\text{H}_{22}$ ($M = 190$).

$(\text{dmpd})_2\text{U}(\text{BH}_4)_2$ (IV). (a) A 50 ml two-necked round bottom flask was charged with UCl_4 (500 mg) and NaBH_4 (110 mg), and a solid addition tube containing dmpdK (360 mg) was attached to the flask through a valve. THF (20 ml) was condensed into the flask under vacuum at -78°C and the mixture was stirred for 3 h at 20°C . The THF was evaporated off and replaced by toluene (20 ml), and dmpdK was slowly added. The mixture was stirred for 2 h at 20°C then filtered, and the red solution was evaporated to dryness to leave red microcrystals. These were washed with pentane (20 ml) and dried under vacuum. Complex IV thus obtained (210 mg, 35%) was found to be pure (^1H NMR) and was used without further treatment. Compound IV immediately decomposed in $\text{THF}-d_8$; the signals corresponding to VI and $\text{U}(\text{BH}_4)_3(\text{THF})_n$ could be detected in the complicated NMR spectrum.

(b) A 50 ml round bottom flask was charged with VI (450 mg) and TiBH_4 (385 mg) and toluene (20 ml) was condensed into it under vacuum at -78°C . The

Table 3

Behaviour of the complexes in toluene or tetrahydrofuran solution

Compound	In toluene	In tetrahydrofuran
$(\text{dmpd})\text{U}(\text{BH}_4)_3$ (II)	stable up to 90°C	reduction
$\text{CpU}(\text{BH}_4)_3$ (III)	stable up to 110°C	disproportionation
$(\text{dmpd})_2\text{U}(\text{BH}_4)_2$ (IV)	stable up to 70°C	reduction
$\text{Cp}_2\text{U}(\text{BH}_4)_2$ (V)	stable up to 100°C	stable up to 65°C
$[(\text{dmpd})_2\text{U}(\text{BH}_4)_2]\cdot$ $[\text{K}(18\text{-crown-6})]$ (VII)		slow decomposition; not stable in the absence of 18-crown-6 ether
$[\text{Cp}_2\text{U}(\text{BH}_4)_2]\cdot$ $[\text{K}(18\text{-crown-6})]$ (VIII)		stable up to 65°C ; also stable in the absence of 18-crown-6 ether.

mixture was stirred for one hour at room temperature then filtered, and the red solution was evaporated to dryness to leave red microcrystals of IV (250 mg, 63%). An analytical sample was obtained by recrystallisation from a 1/1 mixture of toluene and pentane.

$(dmpd)_3U$ (VI). A 50 ml round bottom flask was charged with UCl_4 (286 mg) and $dmpdK$ (403 mg) and THF (20 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred for 2 h at $20^\circ C$ then the solvent was evaporated and the product was extracted with toluene (20 ml). The red-brown solution was filtered then evaporated to dryness to give a red brown powder of VI (240 mg, 61%), which was found to be identical (1H NMR) to the compound described previously [5].

$[(dmpd)_2U(BH_4)_2][K(18-crown-6)]$ (VII). (a) A 50 ml two necked round bottom flask was charged with IX (200 mg) and $dmpdK$ (134 mg) and a solid addition tube containing 18-crown-6 ether (138 mg) was attached to it. THF (20 ml) was condensed into the flask under vacuum at $-78^\circ C$ and after 15 min at $20^\circ C$, the crown ether was added. The mixture was stirred for 30 min then filtered, a 15 ml portion of the solvent was evaporated, and pentane (10 ml) was added to give red brown crystals of VII. These were filtered off and dried under vacuum (340 mg, 90%). The NMR spectrum of the THF- d_8 solution of VII after 20 min indicated the formation of VI ($< 5\%$) and the $(dmpd)U(BH_4)_3^-$ anion (5%). A similar reaction between IX and 2 equiv. of $dmpdK$ was performed in an NMR tube in the absence of the crown ether; after 10 min the NMR spectrum exhibited the signals corresponding to VI and the anion $(dmpd)U(BH_4)_3^-$, in the ratio 1.5.

(b) An NMR tube was charged with VI (10 mg) and 18-crown-6 ether (6 mg) and THF- d_8 was condensed into the tube. The NMR spectrum was recorded. KBH_4 (1.5 mg) was added into the tube and after 30 min the NMR spectrum showed the formation of VII (65%).

