

Electron-deficient organouranium chemistry: synthesis and reactivity of monocyclopentadienyldiphenylphosphidouranium trisborohydrides $[(C_5R_4PPh_2)U(BH_4)_3]$ ($R = H$ or CH_3) and of their borane adducts

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Abstract

The reactivity of the monocyclopentadienyl complex $[(C_5H_4PPh_2)U(BH_4)_3]$ and of its borane adduct $[(C_5H_4PPh_2 \cdot BH_3)U(BH_4)_3]$ strongly suggest that in solutions these complexes are in equilibrium with the biscyclopentadienyls $[(C_5H_4PPh_2)_2U(BH_4)_2]$ and $[(C_5H_4PPh_2 \cdot BH_3)_2U(BH_4)_2]$ and uranium tetraborohydride $[U(BH_4)_4]$ which is the most reactive species in such systems.

Both rearrange in the presence of neutral ligands and are only characterizable in solution. The analogue tetramethylcyclopentadienyl $[(C_5Me_4PPh_2 \cdot BH_3)U(BH_4)_3]$ a model of monolinked dimetallics, is stable and has been isolated.

Keywords: Uranium; Borane adducts; Heterodimetallics; Electron-deficient compounds

1. Introduction

In preliminary work [1], we reported the modelling of f–d heterodimetallics with a phosphorus–d metal linkage by the borane adduct of (diphenylphosphidocyclopentadienyl)uranium complexes.

The classical phosphidocyclopentadienyl $C_5R_4PPh_2$ ($R = H$ or Me) has been widely used [2] to build dimetallic compounds. In most of these molecules, a d metal is doubly bridged to another d or f transition metal. These doubly linked complexes exhibit an enhanced stability, but suffer the major drawbacks of a structural rigidity and an invariant metal–metal distance which sometimes causes direct metal–metal interaction [3] and low reactivity in catalysis [4].

The linking of two metal atoms by only one phosphidocyclopentadienyl group should keep the flexibility of the molecule and allow a variable metal–metal length, as reported in previous work on a samarium–rhodium complex [5].

In these complexes, each metal may be less hindered,

and therefore more reactive than in a doubly linked species. First experiments showed that such monolinked dimetallic compounds are so reactive towards neutral molecules (or rearrange easily) that their complete characterization is difficult. In this paper we describe the synthesis of a simple isolable borane adduct modelling monolinked dimetallic compounds and the characterization in solution of the non-isolable mono- and bis-diphenylphosphinocyclopentadienyluranium borohydride complexes.

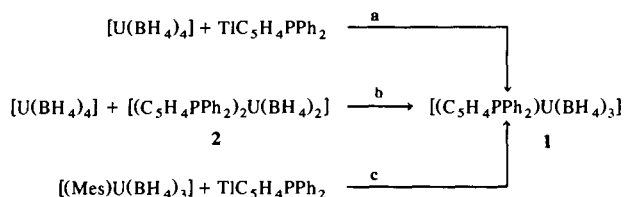
2. Results and discussion

2.1. Syntheses

2.1.1. Synthesis of $[(C_5H_4PPh_2)U(BH_4)_3]$ 1

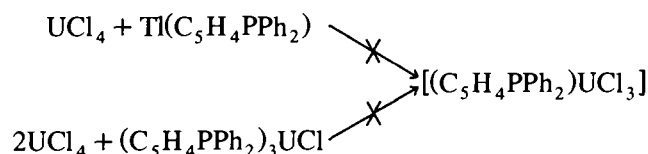
The synthesis of $[(C_5H_4PPh_2)UCl_3]$ has been attempted from UCl_4 and the stoichiometric amount of $Li(C_5H_4PPh_2)$ or $Tl(C_5H_4PPh_2)$. In every case, the only compound isolated was the triscyclopentadienyl $[(C_5H_4PPh_2)_3UCl]$. This latter complex seems to be very stable and disproportionation did not occur with UCl_4 in THF. No the transient formation of

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Scheme 1.

