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Derivatives of $U(BH_4)_4$ and its Lewis base adducts; synthesis of monocyclopentadienyl- and hydride-uranium(IV) complexes: $(\eta\text{-}C_5H_5)U(BH_4)_3$ and $(CH_3OCH_2CH_2OCH_3)U(BH_4)_3H$

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Abstract

In solution, $(THF)_2U(BH_4)_4$ and $(HMPA)_2U(BH_4)_4$ adopt a *trans*-configuration, whereas $(Ph_3PO)_2U(BH_4)_4$ exists as an equilibrium mixture of two isomers. Thermolysis of $(DME)U(BH_4)_4$ gives the corresponding uranium (IV) hydride $(DME)U(BH_4)_3H$. Reaction of $U(BH_4)_4$ with TlCp or cyclopentadiene in toluene gives $CpU(BH_4)_3$.

Introduction

The structural properties of the covalent uranium tetraborohydride $U(BH_4)_4$ (I) have received much attention [1], and especially, because of its volatility [2], in the context of the Manhattan project. However, the chemical transformations of I were limited to the synthesis of $U(BH_3CH_3)_4$ [3] and the preparation of some adducts of $U(BH_3R)_4$ or $U(BH_3R)_3$ (R = H, Me) [4,5,6]. It seemed to us that I and its adducts might be useful for the synthesis of new organouranium compounds. In contrast to the *d* transition metal borohydrides, which, with some exceptions, exist only at low temperature [1], these thermally stable uranium borohydrides should be good models for studies of the structure and the reactivity of the BH_4 ligand.

In the course of the preparation of I we isolated a novel crystalline form of this complex [7]. We synthesized from I the adducts $L_2U(BH_4)_4$ (II–V) with triphenylphosphine oxide, hexamethyl phosphoramide (HMPA), tetrahydrofuran (THF) [5,8], and dimethoxyethane (DME), respectively. These compounds were found to undergo novel reactions of the borohydride ligands, viz. (a) elimination of a BH_4 molecule from the adducts IV and V led to the uranium(IV) hydrides $L_2U(BH_4)_3H$ (L = THF; L = DME: VI), and (b) replacement of a BH_4 group of I by a cyclopentadienyl ligand gave $CpU(BH_4)_3$ (VIII) (Cp = η-C_5H_5).

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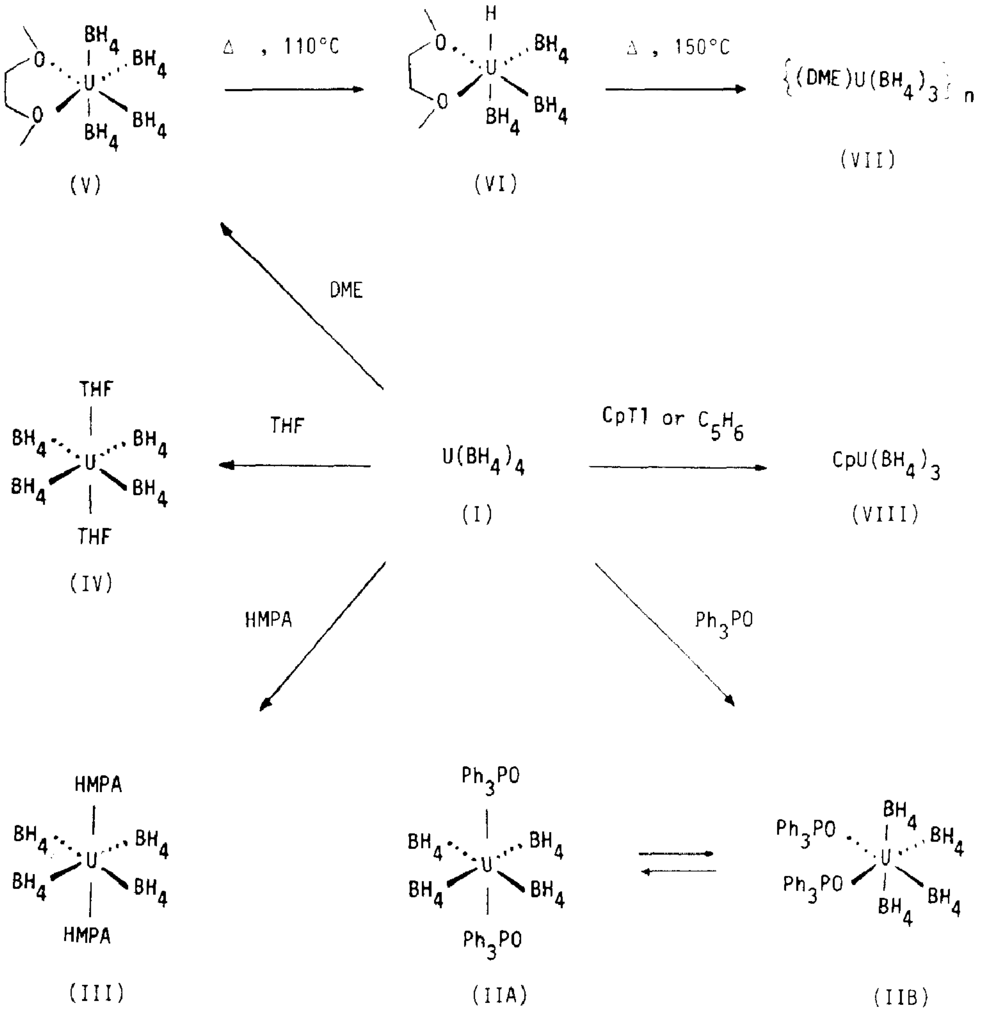
The X-ray crystal structures of $(Ph_3PO)_2U(BH_4)_4$ and $(THF)_2U(BH_4)_4$, which have already been published [8,9], revealed some distortion of the BH_4 ligand. In this paper, we suggest an explanation for this structural feature, which can be related to the reactivity of the borohydride group. We also present and discuss the results of the NMR studies on the structure and dynamic behaviour of the $L_2U(BH_4)_4$ complexes in solution. The synthesis and X-ray crystal structures of the cyclopentadienyl and hydride uranium complexes VI and VIII were previously reported in preliminary communications [10,11], and we give here the full details of their preparation, characterization, and reactions.