$[Cp_2U(BH_4)_2][Na(18-crown-6)]$ (VIII). (a) a 100 ml round bottom flask was charged with V (402 mg) and 2% sodium amalgam (1.2 g) and THF (50 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred for 3 h at $20^\circ C$ and the red solution was then filtered and evaporated. The red powder was washed with toluene (10 ml) and dried under vacuum (470 mg). The NMR spectrum showed the product was $[Cp_2U(BH_4)_2][Na(THF)_n]$. Another 50 ml round bottom flask was charged with this powder (100 mg) and 18-crown-6 ether (65 mg) and THF (10 ml) was condensed into it. Ether (10 ml) was then added to the red solution, and red crystals of VIII separated within a few minutes. These were filtered off and dried under vacuum (127 mg, 86% from V).

(b) A 50 ml round bottom flask was charged with IX (100 mg) and $CpNa$ (44 mg) and THF (10 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred for 2 h at $20^\circ C$ then filtered and the solution was evaporated to dryness. The red powder was washed with toluene (10 ml). The anionic compound $[Cp_2U(BH_4)_2][Na(THF)_n]$ thus obtained (102 mg) was contaminated with ca. 3 % $[CpU(BH_4)_3][Na(THF)_n]$ (by NMR). Treatment of this mixture (10 mg) with an excess of $TiBH_4$ (ca. 10 mg) in toluene- d_8 (0.5 ml) immediately gave V and III ($[V]/[III] = 97/3$ by NMR).

$[U(BH_4)_4][Na(18-crown-6)]$ (X). A round bottom flask was charged with IX (158 mg), $NaBH_4$ (15 mg) and 18-crown-6 ether (106 mg) and THF (20 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred at $20^\circ C$ for 2

h. The pale orange crystals formed were filtered off and washed with THF (20 ml). The yield was almost quantitative.

Reactions of $U(BH_4)_4$ with other dienyl reagents

(a) *With $(C_5H_7)K$.* A 50 ml round bottom flask was charged with I (73 mg) and $(C_5H_7)K$ (26 mg) and pentane (20 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred for 1.5 h at $20^\circ C$ and the red precipitate was filtered off. The green filtrate was evaporated to dryness below $20^\circ C$ and the residue sublimed (10^{-2} mmHg; $40^\circ C$) to give a pale green oily solid (ca. 5 mg). The NMR spectrum showed the presence of $(C_5H_7)U(BH_4)_3$. δ (Toluene- d_8 , $30^\circ C$): 107.04 (q, 85, 12H, BH_4); 18.53 (br, 30, 2H, 2,4-H); -9.88 (br t, 18, 1H, 3-H); -37.49 (d, 10, 2H, 1,5-*syn*H); -68.51 (d, 15, 2H, 1,5-*anti*H). The compound was contaminated with I (δ 135 ppm) and diamagnetic organic impurities.

(b) *With $(3Me-C_5H_6)K$.* An NMR tube was charged with I (10 mg) and $(3Me-C_5H_6)K$ (4 mg) and toluene- d_8 was condensed into it. A red precipitate was immediately formed. The NMR spectrum showed the transient presence of $(3Me-C_5H_6)U(BH_4)_3$ which had totally decomposed after 40 min at $20^\circ C$. δ (toluene- d_8 , $30^\circ C$): 137(br, 340, 12H, BH_4); 48.90(s, 3H, CH_3); 16.43(br t, 29, 2H, 2,4-H);

Table 4

Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

$U(BH_4)_3(2,4-Me_2C_5H_5)$ (II)	$U(BH_4)_3(C_5H_5)$ (III)
U-B(1)	2.50(3)
U-B(2)	2.52(3)
U-B(3)	2.54(3)
U-C(1)	2.79(3)
U-C(2)	2.77(3)
U-C(3)	2.63(2)
U-C(4)	2.80(2)
U-C(5)	2.78(2)
U-2 ^b	1.04(3)
C(1)-C(2)	1.37(3)
C(2)-C(3)	1.43(3)
C(3)-C(4)	1.45(4)
C(4)-C(5)	1.34(4)
C(2)-C(7)	1.53(3)
C(4)-C(6)	1.44(4)
B(1)-U-B(2)	105.0(8)
B(1)-U-B(3)	106(1)
B(2)-U-B(3)	102(1)
C(1)-C(2)-C(3)	124(2)
C(2)-C(3)-C(4)	133(2)
C(3)-C(4)-C(5)	122(3)
C(1)-C(2)-C(7)	122(2)
C(3)-C(2)-C(7)	115(2)
C(3)-C(4)-C(6)	120(2)
C(6)-C(4)-C(5)	118(2)
U-B(1)	2.56(5)
U-B(2)	2.45(5)
U-C(1)	2.60(3)
U-C(2)	2.64(3)
U-C(3)	2.72(3)
U-1 ^a	2.43(2)
U-2 ^b	1.03(4)
C(1)-C(2)	1.32(5)
C(2)-C(3)	1.26(5)
C(3)-C(3')	1.31(7)
B(1)-U-B(2)	101(1)
B(1)-U-1	120(1)
B(2)-U-1	112(1)
1-U-2	178(3)
C(1)-C(2)-C(3)	107(3)
C(2)-C(1)-C(2')	108(5)
C(2)-C(3)-C(3')	109(3)

