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Structure and ligand exchange reactions of the complexes $(\eta\text{-}C_5H_5)U(BH_4)_3L_2$ in solution (L = tetrahydrofuran, dimethoxyethane, hexamethylphosphoramide, triphenylphosphine oxide)

Denise Baudry, Patrick Dorion and Michel Ephritikhine

Service de Chimie Moléculaire, IRDI/DESICP/DPC/CNRS UA 331, CEA CEN Saclay, 91191 Gif sur Yvette Cédex (France)

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Abstract

The $CpU(BH_4)_3L_2$ compounds (L = THF, II; DME, III; HMPA, IV) (but not that with L = Ph_3PO, V) undergo ligand redistribution reactions to give $Cp_2U(BH_4)_2$ and $L_2U(BH_4)_4$. The dynamic behaviour in solution of compounds II–V has been studied by low temperature ^1H NMR. The L ligands of II and V are respectively in *trans* and *cis* positions in an octahedral configuration, whereas complexes III and IV exist in solution as two equilibrating isomers. Dissociation of the THF ligands of II takes place; complexes III–V exchange their L ligands with the corresponding free molecules by an associative mechanism.

Introduction

The structure and dynamic behaviour in solution of hexacoordinate uranium(IV) complexes have been examined only in the case of the monocyclopentadienyluranium(IV) trichloride compounds $CpUCl_3L_2$ ($Cp = \eta\text{-}C_5H_5$, L = ether or phosphine oxide) [1,2]. It is clear that a greater knowledge of such complexes would be gained by studying the charges in their properties as the ligands are varied. Here we describe, and discuss the stability, the structure, and the ligand exchange reactions of the borohydride compounds $CpU(BH_4)_3L_2$ (II–V), the bis-Lewis base adducts of $CpU(BH_4)_3$ (I) with tetrahydrofuran, dimethoxyethane, hexamethylphosphoramide, and triphenylphosphine oxide.

Results and discussion

Stability of the $CpU(BH_4)_3L_2$ complexes

The synthesis of the monocyclopentadienyluranium(IV) borohydride $CpU(BH_4)_3$ (I) was recently described [3]. This complex, which is monomeric in the solid state

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[4], is coordinatively and sterically unsaturated, and should be able to accommodate a number of auxiliary ligands. However, we pointed out that coordinating solvents must be avoided in the preparation of I [5*]; in tetrahydrofuran (THF), this compound was immediately and completely transformed into an equimolecular mixture of $Cp_2U(BH_4)_2$ [6] and $(THF)_2U(BH_4)_4$ [3] (eq. 1).

$$CpU(BH_4)_3 \xrightarrow{L} Cp_2U(BH_4)_2 + L_2U(BH_4)_4 \quad (1)$$

This disproportionation was also found to occur, but less rapidly, in toluene or dichloromethane in the presence of 2 equiv. of THF. The same reaction was observed with dimethoxyethane (DME). With hexamethylphosphoramide (HMPA) a mixture of unidentified products, which presumably result from the further reaction of $Cp_2U(BH_4)_2$ and $(HMPA)_2U(BH_4)_4$ (see Experimental), was obtained. The triphenylphosphine oxide adducts $CpU(BH_4)_3(OPPh_3)$ and $CpU(BH_4)_3(OPPh_3)_2$ (V) were fairly stable in solution, and were isolated as pale green air-sensitive crystals.

