Inorganica Chimica Acta, *144* (1988) 129–134

Chemical and Structural Aspects of Cyclopentadienyl Uranium(IV) Tetrahydroborato Complexes

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(Received July 28, 1987)

Abstract

Several new or partially described complexes of uranium(IV) of the series $Cp_{4-n}U(BH_4)_n$ [Cp = η^5-C_5H_5, η^5-$C_5H_4CH_3$ or η^5-$C_5H_4Si(CH_3)_3$] are reported, mainly in order to systematically compare their physical, chemical and spectroscopic properties. X-ray data of the crystal structure of Cp_3UBH_4 are also reported.

Introduction

The coordinating ability of the boron hydride ligands to the transition metal ions and particularly the possibility of the BH_4 group to form mono-, bi- and tridentate species have been widely investigated during the last two decades [1]. The mode of ligation seems mainly connected both with the metal radius and with the steric demands of other coordinated ligands present in the complex. Thus the large actinide ions generally favour trihapto mononuclear organometallic species, while bidentate structures have been observed, e.g. for crowded polymeric hydride-bridged species [2]. Since a close interconnection may exist between the structural features and the physicochemical properties of these compounds, we undertook investigations on several uranium(IV) and thorium(IV) complexes of the series $Cp_{4-n}M^f(BH_4)_n$ [$M^f = U^{IV}$ and Th^{IV}; $n = 1, 2, 3$; Cp = η^5-C_5H_5, η^5-$C_5H_4CH_3$ and η^5-$C_5H_4Si(CH_3)_3$]. Here we describe their syntheses as well as their chemical reactivities and some spectroscopic properties. In addition, data on the crystal structure of Cp_3UBH_4 are presented.

Experimental

All the operations were carried out in nitrogen-filled glove boxes. Solvents were dried and purified according to described procedures [3]. $Cp^{Me}H$ ($Cp^{Me} = C_5H_4CH_3$) was distilled before use. $LiBH_4$ (Janssen Chimica) was purified by crystallization from diethyl ether and $NaBH_4$ (Janssen Chimica) from isopropylamine; the purity of both was checked by titration with H_2SO_4. Samples of UCl_4, $ThCl_4$-TlCp (Cp = C_5H_5), $TlCp^{Me}$, $Cp_2U(BH_4)_2$, Cp_3UBH_4 and Cp_3UCl were prepared by published procedures.

^1H, ^{13}C and ^{11}B NMR spectra were recorded on a Varian FT80A spectrophotometer. Chemical shifts for ^1H and ^{13}C refer to TMS, calculated with respect to C_6D_5H as internal standard, and for ^{11}B to $BF_3 \cdot OEt_2$ as external standard. They are collected in Table III. Infrared spectra (4000–400 cm^{-1}) were recorded with a Perkin-Elmer 580B apparatus using Nujol mulls (except for $Cp_2^{Si}U(BH_4)_2$ which was used neat) sandwiched between KBr or CsI plates in sealed air-tight σ-holders. Near IR–Vis spectra were recorded with a Cary 17D spectrometer.

Elemental analyses were performed by Dornis und Kolbe mikroanalytisches Laboratorium, Mulheim (F.R.G.).

X-ray fluorescence analyses were carried out as described in ref. 4. Mass spectra were obtained with a ZAB 2F instrument (EI 70eV) (VG Organic, Ltd.).

Syntheses of $Cp^{Si}H$ and $TlCp^{Si}$

To a diethyl ether suspension of KCp (10 mmol) prepared *in situ* from K and CpH, 10 mmol of $(CH_3)_3SiCl$ were added and the mixture was stirred for about 10 h, after which all volatiles (mainly Et_2O and $Cp^{Si}H$) were fractionally distilled. $Cp^{Si}H$ (40%) was collected as a brown–yellow oily liquid at 140–143 °C (1 atm). $TlCp^{Si}$ was obtained as an insoluble white–silver solid by reacting a n-hexane solution of $Cp^{Si}H$ and TlOEt. It was separated by filtration.