Synthesis and characterization of the $L_2U(BH_4)_4$ complexes

Treatment of I in toluene with 2 equivalents of Ph_3PO, HMPA, THF, or DME gave the Lewis base adducts II–V, respectively, isolated as pale green air-sensitive crystals (Scheme 1).



Scheme 1

Table 1

^{1}H NMR spectra of the complexes [a]

Compound	T(°C)	BH_4 ligands	Other ligands
$(Ph_3PO)_2U(BH_4)_4$(II)	30	23.3(br,400,16H)	14.1(br,50,12H,*o*-Ph)
			8.6(br,30,18H,*m*- and *p*-Ph)
isomer IIA [b]	−90	−64.2(br,100,16H)	31.9(br,27,12H,*o*-Ph)
			12.0(brt,8,12H,*m*-Ph)
			11.1(brt,8,6H,*p*-Ph)
isomer IIB [b]	−90	163.7(br,100,8H)	9.9(br,27,12H,*o*-Ph)
		−25.4(br,90,8H)	8.0(br,35,18H,*m*- and *p*-Ph)
$(HMPA)_2U(BH_4)_4$(III)	30	−61.1(br,370,16H)	18.48(d,10,36H)
	−50	−148.0(br,350,16H)	31.8(br,200,36H)
$(THF)_2U(BH_4)_4$(IV)	25	171.9(br,350,16H)	−15.8(br,35,8H,β-THF)
			−33.1(br,90,8H,α-THF)
	−80	225.6(br,100,16H)	−26.8(br,20,8H,β-THF)
			−53.8(br,20,8H,α-THF)
$(DME)U(BH_4)_4$(V)	25	[c]	−31.7(br,25,4H,CH_2)
			−41.4(br,25,6H,CH_3)
	−60	596.9(br,370,8H)	−46.2(s,4H,CH_2)
		−94.3(br,175,8H)	−61.1(s,6H,CH_3)
$(DME)U(BH_4)_3H$(VI)	30	[c]	−35.4(br,180,4H,CH_2)
			−45.1(br,25,6H,CH_3)
	−60	752.6(br,530,4H)	−31.6 and −52.3(s,2H and 2H, CH_2)
			−62.8(s,6H,CH_3)
$CpU(BH_4)_3$(VIII)	30	53.20(q,78,12H)	14.63(s,5H,Cp)

[a] In toluene-d_8, except II and III in CD_2Cl_2; reported as δ (ppm) from TMS; given successively in parentheses: multiplicity, most signals are broad (br); half height width or J in Hz, intensity and assignment. [b] The equilibrating isomers IIA and IIB are in the ratio 30/70. [c] BH_4 peaks broadened into base line due to rapid exchange.