$[(\text{C}_5\text{H}_4\text{PPh}_2)\text{UCl}_3]$ was detected by NMR spectroscopy of the reaction mixtures.



Nevertheless, we hoped to obtain the analogous borohydride because the complete series $[(\text{C}_5\text{H}_5)_{4-n}\text{U}(\text{BH}_4)_n]$ has been reported [6].

The borohydride **1** $[(\text{C}_5\text{H}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ can be obtained (Scheme 1) by three methods in C_6D_6 (NMR scale) or in toluene (preparative scale). (a) Reaction of $[\text{U}(\text{BH}_4)_4]$ with one equivalent of $\text{Ti}(\text{C}_5\text{H}_4\text{PPh}_2)$, (b) comproportionation between $[\text{U}(\text{BH}_4)_4]$ and $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$ **2**, (c) oxidation of $[(\text{Mes})\text{U}(\text{BH}_4)_3]$ with $\text{Ti}(\text{C}_5\text{H}_4\text{PPh}_2)$ (Mes = 1,3,5-trimethylbenzene).

The reactions are monitored by ^1H and ^{31}P NMR spectroscopies. The formation of **1** is complete, and clean solutions containing only **1** are obtained (path b). These solutions are stable for a few days at room temperature. However, all attempts to isolate **1** pure in the solid state failed. Rapid evaporation of toluene solution leads to a mixture of **1** (80%) and of the bisdiphenylphosphinocyclopentadienyl borane adduct $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)_2\text{U}(\text{BH}_4)_2]$ **3** (20%). Slow crystallization (from toluene pentane) leads only to yellow crystals of **3**.

Compound **1** is formulated on the basis of spectroscopic data (Table 1) and chemical correlations (paths b and c, Scheme 1)

Table 1
 ^1H and ^{31}P NMR data of monocyclopentadienyl complexes **1–4** and **9, 10** (C_6D_6 , 25°C)

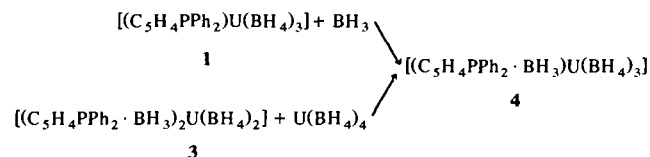
Complex	$\delta \text{C}_5\text{H}_4$	δBH_4	δBH_3	^{31}P
1	11.82 ^a	61	–	–179
2	13.67	–12.0	–	–251
3	2.40	(br, 260) ^b	–	–
	19.1	–20.2	5.5	–95
4	–2.44	(br, 270)	(br, 260)	–
	15.69	73	–13.0	–76
9	2.66	–	–	–
	3.00	–	–	–197
	–11.40	–	–	–
10	19.6	69.5	–	–67
	4.95	(br, 250)	–	–

^a Two signals at 327 K (9.35; 9.05).

^b br: broad signal, W 1/2 in hertz.

2.1.2. Borane-adduct formation, synthesis of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **4**

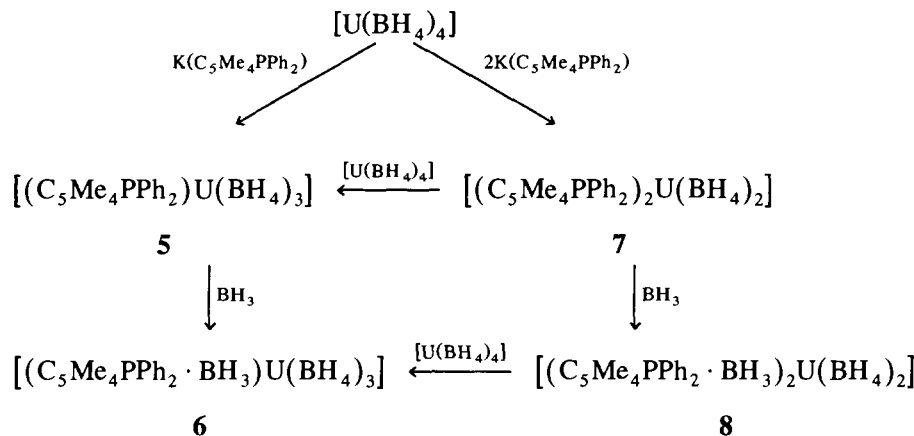
The borane adduct **4** can be obtained directly from **1**, but large-scale syntheses were performed by mixing **3** with equimolar amounts of $[\text{U}(\text{BH}_4)_4]$ in non-coordinating solvents.