Synthesis of $Cp_2^{Me}U(BH_4)_2$

To 570 mg of UCl_4 (1.5 mmol) in 30 ml of Et_2O, 100 mg of $LiBH_4$ (4.5 mmol) was added at room

0020-1693/88/$3.50

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temperature. After stirring for about 20 h, 850 mg of $TlCp^{Me}$ (3 mmol) were added to the solution. Two hours later the solution was filtered from TlCl, LiCl and the excess of $LiBH_4$, then Et_2O was removed under vacuum. The residue was transferred under nitrogen in a sublimer and sublimated at 0.2 torr, 55 °C. The sublimation continued for 2 days, giving a brown–yellow product. Its uranium content was determined by gravimetric analysis and X-ray fluorescence: *Anal.* Calc. for $C_{12}H_{22}UB_2$: U, 55.9. Found: U, 56.3%. ^1H NMR: 9.8 (s, 6H, CH_3), 15.83 (s, 4H), −12.76 (s, 4H); −21.15 (q, 8H, BH_4). ^{11}B NMR: 86.9 (quintet). IR (Nujol mull, CsI): 3090m, 2480s, 2180m, 2110m, 1170m, 1010m, 930m, 890m, 790s, 670m.

Synthesis of $Cp_2{}^{Si}U(BH_4)_2$

UCl_4 (760 mg, 2 mmol) and $LiBH_4$ (100 mg, 4.5 mmol) were stirred in Et_2O for 20 h, then $TlCp^{Si}$ (682 mg, 2 mmol) was added and stirring was continued for an additional 20 h. Et_2O was stripped away and the residue was washed with hexane and filtered. The collected fractions gave, after removal of n-hexane, $Cp_2{}^{Si}U(BH_4)_2$ (50–60% yield) as a red oily liquid. Gravimetric analysis and X-ray fluorescence gave: U, 44.2. Calc. for $C_{16}H_{34}UB_2Si$: U, 43.9%. ^1H NMR: 0.0 (s, 18H, CH_3), 18.38 (s, 4H), −16.52 (s, 4H), 18.07 (q, 8H, BH_4) ^{11}B: 92.1 (quintet). IR (neat): 3090w, 2940s, 2890sh, 2850sh, 2485s, 2200m, 2120m, 1440m, 1400m, 1370m, 1310m, 1250s, 1170s, 1040s, 1010m, 900s, 830s, 785s, 750s, 680m, 630s, 615sh.

Synthesis of $Cp_2Th(BH_4)_2$

$ThCl_4$ (1106 mg, 2 mmol) was suspended in 20 ml of DME and 154 mg of $NaBH_4$ (4 mmol) were added. After stirring for 3 days at room temperature, 1076 mg of TlCp (4 mmol) were added to the mixture. The solution was stirred for 24 h and then TlCl and NaCl were filtered off. DME was removed by prolonged pumping and the white residue, after washing several times with n-hexane, was analysed. Complete purification was achieved by slow sublimation (low yield, 10%) at 10^{-3} Torr and 150 °C. *Anal.* Calc. for $C_{10}H_{18}ThB_2$: C, 30.61; H, 3.0. Found: C, 30.53; H, 3.10%. Due to the low solubility in C_6D_6 we were not able to obtain good ^1H NMR spectra. IR (Nujol mull, KBr): 2480s, 2200m, 2140m, 1080m, 1010m, 790s.