The structures and dynamic behaviour of these complexes in solution were studied by ^{1}H NMR spectroscopy (Table 1). The spectra of the HMPA and THF derivatives III and IV, between 30 °C and −80 °C show one signal corresponding to the BH_4 ligands, indicating that in solution the complexes adopt an octahedral configuration with the two L ligands in *trans* positions. This structure was also found for the crystalline form of IV [5,8]. The dynamic behaviour in solution of the DME adduct V is identical to that of the methyl borohydride analogue $(DME)U(BH_3CH_3)_4$ [6]: rapid exchange of the BH_4 sites occured at 25 °C, whereas two inequivalent pairs of borohydride ligands were observed at low temperature. The low field NMR signal was assigned to the BH_4 groups, which are mutually *trans* (*cis* to the oxygen atoms of the DME molecule) [12]. The two possible octahedral isomers of $(Ph_3PO)_2U(BH_4)_4$, (IIA) and (IIB), were detected in CD_2Cl_2 at −80 °C; the Ph_3PO ligands of the most abundant isomer IIB (70%) are in a *cis* disposition, whereas they were found to be in a *trans* disposition in the crystalline form of II [9]. The tendency of octahedral uranium complexes, such as $CpUCl_3(Ph_3PO)_2$ [13] and $(Ph_3PO)_2UCl_4$ [14], to adopt stable configurations with *cis* triphenyl phosphine oxide ligands was tentatively explained in terms of π-interactions between the phenyl rings [14]. Spin saturation transfer experiments [15] showed that IIA and IIB are in rapid equilibrium even at −80 °C. This equilibrium is another example of isomerization of octahedral uranium compounds [13]. Varia-

Table 2

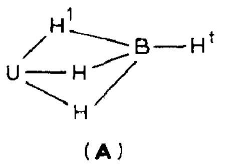
Elemental analyses and IR (ν(BH)) frequencies of the complexes

Compound	Analyses (Found (calcd) (%))				ν(BH) [a] (cm^{-1})
	C	H	B	P	
II	50.44	4.98		7.41	2473, 2418,
	(50.63)	(5.43)		(7.25)	2220, 2172
III	21.75	6.61		9.17	2453, 2412,
	(21.98)	(7.99)		(9.45)	2217, 2178
V	12.33	6.67	10.93		2490, 2200,
	(12.40)	(6.76)	(11.16)		2140
VI [b]	13.70	5.14	9.23		2480, 2210,
	(12.86)	(6.20)	(8.68)		2140
VII	12.67	5.50	8.86		2462, 2264,
	(12.89)	(5.95)	(8.70)		2203, 2140
VIII	17.05	4.71	9.38		2528, 2156
	(17.25)	(4.92)	(9.32)		2087

[a] In Nujol mull. [b] The discrepancies between calculated and observed analytical data are commented on in the experimental section.

tions in the NMR chemical shifts and broadening of the resonances showed that complexes IV and V undergo exchange of their L ligands with the corresponding free molecules; however, no intermolecular exchange of the Ph_3PO ligands of II could be detected, and III reacted with HMPA to give a mixture of unidentified products.

Infrared spectra [1] indicated that both bidentate and tridentate borohydride ligands are coordinated to II and III, whereas all the BH_4 groups of IV and V adopt a tridentate coordination (Table 2); these indications were confirmed by the X-ray crystal structures of II [9] and IV [8]. These structures also revealed an additional interesting feature in the geometry of the tridentate BH_4 ligands, which are not symmetrically oriented (A), namely that one of the three bridging hydrogen atoms is closer to the uranium center (U–H_1 2.0–2.1 Å) than the other two (2.4–2.8 Å), and the value of the U–B–H^t angle is around 160°. A similar distortion of the tridentate borohydride ligand was also found in the second crystalline form of



(A)

$U(BH_4)_4$ [7*]. This situation resembles that encountered with recently reported *d* transition metal aluminohydrides [16], and suggests that some uranium borohydrides can be regarded as uranium hydrides coordinating to a BH_3 molecule. This hypothesis was confirmed by the reactions of complexes IV and V.

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* Reference marked by an asterisk indicates a note in the list of references.

Synthesis and characterization of the uranium(IV) hydride (DME)U$(BH_4)_3$H (VI)