As for **1**, it was also not possible to obtain **4** pure in the solid state; all attempts at crystallisation from solutions of pure **4** led to significant formation of **3**. The ^1H and ^{31}P NMR data of compounds **1–4** are reported in Table 1.

2.1.3. Formation of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)_2\text{U}(\text{BH}_4)_2]$ **3**

Compound **3** has been isolated analytically pure [1]. A first crop was obtained as large yellow crystals from a pentane solution of $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$ stored at room temperature. In a large-scale synthesis, the stoi-



Scheme 2.

chiometric amount of borane ($\text{BH}_3 \cdot \text{SMe}_2$) was added to a crude toluene solution of $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$. After concentration of the solution and addition of cold pentane, a yellow microcrystalline powder was obtained.

The formation of **3** from **1** or **4** was invariably observed, especially when solutions of these complexes are concentrated.

2.1.4. Synthesis of $[(\text{C}_5\text{Me}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ **5** and $[(\text{C}_5\text{Me}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **6**

To obtain monophosphidocyclopentadienyl complexes suitable to synthesize dimetal species, it is necessary to prevent the rearrangements leading to biscyclopentadienides. It is well known that redistribution reactions are more difficult from the permethylated complexes, so the $\text{C}_5\text{Me}_4\text{PPh}_2$ analogues were synthesized.

The reaction of $[\text{U}(\text{BH}_4)_4]$ with one equivalent of $\text{KC}_5\text{Me}_4\text{PPh}_2$ in toluene or benzene afford the corresponding monodiphenylphosphidotetramethylcyclopentadienyluranium borohydride, **5**. Addition of $\text{BH}_3 \cdot \text{SMe}_2$ affords **6** (Scheme 2).

These complexes are stable in solution at room temperature, but all attempts to crystallize **5**, by removal of the solvent or addition of pentane after concentration, afford a mixture of the expected compounds and 5–20% of the borane adduct **6** and of the biscyclopentadienyl **8** as well as unidentified products.

6 was isolated analytically pure after addition of $\text{BH}_3 \cdot \text{SMe}_2$ to a solution of **5**, and slow removal of

Table 2
 ^1H and ^{31}P NMR data of tetramethylcyclopentadienylphosphido complexes **5–8** (C_6D_6 , 25°C)

Complex	Me	BH_4	BH_3	^{31}P
5	4.09	50.9	–	– 225
	4.52			
6	1.26	67.3	– 18.14	– 125
	3.35			
7	3.52	– 53	–	– 158
	17.83			
8	1.04	–	– 24.7	– 111
	22.08			

toluene at 0°C , and washing the brown powder thoroughly with pentane.

The usual workup of solutions of **5** as for **1** and **4** led to the formation of **8**.

The formation of the biscyclopentadienyl compounds $[(\text{C}_5\text{Me}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$ **7** and $[(\text{C}_5\text{Me}_4\text{PPh}_2 \cdot \text{BH}_3)_2\text{U}(\text{BH}_4)_2]$ **8** was monitored by NMR spectroscopy (Table 2). The reaction of $[\text{U}(\text{BH}_4)_4]$ with 2 equivalents of $\text{KC}_5\text{Me}_4\text{PPh}_2$ afforded **7**, whereas **8** was obtained after subsequent addition of BH_3 . **7** and **8** react with $[\text{U}(\text{BH}_4)_4]$ to give **5** and **6** respectively. The ^1H and ^{31}P NMR data of compounds **5–8** are reported in Table 2.