Syntheses of $CpU(BH_4)_3$ *and* $Cp^{Me}U(BH_4)_3$

$CpU(BH_4)_3$ was prepared by an alternative route with respect to ref. 5. In particular UCl_4 (700 mg, 2 mmol) and $NaBH_4$ (300 mg, 8 mmol) were stirred in Et_2O at room temperature for 24 h, then TlCp (540 mg, 2 mmol) was added. After 2 days stirring the ^1H NMR spectrum revealed the presence in solution of $CpU(BH_4)_3$ (>80%) and $Cp_2U(BH_4)_2$ (<20%). The solution was filtered, Et_2O was removed and $CpU(BH_4)_3$ purified by sublimation. The amount of $Cp_2U(BH_4)_2$ varied on varying the excess of $NaBH_4$ used and its presence was probably due to disproportionation of $CpU(BH_4)_3$ into $Cp_2U(BH_4)_2$ and $U(BH_4)_4$, favoured by the coordinating ability of Et_2O [5]. ^{11}B NMR: 129 (br). In the same way we prepared $Cp^{Me}U(BH_4)_3$ but we did not succeed in purifying it from the $Cp_2{}^{Me}U(BH_4)_2$ formed in the course of the reaction. $Cp^{Me}U(BH_4)_3$ was identified in solution on the basis of ^1H NMR signals: 16.5 (s, 2H), 41.8 (q, 12H), −2.3 (s, 3H), 7.3 (s, 2H).

Reactivity

Reactions of $Cp_2U(BH_4)_2$ and Cp_3UBH_4 with various reagents (alcohols, acetone, acetylacetone, $HSnPh_3$) have been studied by adding the reagent to an Et_2O solution of the tetrahydroborate complex at room temperature. The products were identified from the ^1H NMR spectrum of a C_6D_5H solution of the residue obtained after removing Et_2O. Generally both the uranium compounds and the reagent were mixed in approximate stoichiometric ratios, except for CH_3COCH_3 and $Cp_2U(BH_4)_2$, in which different behaviour was observed depending on the molar ratio of the reagents, as follows:

(1) $Cp_2U(BH_4)_2$ + CH_3COCH_3*, molar ratio 1:1*

To $Cp_2U(BH_4)_2$ (1 mmol) in Et_2O, 1 mmol of CH_3COCH_3 was added dropwise. The solution gradually turned green and after 1 h the ^1H NMR spectrum revealed the presence in solution of $Cp_2U(OPr^i)BH_4$ as the main product, together with a small amount of $Cp_3U(OPr^i)$ and Cp_3UBH_4. $Cp_2U(OPr^i)BH_4$ was identified on the basis of ^1H NMR signals but we never succeeded in isolating it, either by extraction in different solvents or by sublimation (we obtained only Cp_3UOPr^i).

(2) $Cp_2U(BH_4)_2$ + CH_3COCH_3*, molar ratio 1:2*

Two mmol of CH_3COCH_3 were added to $Cp_2U(BH_4)_2$ (1 mmol) in n-hexane at room temperature. After 10 min the ^1H NMR spectrum showed that the reaction was complete: $Cp_2U(OPr^i)_2$ [6] was present in solution together with traces of $Cp_3U(OPr^i)$.

(3) $Cp_2U(BH_4)_2$ + CH_3COCH_3*, molar ratio 1:3*

When an excess of CH_3COCH_3 was added to $Cp_2U(BH_4)_2$ in Et_2O, the main product detectable by ^1H NMR was Cp_3UOPr^i together with Cp_3UBH_4.

Other results are summarized in Scheme 1.

X-ray Data

Crystals of Cp_3UBH_4 were obtained by crystallization from toluene. Cell parameters were determined from a least-squares refinement of the setting angles of 25 medium angle reflexions carefully centered on a Philips four-circle diffractometer with Mo Kα radiation.

Results and Discussion

The cyclopentadienyl tetrahydroborate complexes can be easily prepared by stepwise replacement of the chloride atoms of UCl_4 (or $ThCl_4$) with the Cp and BH_4 groups, *i.e.* by the reaction sequences:

$$UCl_4 + (4-n)TlCp \longrightarrow UCp_{4-n}Cl_n + (4-n)TlCl$$

$$UCp_{4-n}Cl_n + nMBH_4 \longrightarrow UCp_{4-n}(BH_4)_n + nMCl$$

(where M = Li, Na)

Tetrahydrofuran (THF), dimethoxyethane (DME) and diethyl ether have been used as the solvents, but for the synthesis of $CpU(BH_4)_3$ non-coordinating solvents had to be employed as in THF (and partially in Et_2O) disproportionation occurs as follows:

$$2CpU(BH_4)_3{\cdot}S \longrightarrow Cp_2U(BH_4)_2 + U(BH_4)_4{\cdot}S$$

(S = THF, Et_2O)