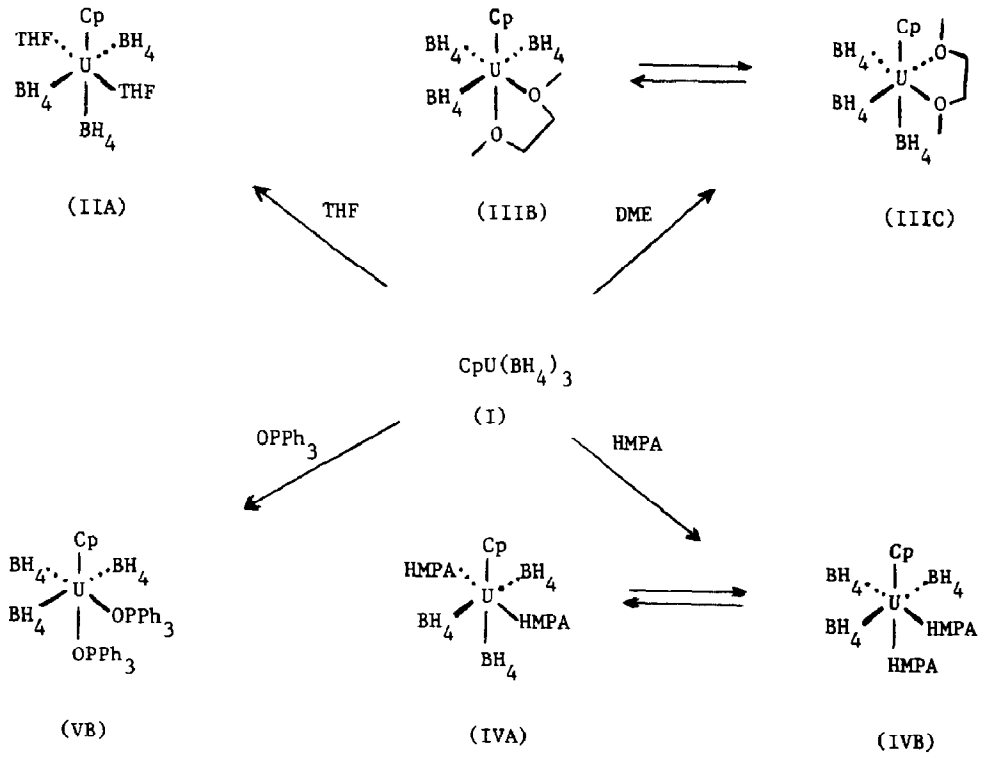
The complexes $CpU(BH_4)_3L_2$ (II–IV) are the first intermediates in reaction 1, and by working at low temperature to slow down the ligand redistribution, these compounds could be studied in solution (vide infra). The behaviour of these products is in striking contrast to that of the $CpUCl_3L_2$ analogues, which are very stable in THF; moreover, all attempts to prepare Cp_2UCl_2 in this solvent or in dimethoxyethane [1] gave a mixture of $CpUCl_3L_2$ and Cp_3UCl. In addition to $Cp_2U(BH_4)_2$, other Cp_2UX_2 compounds were synthesized, having $X = NEt_2$ or a thiolate [7], acetylacetonate [8], alkoxide or aryloxide ligand [9]; the relative stability of these compounds reflects the ability of the X ligand to saturate the uranium coordination sphere [10].

Structure in solution of the $CpU(BH_4)_3L_2$ complexes

Solutions of complexes II–V were prepared by addition of a small excess of THF or DME or a stoichiometric amount of HMPA or Ph_3PO to I in toluene or dichloromethane (Scheme 1). These solutions were sufficiently stable below $-30\,^{\circ}C$ to be studied by NMR spectroscopy; the spectral data are listed in Table 1.

In solution compound II adopts the octahedral configuration A, with the two magnetically equivalent THF ligands in *trans* positions (Scheme 1); the borohydride groups give rise to two signals of relative intensity 2/1. The paramagnetic chemical shifts of the signals corresponding to the axial ligands of IIA (low field resonances of Cp and 1 BH_4) lie in the opposite direction from those assigned to the equatorial groups (high field resonances of $2BH_4$ and 2THF). This situation, which is predicted from the theoretical expression for the pseudo-contact shifts in axial symmetry [11], was previously encountered with the octahedral $CpUCl_3L_2$ [2] and $L_2U(BH_4)_4$ [3] compounds. The two possible isomers of $CpU(BH_4)_3(DME)$, IIIB and IIIC, were detected in solution at $-80\,^{\circ}C$. Except for the borohydride resonances, the ^1H NMR spectrum of IIIB resembles that of the *mer*-octahedral $CpUCl_3(DME)$ compound [1], in which the CH_3 and CH_2 groups of the dimethoxyethane molecule are magnetically different. In isomer IIIC, the two CH_3 groups of the DME ligand are equivalent, but the CH_2CH_2 fragment presents two

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



Scheme 1.

distinct pairs of vicinal hydrogen atoms. Spin saturation transfer experiments [12] showed that IIIB and IIIC are in rapid equilibrium. The HMPA derivative IV exists in solution in the form of the two equilibrating isomers IVA and IVB in the proportions 45/55, whereas the two triphenylphosphine oxide ligands of V are mutually *cis* in the *mer* octahedral configuration B.