6 bind one molecule of THF reversibly. The reaction was monitored by ^{31}P NMR spectroscopy. The P signal of **6** (– 125 ppm) shifted to – 159 ppm after progressive addition of THF. After removal of the solvent and redissolution in C_6D_6 , the signal was recovered unchanged at – 125 ppm. $[(\text{C}_5\text{H}_5)\text{U}(\text{BH}_4)_3]$ also coordi-

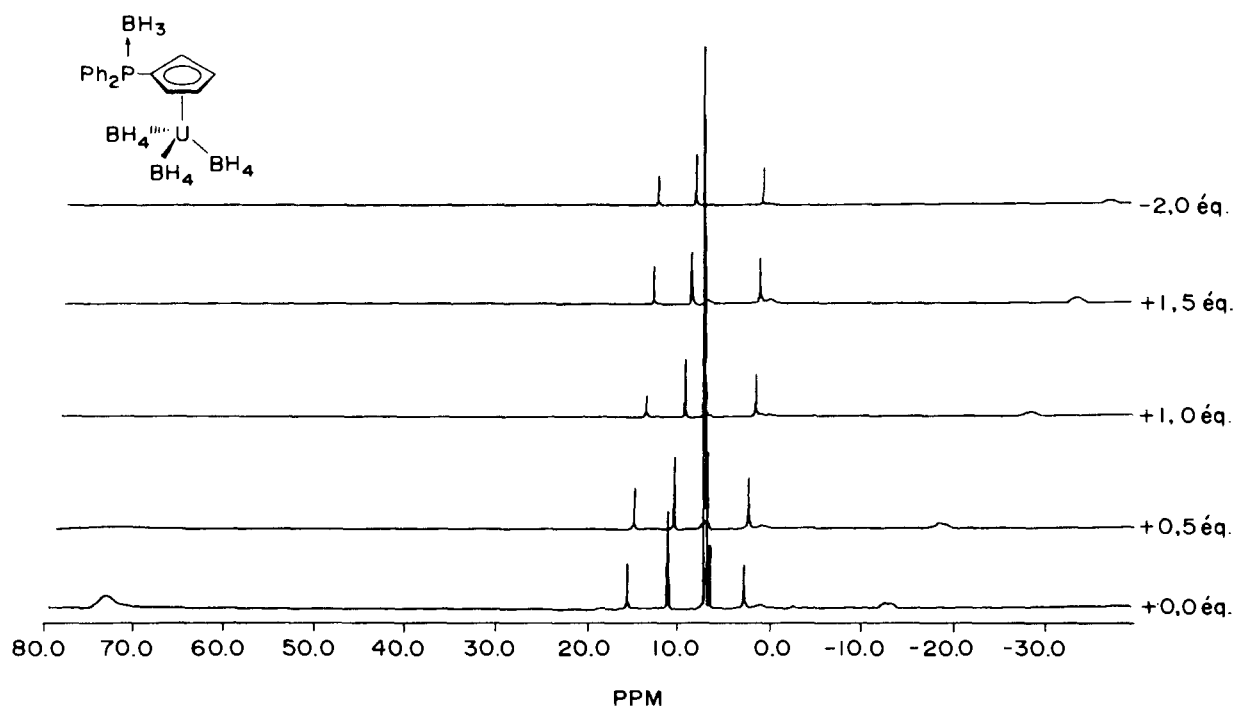


Fig. 1. ^1H NMR spectra of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **4** after progressive addition of $[\text{U}(\text{BH}_4)_4]$.

Table 3
 ^1H and ^{31}P NMR data of $(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3$ after progressive addition of $\text{U}(\text{BH}_4)_4$ (C_6D_6 , 25°C)