The yields are usually very high and in any case pure products can be easily obtained by sublimation; in fact the prepared compounds are very volatile; the volatility increases with the number of BH_4 groups present in the molecule and with the crowding of the substituted Cp ligands, *i.e.* following the series:

$$Cp_3UBH_4 < Cp_2U(BH_4)_2 < CpU(BH_4)_3$$

$$\text{and } Cp_2U(BH_4)_2 < Cp_2{}^{Me}U(BH_4)_2 < Cp_2{}^{Si}U(BH_4)_2$$

as reported in Table I.

$Cp_2U(BH_4)_2$ can be quantitatively prepared also by reaction of $Cp_2U(NEt_2)_2$ [7] with $BH_3{\cdot}SMe_2$, probably by the same mechanism as described elsewhere [8]. $Cp_2Th(BH_4)_2$ is far less volatile than uranium compounds and it is more difficult to obtain free from coordinated THF or DME.

Spectroscopic Properties

Visible and infrared spectra

The infrared spectra of the prepared compounds show the bands typical of the Cp and BH_4 groups, thus providing useful information on their coordination mode. In fact, those at 1000–1020 indicate η^5-coordination of the cyclopentadienyl ligands, while absorptions at 2450–2600, 2100–2200 and 1150–1250 cm^{-1} can be ascribed to a trihapto ligation mode of the BH_4 groups to the uranium atom, following the criteria established by Marks and generally confirmed by structural determinations [1, 2]. The substituents R (CH_3, $(CH_3)_3Si$) of the Cp group slightly modify only the position but not the shape of the absorptions typical of the BH_4 groups; of course their spectra present additional bands due to the R groups themselves.

The $Cp_2Th(BH_4)_2$ IR absorption bands are identical to those of its uranium analogues, indicating a striking similarity both in structure and bonding; however, unlike the corresponding uranium compound, it is usually obtained coordinated to THF and DME (as indicated by IR bands appearing in the range 1050–1150 cm^{-1}) from which it can be easily liberated by prolonged vacuum pumping or sublimation. Here probably the larger ion size of Th^{4+} with respect to that of U^{4+} plays a role in allowing the coordination of one extra ligand.

$Cp_2U(BH_4)_2$, $Cp_2{}^{Me}U(BH_4)_2$ and $Cp_2{}^{Si}U(BH_4)_2$ show very similar solvent independent spectra in the visible–near-IR region (Fig. 1), indicating similar coordination around the central metal (for the solid $Cp_2U(BH_4)_2$ the structure corresponds to a distorted tetrahedron formed by the vertices of the Cp group centroids and the boron atoms [9]). These tetrahydroborato complexes display very narrow absorption bands and their spectra look rather different from those of $Cp_2U(NEt_2)_2$ which are very broad. Such behaviour may reflect different structural conformations in solution in that tetra-

TABLE I. Physical Properties of Different Tetrahydroborate Complexes

Compound	Appearance	Sublimation condition T (°C) (P (torr))	Solubility[a] (27 °C)			Reference
			n-hexane	benzene toluene	THF–DME	
$CpU(BH_4)_3$	yellow–orange solid	20 (10^{-2})	ss	+	dec	5
$Cp_2U(BH_4)_2$	red solid	60–100 (10^{-2}–10^{-3})	–	+	++	8
$Cp_2{}^{Me}U(BH_4)_2$	red solid	50–60 (10^{-2}–10^{-3})	ss	+	++	This work
$Cp_2{}^{Si}U(BH_4)_2$	red oily liquid		+	++	++	This work
$Cp_3U(BH_4)$	red solid	170 (10^{-4})	–	+	+	13
$Cp_3{}^{Me}UBH_4$	reddish solid	120–130 (10^{-4})	–	+	+	14
$Cp_2Th(BH_4)_2$	white solid	150–200 (10^{-4})	–	ss	+	This work

[a] – insoluble; ss slightly soluble; + soluble; ++ very soluble.