Thermolytic of photolytic reduction of the uranium(IV) borohydrides to the corresponding U$(BH_4)_3$ derivatives, with evolution of hydrogen and diborane, was previously observed [2], and reflects the ready accessibility of the uranium(III) oxidation state. Thermal decomposition of V in toluene at 150 °C gave dark red crystals; the elemental analyses of which indicated the formula $[(DME)U(BH_4)_3]_n$ (VII). The insolubility of these crystals in the usual organic solvents, which precluded NMR studies, suggests a polymeric structure. A different reaction occurred when a solution of V in toluene was kept at 110 °C; no precipitation of VII was noted, but green crystals of VI were formed after addition of pentane to the toluene solution (Scheme 1). In a separate experiment with triphenylphosphine present, formation of the adduct PPh_3-BH_3 was observed. That VI is an intermediate in the reduction of V was confirmed by its thermal conversion into VII. The ^1H NMR spectrum (Table 1) indicates that VI is derived from V by replacing one of the two *trans* BH_4 groups by a hydride ligand, but the latter was not observed [17]. In this configuration the CH_2CH_2 fragment of the DME ligand has two magnetically inequivalent pairs of vicinal hydrogen atoms. X-ray diffraction studies revealed that VI adopts a dimeric structure in the crystalline form, the pseudo octahedral monomeric units being bridged by the hydride ligands [11]. In similar experiments NMR studies showed the presence of the compound $(THF)_2U(BH_4)_3H$ as an intermediate in the reduction of the THF derivative IV. This hydride could not be obtained pure, free from IV or reduced products [18].

Synthesis of *d* transition metal hydrides from the corresponding borohydrides is very well-known but the preparation of VI represents the first example of such a reaction in the actinide series. Up to now, uranium hydrides, which are very rare, have been obtained from alkyl or amide uranium compounds [19]. Reactions of VI and formation of (DME)U$(BH_4)_3$X derivatives (X = alkyl, halide) will be described in a subsequent paper.

Synthesis and characterization of the monocyclopentadienyl uranium complex CpU$(BH_4)_3$ (VIII)

Treatment of I with one equivalent of CpTl in toluene gave the complex VIII, a rare example of a monocyclopentadienyluranium compound [13]. The latter was also obtained by the reaction of I with cyclopentadiene in toluene (Scheme 1). Compound VIII could not be prepared in THF; in this solvent, it was totally transformed into a 1/1 mixture of $Cp_2U(BH_4)_2$ [10] and IV. This clearly illustrates the major influence of the solvent on the stability of uranium complexes, the ligands of which can readily be displaced by coordinating molecules. Consistently, an equimolecular mixture of $Cp_2U(BH_4)_2$ and I in toluene was completely converted into VIII. Whatever its mode of preparation, VIII was easily purified by sublimation (10^{-2} mmHg, 20 °C) and isolated as orange crystals. X-ray diffraction studies [10] showed that VIII is monomeric in the solid state, with the uranium atom in a tetrahedral environment. In this structure the complex is coordinatively and sterically unsaturated, and could accomodate a number of additional ligands. Compound VIII did not react with olefins, phosphines, or carbon monoxide, but with 2 electron oxygen ligands, the complexes CpU$(BH_4)_3$L and CpU$(BH_4)_3L_2$ were formed; in some cases this coordination induced intermolecular rearrangements, and the adducts were only observable at low temperature.

The characterization, dynamic behaviour, and ligand exchange reactions of the derivatives of VIII will be described in a forthcoming paper. The BH_4 groups of VIII are easily replaced by cyclopentadienyl ligands; use of an excess of CpTl in the synthesis of VIII led to the formation of $Cp_2U(BH_4)_2$, which was also formed by the reaction of VIII with Cp_3U-2-Bu [23].

Experimental

General methods. Microanalyses were carried out in the Analytisches Laboratorien at Engelskirchen (FRG) or the Laboratoire d'Analyses du CNRS (Gif sur Yvette, France). The infrared spectra were recorded on a Perkin–Elmer 782 instrument and the ^1H NMR spectra on a Bruker W60 (FT) instrument fitted with a temperature control unit. Deuterated solvents were dried over molecular sieves (3 Å). The paramagnetic chemical shifts are shown relative to tetramethylsilane ($\delta = 0$), with positive values denoting shifts to low field. ^1H NMR spectra and analytical data are given in Tables 1 and 2.

All experiments were carried out under argon by standard Schlenck techniques or in a glove box. Evaporation was under reduced pressure. Toluene, pentane, THF, and DME were distilled from sodium. $OPPh_3$ (Schuchart), HMPA (Merck), PPh_3 (Prolabo) were used without purification. TlCp [21], $U(BH_4)_4$ [22], $Cp_2U(BH_4)_2$ [20] and Cp_3UnBu [23] were prepared by published methods.

$(Ph_3PO)_2U(BH_4)_4$ (II). A solution of Ph_3PO (250 mg) in toluene (15 ml) was added to a solution of I (140 mg) in toluene (15 ml). Pale green microcrystals of II were formed within 5 min. These were filtered off, washed with toluene (20 ml) then pentane (10 ml), and dried under vacuum (300 mg, 75%).