The structure of V in solution is identical to that of $CpUCl_3(OPPh_3)_2$ [2], and provides a further example (compare $(Ph_3PO)_2UCl_4$ [13] and $(Ph_3PO)_2U(BH_4)_4$ [3]) of the tendency for such octahedral uranium complexes to adopt stable configurations with *cis*-triphenylphosphine oxide ligands; this geometry was tentatively attributed to π-interactions between the phenyl rings [13]. The structures in solution of complexes II–IV differ markedly from those of the corresponding $CpUCl_3L_2$ compounds, which, for X = THF and DME, adopt exclusively the *cis* configuration B, and for X = HMPA, predominantly exist in this form. Complex III is unique among the series of the $CpUX_3L_2$ and (indenyl)UX_3L_2 [14] compounds in adopting the isomer form C, with two equatorial L ligands in mutually *cis* positions.

The *cis* arrangement of the L ligands in the $CpUCl_3L_2$ complexes has been attributed to intramolecular non-bonded repulsions, which would be at a minimum when the ligand with the smallest coordination atom is *trans* to the cyclopentadienyl ligand [1]. Another explanation invokes the electronic effect of the Cl ligand: the electron withdrawal by this ligand would weaken the *trans*-metal–cyclopentadienyl bond in configurations A and C [15]. From consideration of the cone angle factors (caf) [16] of the Cl (caf = 0.14), THF (caf = 0.09) and BH_4

ligands (caf = 0.11 or 0.16 for a bidentate or a tridentate ligation), it is not obvious, in light of the first explanation that the borohydride group should occupy the polyhedral site *trans* to the Cp ring in complex II. The differing structures of the $CpUX_3L_2$ compounds (X = Cl, BH_4) seem instead to be attributable to electronic factors, and it is possible that configurations A and C of the $CpU(BH_4)_3L_2$ compounds are not destabilized, as they are in the case of the chloride analogues, because of the electron-donating ability of the BH_4 ligand [17].

Ligand exchange reactions of the $CpU(BH_4)_3L_2$ complexes

In contrast to $CpUCl_3(THF)_2$ [1], the THF ligands of II are not firmly attached to the metal centre, and evaporation of a toluene solution of this compound gave crystals of I; this distinct behaviour is clearly related to the coordination mode of the polydentate BH_4 groups [17]. It is therefore not surprising that the THF ligands of II are in rapid exchange with free tetrahydrofuran molecules. As is usually observed for organouranium complexes, the DME, HMPA, and Ph_3PO ligands are more strongly bonded than THF, and their dissociation was not found to occur in complexes III–V; no exchange of L ligands was detected between the mono- and bis-base adducts $CpU(BH_4)_3L$ and $CpU(BH_4)_3L_2$ (L = HMPA, Ph_3PO). However, spin saturation transfer experiments and broadening resonances showed that complexes III–V exchange their L ligands with the corresponding free species. As in the case of the chloride analogues [2], these reactions are stereoselective, only the equatorial L ligands are involved at low temperature, and for L = HMPA the rate of the exchange increases with the concentration of free ligand, suggesting an associative mechanism [18*].

Experimental

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (FRG). The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over molecular sieves (3 Å). The paramagnetic chemical shifts were calculated with respect to tetramethylsilane ($\delta = 0$); positive values denote shifts to low field. ^1H NMR spectra are given in Table 1.

All experiments were carried out under argon by Schlenck techniques or in a glove box. Solvents, THF, and DME were distilled from sodium. Ph_3PO (Schuchardt) and HMPA (Aldrich) were used without purification. $CpU(BH_4)_3$ was prepared as described in ref. 3, as were the compounds $L_2U(BH_4)_4$.