Equivalents of $\text{U}(\text{BH}_4)_4$	^{31}P ($W_{1/2}$)	C_5H_4 ($W_{1/2}$)	BH_4	BH_3 ($W_{1/2}$)
0	-76 (140)	15.69 (2.66)	73 (350)	-13.05 (300)
0.5	-66.6 (145)	14.89 (2.23)	73.5 (1000)	-18.9 (320)
1	-50.1 (160)	13.59 (1.49)	-	-28.6 (315)
1.5	-40.4 (170)	12.87 (1.09)	-	-33.7 (310)
2	-33.2 (180)	12.34 (0.78)	-	-37.4 (315)

nates reversibly one molecule of THF [7] (at -50°C to avoid a disproportionation reaction), whereas neither $[(\text{C}_5\text{Me}_5)\text{U}(\text{BH}_4)_3]$ nor $[(\text{C}_5\text{Me}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ is able to form an adduct [8]. The coordination of THF is only possible on an electron-deficient metal, the bulky $\text{C}_5\text{Me}_4\text{PPh}_2 \cdot \text{BH}_3$ showing the same electron behaviour as the small C_5H_5 ring. The electron-withdrawing effect of the $\text{PPh}_2 \cdot \text{BH}_3$ group counterbalances the effects of the four Me groups. This has been established by NMR spectroscopy. Correlations between both ^{11}B and ^1H chemical shifts and electron-richness of uranium complexes have been emphasised [9].

2.2. Reactivity of **4** and rearrangements in solution

2.2.1. Coordination of $[\text{U}(\text{BH}_4)_4]$ to **4**

The identification of **4** in the crude solutions is not easy. The ^{31}P chemical shifts of the signals of **4** change with concentration. This indicates the presence of associated forms in solution and is a consequence of the electronic paucity of the metal. Such behaviour has already been reported for the 'tritox' derivative $[(^t\text{Bu}_3\text{CO})\text{U}(\text{BH}_4)_3]$ [10]. Moreover, the chemical shifts of all the signals, and especially H(-B) and P, depend on the origin of the sample. It has been further established that these changes are due to impurities able to act as ligands, such as NEt_3 and $[\text{U}(\text{BH}_4)_4]$. It has already been reported that $[\text{U}(\text{BH}_4)_4]$ can act as a ligand. The coordinatively unsaturated polymeric $[(\text{COT})\text{U}(\text{BH}_4)_2]$ ($\text{COT} = \text{C}_8\text{H}_8$) is insoluble in toluene but dissolves immediately after addition of one equivalent of THF, phosphine oxide, or $\text{U}(\text{BH}_4)_4$ [11].

The changes of the chemical shifts of the signals of **4** after progressive addition of $\text{U}(\text{BH}_4)_4$ are reported in Table 2 and Figs. 1 and 2.

To avoid the presence of traces of $[\text{U}(\text{BH}_4)_4]$, the spectra of 'pure' **4** were recorded in solutions containing a small excess of the bicyclopentadienyl complex **3**.

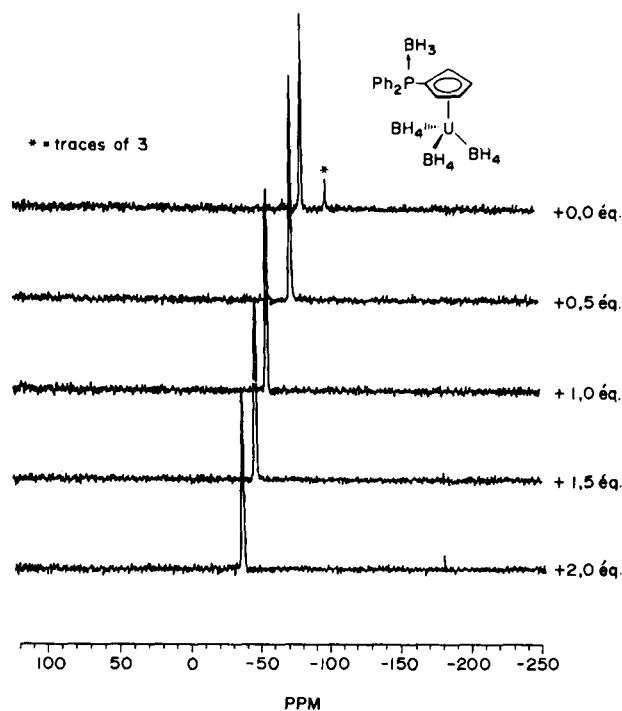
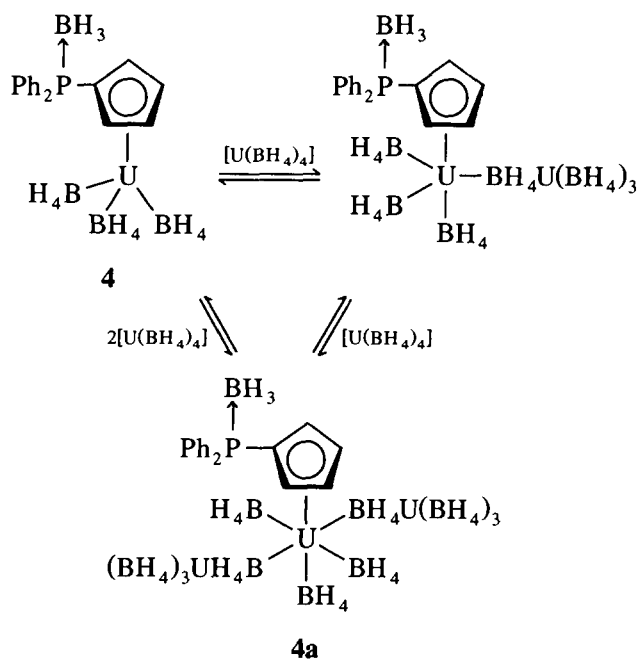