$(HMPA)_2U(BH_4)_4$ (III). A solution of HMPA (200 μl) in toluene (10 ml) was added to a solution of I (180 mg) in toluene (15 ml). Pale green microcrystals of III were formed within 5 min. These were filtered off, washed with toluene (5 ml) then pentane (10 ml), and dried under vacuum (170 mg, 43%).

$(THF)_2U(BH_4)_4$ (IV). THF (150 μl) was added from a syringe to a solution of I (120 mg) in toluene (10 ml). After 10 min the solution was evaporated to dryness to give a pale green solid (160 mg). The NMR spectrum showed this to be pure IV. Crystals of IV were obtained from a concentrated toluene solution. The product is identical to that described in ref. 5.

$(DME)U(BH_4)_4$ (V). DME (400 μl) was added from a syringe to a solution of I (150 mg) in toluene (20 ml). After 10 min, the solution was evaporated to dryness; the residual green solid was dissolved in toluene (8 ml), and pentane (15 ml) was added. After 16 h at 20 °C, green crystals of V were formed and were filtered off and dried under vacuum (100 mg, 50%).

$(DME)U(BH_4)_3H$ (VI) and $(DME)U(BH_4)_3$ (VII). A solution of V (prepared from 140 mg of I) in toluene (15 ml) was kept at 110 °C for 1.5 h. The pale orange mixture was dried under vacuum and the residue extracted with toluene (20 ml), leaving a small quantity of an insoluble tan product. Green crystals of VI (90 mg, 49%) were obtained by addition of pentane to the toluene extract (90 mg, 49%). A good elemental analysis for VI could not be obtained (Table 2). Partial decomposition occurred in vacuo, and so, VI was dried under a flow of argon. The observed

deviations are due to the presence of residual toluene (3–5% determined by the NMR) and probably a small amount of decomposition. Such a desolvation–decomposition problem was encountered with other complexes [25]. In a separate experiment (20 °C, 16 h) in the presence of PPh_3, formation of the adduct PPh_3-BH_3, identified by comparison of the spectroscopic data with those of sample (Aldrich), was observed by NMR spectroscopy.

Similar thermolysis of V at 150 °C for 1 h gave a bright orange solution and dark red crystals of VII. These were filtered off, washed with toluene (15 ml), and dried under vacuum (100 mg, 55%). A solution of VI (60 mg) in toluene (10 ml) was kept at 150 °C for 1 h, to give crystals of VII (25 mg, 42%).

Thermolysis of IV. When a solution of IV (12 mg) in toluene-d_8 (0.5 ml) was placed in an NMR tube and kept at 120 °C, a red precipitate was progressively formed. NMR spectroscopy indicated the transient formation of $(THF)_2U(BH_4)_3H$. δ (toluene-d_8, -60 °C): 329.2 (br, 100, 4H, BH_4); 202.4 (br, 400, 8H, BH_4); -31.2 (br, 20, 8H, β-THF); -63.0 (br, 20, 8H, α-THF) ppm.

$CpU(BH_4)_3$ (VIII). (a) TlCp (140 mg) was added to a solution of I (163 mg) in toluene or pentane (40 ml). The mixture was stirred at 20 °C for 18 h, filtered, and evaporated under vacuum below 20 °C. Sublimation (10^{-2} mmHg, 20 °C) of the residue gave orange crystals of VIII (190 mg, 55%).

(b) Freshly distilled cyclopentadiene (0.4 ml) was added to a solution of I (90 mg) in toluene (10 ml). After 3 h at 80 °C the solution was evaporated to dryness below 20 °C and the residue was extracted with pentane (30 ml). Evaporation of the extract, followed by sublimation of the residue gave VIII (105 mg, 60%).

(c) a solution of $Cp_2U(BH_4)_2$ (65 mg) in toluene (15 ml) was added to a solution of I (48 mg) in toluene (10 ml). After 2 h at 20 °C, the solution was carefully evaporated to dryness. Sublimation of the residue gave orange crystals of VIII (60 mg, 53%). A similar experiment in an NMR tube showed quantitative formation of VIII; subsequent addition of THF (ca. 20 equiv.) regenerated $Cp_2U(BH_4)_2$ and the THF adduct of I in a 1/1 ratio.

Reaction of VIII with Cp_3UnBu. Cp_3UnBu (3.5 mg) was added in an NMR tube to a solution of VIII (5 mg) in toluene-d_8 (0.5 ml) at -10 °C. After 10 min, an unidentified precipitate was formed; the NMR signals of Cp_3UnBu were not visible in the spectrum, and 50% of VIII was transformed into $Cp_2U(BH_4)_2$.

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