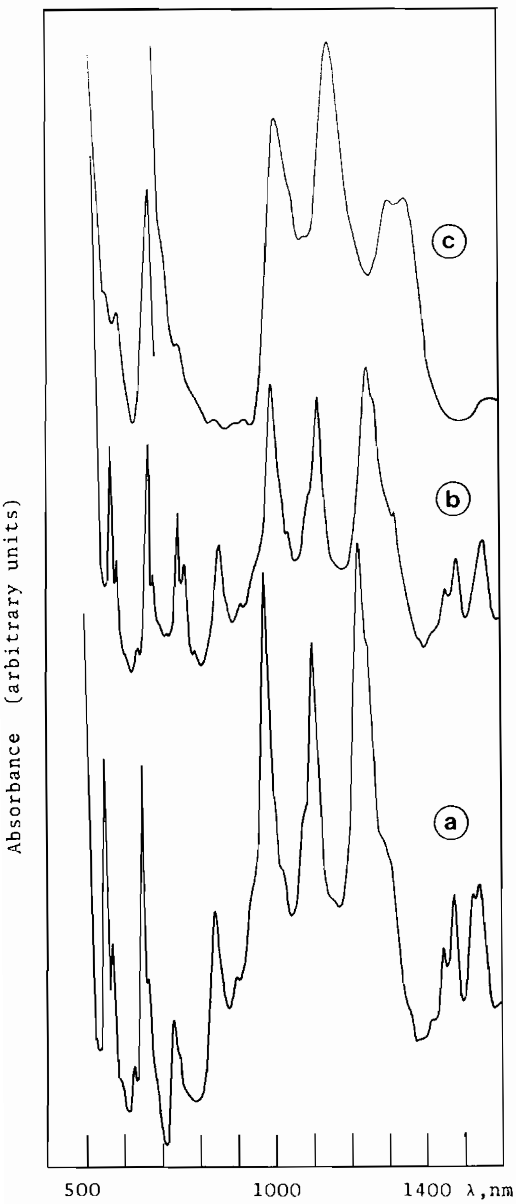


Fig. 1. Vis–near-IR spectra of: (a) $Cp_2U(BH_4)_2$ in toluene; (b) $Cp_2{}^{Me}U(BH_4)_2$ in toluene; (c) $Cp_2U(NEt_2)_2$ [7] in n-hexane.

hydroborate complexes probably are monomeric, while $Cp_2U(NEt_2)_2$ may form oligomeric nitrogen-bridged species.

Mass spectra

In Table II the main peaks of the mass spectra of $Cp_2U(BH_4)_2$ and $Cp_2{}^{Si}U(BH_4)_2$ are collected. It is noteworthy that ions containing BH_4 groups are abundantly present in both fragmentation patterns and for $Cp_2{}^{Si}U(BH_4)_2$ the ion $(Cp_2{}^{Si}UBH_4)^+$ is the most abundant one, thus indicating that the $U–BH_4$ bond is rather robust. Easy loss of CH_3 groups from the $C_5H_4Si(CH_3)_3$ moiety took place; in fact, no appreciable amount of $(Cp_2{}^{Si}U)^+$ was detected but only $[(Cp_2{}^{Si}U) - CH_3]^+$ and species obtained by subsequent loss of CH_3.

TABLE II. Outline of the Most Significant Fragments in the Mass Spectra of (a) $Cp_2U(BH_4)_2$ and (b) $Cp_2{}^{Si}U(BH_4)_2$

m/e	I_{rel}	Fragment
(a) $Cp_2(UBH_4)_2$		
398	20	M^+
383	15	$(M - BH_4)^+$
368	100	$(M - 2BH_4)^+$
318	60	$(M - BH_4 - Cp)^+$
303	43	$(CpU)^+$
66	60	$(CpH)^+$
65	70	$(Cp)^+$
39	30	$(C_3H_3)^+$
(b) $((CH_3)_3SiC_5H_4)_2U(BH_4)_2$		
542	20	M^+
527	100	$(M - BH_4)^+$
497	30	$(M - 2BH_4 - CH_3)^+$
482	40	$(M - 2BH_4 - 2CH_3)^+$
452	55	$(M - 2BH_4 - 4(CH_3))^+$
439	65	$(M - 2BH_4 - Si(CH_3)_3)^+$
138	50	$((CH_3)_3SiC_5H_5)^+$
123	80	$((CH_3)_2SiC_5H_5)^+$
73	30	$((CH_3)_3Si)^+$