Fig. 2. ^{31}P NMR spectra of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **4** after progressive addition of $[\text{U}(\text{BH}_4)_4]$.

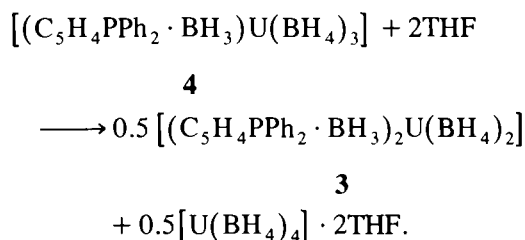
The broadening and subsequent disappearance of the BH_4 signal of **4** in the presence of $[\text{U}(\text{BH}_4)_4]$ indicates inter- or intra-molecular exchange. The tendency of uranium to increase its coordination number is well known [12]. Therefore, the formation of penta- or hexacoordinate complexes in rapid equilibrium with **4** may explain the observed variations of chemical shift (Scheme 3).



Scheme 3.

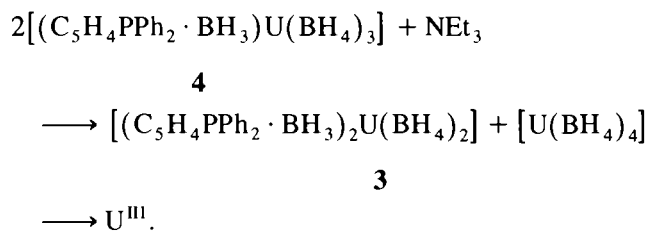
2.2.2. Reactions with Lewis bases

When THF (2 eq) is added to a benzene solution of **4**, a disproportionation reaction occurs at room temperature. After 30 min., only **3** and $[\text{U}(\text{BH}_4)_4(\text{THF})_2]$ are present.



A similar disproportionation has been observed for **1**.