^a 1 is the centroid of the cyclopentadienyl ring. ^b 2 is the centroid of the boron atoms.

–41.55 (d, 10, 2H, 1,5-*syn*H); –62.58 (d, 15, 2H, 1,5-*anti*H).

(c) *With (dmpd)₂Zn.* An NMR tube was charged with I (12 mg) and (dmpd)₂Zn (1.5 mg) and toluene-*d*₈ was condensed into it. The NMR spectrum showed the formation of II and a small quantity (ca. 5%) of IV, the proportion of ([IV]/[II] = 80/20 increased when an excess of (dmpd)₂Zn (ca. 10 equiv.) was added.

Reactions of IX with 1 equivalent of dmpdK or CpNa

(a) An NMR tube was charged with IX (10 mg) and dmpdK (3.5 mg) and THF-*d*₈ was condensed into it. After 2 h the NMR spectrum exhibited the signals of VI (2%), U(BH₄)₃(THF)_n (2%), and other peaks which were attributed to the (dmpd)U(BH₄)₃[–] anion (70%). δ (THF-*d*₈, 30 °C): 104.9 (br, 330, 12H, BH₄); –17.29 (s, 2H, CH₂); –18.10 (s, 6H, CH₃); –48.96 (br, 75, 1H, CH); –51.55 (br, 75, 2H, CH₂). Addition of 18-crown-6 ether caused progressive precipitation of [U(BH₄)₄][K(18-crown-6)] and formation of 2,4-dimethylpenta-1,3-diene.

Table 5

Crystallographic data and experimental details

	II	III
<i>Crystal data</i>		
Crystal dimensions (mm)	0.35 × 0.25 × 0.10	0.20 × 0.15 × 0.10
Color	dark green	orange
Crystal system	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Cmc</i> 2 ₁
<i>a</i> (Å)	7.443(3)	11.130(4)
<i>b</i> (Å)	8.035(4)	13.220(7)
<i>c</i> (Å)	11.676(4)	7.550(2)
α (°)	84.19(3)	
β (°)	87.04(3)	
γ (°)	70.69(4)	
<i>V</i> (Å ³)	655(1)	1110(1)
<i>Z</i>	2	4
<i>D</i> _{calc} (Mgm ^{–3})	1.99	2.08
μ (Mo- <i>K</i> α) (cm ^{–1})	116.97	137.92
<i>Data collection</i>		
Radiation	Mo- <i>K</i> α (λ 0.71073 Å)	Mo- <i>K</i> α
θ limits (°)	1–20	2–25
Scan type	$\omega/2\theta$	$\omega/2\theta$
Monochromator	graphite	graphite
Reflections measured		
<i>h</i>	–7, 7	0, 13
<i>k</i>	0, 7	0, 15
<i>l</i>	–11, 11	0, 8
Reflections collected		
total	1420	620
unique	1092	566
with <i>I</i> > 3 σ (<i>I</i>)	990	453
Temperature (K)	294	294
<i>Final values</i>		
<i>R</i> (<i>F</i>)	0.036	0.032
<i>R</i> _w (<i>F</i> ²) (ω = 1)	0.050	0.035

(b) An NMR tube was charged with IX (11 mg) and CpNa (2.5 mg); and THF- d_8 was condensed into it. The NMR spectrum showed the formation of $[\text{Cp}_2\text{U}(\text{BH}_4)_2][\text{Na}(\text{THF})_n]$ (10%) and $[\text{CpU}(\text{BH}_4)_3][\text{Na}(\text{THF})_n]$ (90%). $\delta(\text{THF-}d_8, 30^\circ\text{C})$: 97.7(br, 420, 12H, BH_4); -19.56(br, 50, 5H, Cp). Addition of 18-crown-6 ether led to the formation of VIII and X, which progressively separated out.