$CpU(BH_4)_3(THF)_2$ (II)

THF (3 μl, 0.036 mmol) was introduced into an NMR tube containing a solution of I (5 mg, 0.017 mmol) in toluene-d_8 (0.5 ml) at −60 °C. The NMR spectrum at −80 °C indicated the formation of 27% of II ($\delta(C_7D_8)$: 926 (4H, br, $w_{1/2}$ 250 Hz, BH_4), 75.3 (5H, s, Cp), −36.9 (8H, s, β-THF), −91.1 (8H, s, α-THF), −236 (8H, br, $w_{1/2}$ 80 Hz, BH_4)) and the presence of another species, I or $CpU(BH_4)_3(THF)$ with THF ($\delta(C_7D_8)$: 46 (12H, br, $w_{1/2}$ 700 Hz, BH_4), 40.6 (8H, br, $w_{1/2}$ 185 Hz, α-THF), 22.3 (8H, br, $w_{1/2}$ 105 Hz, β-THF), −8.8 (5H, br, $w_{1/2}$ 60 Hz, Cp)). At −40 °C, irradiation of the α (or β) THF signal of II caused a decrease in intensity of the corresponding signal of the other THF to 50% of its original value. After evaporation to dryness at room temperature, the NMR spectrum of the residue in

Table 1

^{1}H NMR [a] parameters for the complexes $CpU(BH_4)_3L_2$

Compound		BH_4 Ligands	Cp Ligand	L Ligand
IIA [b]	L = THF	959(350, 4H) −251(100, 8H)	77.0	−42.40(25, 8H, β-CH_2) −97.96(25, 8H, α-CH_2)
IIIB [c]	L = DME	310(280, 8H) −96(250, 4H)	−23.4	~ 3(CH_3 [d]); −7.9(80, 2H, CH_2); −36.9(80, 2H, CH_2); −70.3(80, 3H, CH_3)
IIIC [c]		980(400, 4H) −246(200, 8H)	80.9	−48.3(32, 2H, CH); −93.3(40. 2H, CH); −105.0(40, 6H, CH_3)
IVA [e]	L = HMPA	104.2(100, 4H) −76.5(60, 8H)	1.9	9.42(30, 36H, CH_3)
IVB [e]		−85.8(75, 8H) −110.3(80, 4H)	41.9	24.5(30, 18H, ax.CH_3) −8.1(30, 18H, eq.CH_3)
VB	L = $OPPh_3$	−195(80,8H) −230(80, 4H)	77.1	58.7(30, 6H, ax.*o*-Ph); 17.0(25, 6H, ax.*m*-Ph); 15.3(25, 3H, ax. *p*-Ph); 3.98(25, 3H, eq. *p*-Ph); 1.69(25, 6H, eq.*m*-Ph); −21.0(45. 6H, eq.*o*-Ph)

[a] II and IV in toluene-d_8, III and V in CD_2Cl_2; at −80 °C except II (at −85 °C). Reported as δ from TMS. Are given successively in parentheses: half height width in Hz, intensity and assignment. Cp signals ($w_{1/2}$ 10–15 Hz) integrate for 5H. [b] from a mixture of I + 20 equiv. of THF. [c] from a mixture of I + 1.5 equiv. of DME. IIIB and IIIC are in equilibrium; |IIIB|/|IIIC| = 40/60. [d] Masked by free DME. [e] IVA and IVB in equilibrium; |IVA|/|IVB| = 45/55.

toluene indicated the presence of I contaminated with 10% of $Cp_2U(BH_4)_2$ and 10% of $(THF)_2U(BH_4)_2$. Addition of 20 equiv. of THF to a toluene solution of I led to quantitative formation of II (Table 1).

$CpU(BH_4)_3(DME)$ (III)

DME (2.6 μl, 0.02 mmol) was introduced into an NMR tube containing a solution of I (5 mg, 0.014 mmol) in CD_2Cl_2 (0.5 ml). The NMR spectrum at 30 °C showed signals corresponding to I (δ 72.0 (BH_4), 16.8 (Cp)) and DME (δ 2.58 and 2.14). Broad resonances were observed between 25 and −60 °C. The spectrum at −80 °C (Table 1) indicated the presence of the two isomers IIIB and IIIC in the ratio 40/60. At −70 °C, the signals corresponding to the DME ligand of IIIB (*cis*-equatorial isomer) were much broader (250 Hz) than those of IIIC (45 Hz).