NMR spectra

The chemical shifts (Table III) are typical of uranium(IV) paramagnetic organometallic complexes. Interestingly, a general trend to an upfield shift for the signals of all nuclei studied (^1H, ^{11}B, ^{13}C) is observed by progressive replacement of BH_4 groups with cyclopentadienyl groups. The presence of the methyl or trimethylsilyl substituents in the cyclopentadienyl groups induces the splitting of the ring singlet into α and β proton signals in opposite sides with respect to the signal of the protons of the unsubstituted Cp ring. The methyl Cp derivatives show ^{11}B as well as $^1H_{B-H}$ upfield signals compared to the unsubstituted Cp complexes; the replacement of the hydrogen atoms to boron by different groups (Me, Et, Ph, BBN (=q-borabicyclo(3,3,1)nonane)) significantly affects the signals of the ^{11}B spectra, while the signals of both Cp and remaining hydroborate protons are practically unaltered. Clearly, structural and/or electronic parameters are responsible for this behaviour but their exact influence is still under investigation.

Crystal Data of Cp_3UBH_4 ($C_{15}H_{19}BU$, $M = 447.9$)

Red–brown crystals, orthorhombic, space group *Pnma*, with a = 14.773(9), b = 8.226(4), c = 12.183(6) Å, V = 1480.5 Å^3, D_c = 2.01 g cm^{-3} for Z = 4.

The compound has molecular symmetry C_{3v} with the U and B atoms lying on the crystallographic

TABLE III. List of Room Temperature ^{1}H, ^{11}B and ^{13}C NMR Shifts for Various $U(C_5H_4R)_x(H_{4-n}BR_n)_{4-x}$ (^{1}H and ^{13}C Shifts Are Referred to TMS, ^{11}B to $BF_3 \cdot OEt_2$)

Formula	^{1}H of ring protons of C_5H_4R	^{1}H of $H_{4-n}BR_n$	^{1}H of R/R_n	^{11}B	^{13}C
UCp_4[a]	−12.73s				*ca.* 165
UCp_3BH_4[a]	−6.54s	−60q		64.26quint	195
UCp_3H_3BMe[b]	−6.80s	−65.4q	−17.4q	96.7b	
UCp_3H_3BEt[a]	−6.58s	−66.4q	−17.4q; −10.7t	87.8q	
UCp_3H_3BPh[a]	−6.33s	−76.8q	−2.14t; −1.90t; 8.22q	92.5q	
$UCp_3^{Me}BH_4$[c]	7.58s; −22.94s	−62.6q	2.57s	53.95quint	
UCp_3HBBN[e]	−7.09s	62.2b	−6.06b; −9.03q; −43.09b; −10.41b; −13.70b	−55.16b	
$UCp_2(BH_4)_2$[a]	5.30s	−19.34q		90.78quint	310
$UCp_2^{Me}(BH_4)_2$[a]	15.83s; −12.76s	−21.15q	9.8s	86.9quint	
$UCp_2^{Si}(BH_4)_2$[a]	18.38s; −16.52s	−18.07q	0.0s	92.1quint	377, 326, 294, 3.83
$UCp(BH_4)_3$[d]	14.9bs	53.3q		129.1bs	*ca.* 370
$UCp^{Me}(BH_4)_3$[c]	16.5s; 7.3s	41.8q	−2.3s	125bs	
$U(BH_4)_4$[f]		130q		90.1quint	
$U(H_3BMe)_4$[g]		156.4bs	15.8s		