The $\text{CpU}(\text{BH}_4)_3^-$ anion was also prepared by treatment of III (348 mg) with 2% sodium amalgam (1200 mg) in THF (20 ml). The mixture was stirred for 12 h at 20°C then filtered; the filtrate was evaporated to dryness, and the oily residue (350 mg) washed with toluene (20 ml). The NMR spectrum showed the presence of $[\text{CpU}(\text{BH}_4)_3][\text{Na}(\text{THF})_n]$ and $[\text{Cp}_2\text{U}(\text{BH}_4)_2][\text{Na}(\text{THF})_n]$ in the ratio 90/10. Attempts to obtain a pure compound by recrystallization were unsuccessful.

Reactions of VI and $\text{Cp}_3\text{U}(\text{THF})$ with respectively CpK and dmpdK

An NMR tube was charged either with VI and 3 equivalents of CpK or with $\text{Cp}_3\text{U}(\text{THF})$ and 3 equivalents of dmpK. THF- d_8 was then condensed into the tube. The same NMR spectrum (-50°C) was obtained in each case, indicating the presence of $\text{Cp}_3\text{U}(\text{THF})$ as the major organouranium component along with the dmpdK and CpK compounds in the ratio 85/15. A similar experiment in the presence of toluene as an internal standard showed that 90% of the starting uranium complex was in the form of $\text{Cp}_3\text{U}(\text{THF})$.

Table 6

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d. for compound II.

Atom	x	y	z	B ($\text{\AA}^2$) ^a
U	0.0360(1)	0.3156(1)	0.26552(7)	3.39(2) *
B(1)	0.205(4)	0.100(4)	0.427(2)	6.0(7)
B(2)	0.226(4)	0.210(4)	0.087(2)	6.1(7)
B(3)	0.108(4)	0.599(4)	0.285(2)	5.0(6)
C(1)	-0.206(3)	0.123(3)	0.232(2)	5.5(5)
C(2)	-0.265(3)	0.272(3)	0.156(2)	4.1(4)
C(3)	-0.312(3)	0.449(3)	0.187(2)	3.6(4)
C(4)	-0.344(3)	0.526(3)	0.297(2)	5.2(5)
C(5)	-0.297(3)	0.426(3)	0.396(2)	6.1(6)
C(6)	-0.412(4)	0.715(4)	0.299(2)	7.8(7)
C(7)	-0.259(3)	0.258(3)	0.027(2)	6.5(6)

^a * means: $B_{\text{eq}} = 4/3[\sum_i \sum_j \beta_{ij} \vec{a}_i \vec{a}_j]$.

Table 7

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d. for compound III

Atom	x	y	z	B ($\text{\AA}^2$) ^a
U	0.000	0.79345(7)	-0.100	3.89(1) *
C(1)	0.000	0.597(2)	-0.069(8)	14(2) *
C(2)	0.096(2)	0.615(2)	-0.166(5)	13(1) *
C(3)	0.059(4)	0.638(2)	-0.319(4)	14(2) *
B(1)	0.000	0.829(4)	0.233(7)	7(1)
B(2)	0.182(4)	0.884(3)	-0.190(5)	9(1)

^a * means: $B_{\text{eq}} = 4/3[\sum_i \sum_j \beta_{ij} \vec{a}_i \vec{a}_j]$.

X-Ray analysis

Single crystals were introduced into thin-walled Lindemann glass tubes in an inert atmosphere drybox. Data were collected in an Enraf–Nonius CAD4 automatic diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by a least-squares refinement of the setting angles of the 25 reflections with θ between 8 and 12°. Intensities were corrected for Lorentz polarization effects and absorption (using the empirical DIFABS method [22]). The structures were solved by the heavy-atom method and refined by full-matrix least-squares (F). H atoms of the pentadienyl and cyclopentadienyl rings were included in the refinement at calculated positions (C–H 0.95 Å, B 5 Å²); they were not refined but constrained to ride on their C atoms. The absolute structure was determined for III. All calculations were performed on a PDP 11/23 Plus computer with the Enraf–Nonius Structure Determination Package [23]. Analytical scattering factors for neutral atoms [24] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 5. Selected bond lengths and final positional parameters are listed in Tables 4, 6 and 7 for compounds II and III, respectively. A complete list of bond lengths and angles and a table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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