The spectrum of a toluene solution of I in the presence of 10 equivalents of DME was recorded at −80 °C; this spectrum was similar to that for which details are given in Table 1 but the ratio [IIIB]/[IIIC] was equal to 70/30. Irradiation of the signals corresponding to free DME brought about a decrease in intensity of the signals of the DME ligand of IIIB to 5% of their original value, whereas the intensity of signals from the DME ligand of isomer IIIC decreased to 20%. At −70 °C, coalescence of the signals corresponding to the DME ligand of IIIB was observed. After 16 h at room temperature, 50% of III were transformed into $Cp_2U(BH_4)_2$ and $(DME)U(BH_4)_4$.

$CpU(BH_4)_3(HMPA)_2$ (IV)

HMPA was progressively introduced into an NMR tube containing a solution of I (4.8 mg, 0.0138 mmol) in toluene-d_8 (0.5 ml). The NMR spectrum at −50 °C showed initially the presence of I along with another species which is presumably $CpU(BH_4)_3$(HMPA). ($\delta(C_7D_8)$: 33.7 (18 H, d 25 Hz, HMPA), 12.1 (5H, br, $w_{1/2}$ 75 Hz, Cp), −53 (12 H, br, $w_{1/2}$ 700 Hz, BH_4)). Further addition of HMPA led to the disappearance of I and the formation of IVA and IVB. No exchange was detected between the HMPA ligands of IV and $CpU(BH_4)_3$(HMPA). When the total quantity of added HMPA was equal to 4.8 μl (0.027 mmol, 2 equiv.), the NMR spectrum exhibited only the signals of IVA and IVB (Table 1). The half height width of the doublet signals corresponding to the HMPA ligands was 20 Hz. A further addition of HMPA (0.5 μl) caused a broadening of the signal corresponding to the equatorial HMPA ligand of IVB ($w_{1/2} = 30$ Hz), and the intensity of this signal was decreased by 95% when the signal corresponding to free HMPA was irradiated. In the presence of an excess of HMPA (15 μl overall, 0.04 mmol), the half height width of this signal was 35 Hz, whereas those of the other HMPA signals remained unchanged. After 16 h at −30 °C, a solution of I in the presence of two equivalents of HMPA gave ca. 25% of unidentified products; addition of HMPA to $Cp_2U(BH_4)_2$ or $(HMPA)_2U(BH_4)_4$ in toluene also caused formation of unidentified compounds [3].

$CpU(BH_4)_3(OPPh_3)$

Ph_3PO (33.4 mg) was added to a solution of I (43 mg) in toluene (10 ml). After 5 min the yellow solution was reduced to 3 ml by evaporation and pentane (7 ml) was added. After 12 h at room temperature, green crystals were formed and these were filtered off, washed with pentane, and dried under vacuum (35 mg, 45%). ($\delta(C_7D_8$,

30 °C): 31.94 (6H, brs, *o*-Ph), 11.42 (6H, brs, *m*-Ph), 10.31 (3H, t, 8Hz, *p*-Ph), −5.42 (5H, s, Cp), −12.8 (12H, br, $w_{1/2}$ 300 Hz, BH_4)). Analysis. Found: C, 43.84; H, 4.94; P, 5.08. $C_{23}H_{32}B_3POU$ calcd.: C, 44.08; H, 5.11; P, 4.95%.

$Cpu(BH_4)_3(OPPh_3)_2$ (V)

Ph_3PO (272 mg) and I (170 mg) were dissolved in CH_2Cl_2 (18 ml) at −30 °C. The solution was allowed to warm to room temperature, then evaporated to give V as a green powder (410 mg, 92%), which was dried under vacuum. Analysis. Found: C, 54.24; H, 5.05; P, 6.75. $C_{41}H_{47}B_3P_2O_2U$ calcd.: C, 54.46; H, 5.23; P, 6.85%.

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