[a] Ref. 15. [b] Ref. 7. [c] This work. [d] Ref. 5. [e] Ref. 16. [f] Ref. 17. [g] Ref. 18.

mirror. The U atom is tetrahedrally surrounded by the four ligand groups (three Cp and one BH_4) and the U–B distance [10] of 2.48 Å, which compares well with other U–B distances, strongly supports the hypothesis of a trihapto hydride bridge bonding although the H atoms could not be located, in agreement with the conclusion gathered from the infrared absorption [1]. Due to molecular disorder the cyclopentadienyl carbon atoms could not be exactly localized either; they are statistically distributed over two or more positions. The actual *R* factor, based on 1016 (independently) observed reflections, has been calculated by tentatively introducing the carbon atoms with occupancy factors of 0.5 and figures up at 5.6%. In this manner the $U–C_{Cp}$ distances have been found in the range 2.75–2.83 Å, as usually found for this class of molecules. Thus coordination geometry of Cp_3UBH_4 corresponds to the monomeric tetrahedral Cp_3UX [11] molecules as illustrated in Fig. 2, even though a more complete characterization could be achieved by low temperature or neutron diffraction studies.

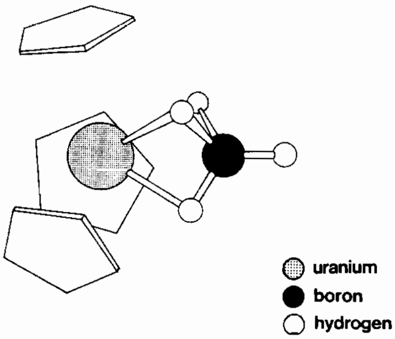
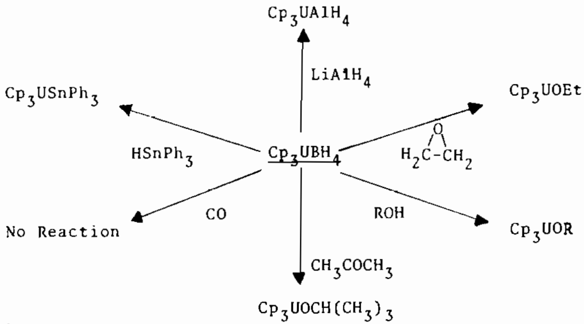


Fig. 2. Proposed structure for Cp_3UBH_4 on the basis of X-ray data.

Reactivity

Several reactivity tests have been performed with Cp_3UBH_4 and $Cp_2U(BH_4)_2$. The results for Cp_3UBH_4 are collected in Scheme 1.



Scheme 1.

It has been observed that this tetrahydroborato complex reacts with alcohols, acetone, acetylacetone and $HSnPh_3$, leading to the final substitution of the BH_4 group with alkoxide, isopropoxide, acetylacetonato and triphenylstannide groups, respectively. The interesting compound $Cp_2U(BH_4)(OCH(CH_3)_2)$ has been detected by ^{1}H NMR in the reaction of $Cp_2U(BH_4)_2$ and CH_3COCH_3.

A small excess of the reagents with respect to the uranium compounds did not attack the U–Cp bonds; moreover CO, pyridine, CH_3CN and isonitriles seem to be unreactive.

In conclusion, the described mixed ligand (cyclopentadienyl and tetrahydroborato) uranium complexes form a stable class and do not generally undergo disproportionation phenomena and have a reasonably high thermal stability. Moreover, the ligation of boron to uranium (and thorium) in the described complexes takes place exclusively through three bridging hydrogen atoms; this behaviour seems to reflect the enhanced coordinating power of actinide elements due to their bigger size with respect to the transition elements (such as Zr, Hf, etc.) in which the BH_4 group is coordinated to the metal through a bidentate bond. Finally, they show very interesting and peculiar ^1H NMR behaviour wich is quite sensitive to the nature of the ligands present in the molecule [12].

Acknowledgements

The authors are indebted to Mr. F. Braga and Mr. V. Corrado for their technical assistance.

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