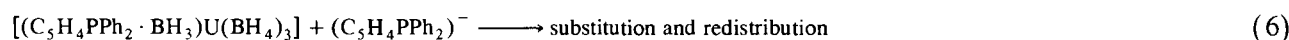
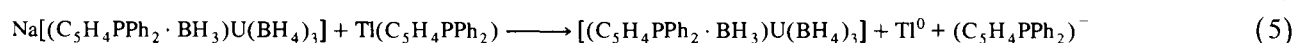
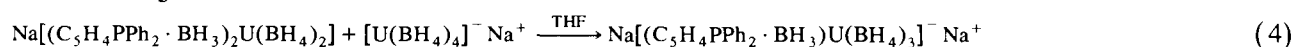
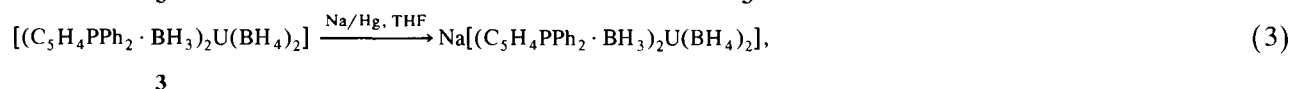
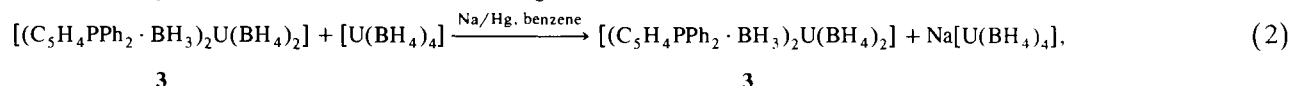
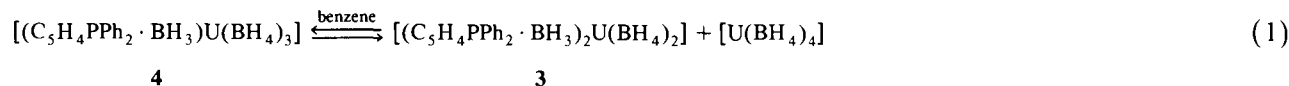
The displacement of coordinated BH_3 from **4** has been attempted by addition of trimethylamine. (The use of the more efficient PMe_3 is not possible as this reagent reduces uranium(IV) borohydride in a short time at ambient temperature [13].) After 3 days at room temperature, the formation of **3** and of an insoluble U^{III} species are observed, along with about 20% of unreacted **4**. This insoluble U^{III} product can be oxidized by addition of $\text{TiC}_5\text{H}_4\text{PPh}_2$ to give a mixture of $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$, **2** (90%) and $[(\text{C}_5\text{H}_4\text{PPh}_2)_3\text{U}(\text{BH}_4)]$, **1** (10%). Thus, it is probably $[\text{U}(\text{BH}_4)_3(\text{NEt}_3)_x]$.



In this reaction, NEt_3 is a neutral ligand and induces the slow disproportionation of **4** with the formation of **3** and of $[\text{U}(\text{BH}_4)_4]$ which is slowly reduced.

2.2.3. Reduction of **4** with sodium amalgam

4 reacts readily with sodium amalgam in C_6D_6 . The reaction was monitored by NMR spectroscopy. After 15



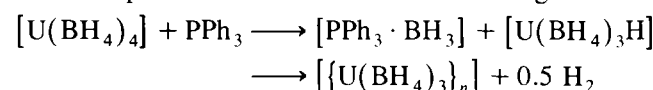
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min stirring by ultrasound, a dark brown U^{III} powder deposited and only **3** was present in the solution. After removal of benzene and addition of THF, the brown solid dissolved and the solution exhibited only one ^{31}P signal at -215 ppm. After addition of $\text{TiC}_5\text{H}_4\text{PPh}_2$ a mixture of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)_2\text{U}(\text{BH}_4)_2]$ **3** (40%); $[(\text{C}_5\text{H}_4\text{PPh}_2)(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_2]$ [**1**] (40%) and $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$, **2** (20%) was obtained.

These results can be rationalized (Scheme 4) if it is assumed that the conproportionation reaction leading to **4** is an equilibrium (Eq. (1)), which may be completely displaced by the irreversible reduction of $[\text{U}(\text{BH}_4)_4]$ (Eq. (2)). Such a reduction is effective at room temperature in benzene. The reduction of **3** by Na/Hg is slow in benzene, but much faster in THF (Eq. (3)). When THF is then added, the reduction of **3** occurs and the U^{III} anion is obtained by a conproportionation reaction (Eq. (4)). This last is oxidized by Ti^+ (Eq. (5)) and the $[\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3]^-$ and BH_4^- ligands of **4** are displaced by the better donor, $[\text{C}_5\text{H}_4\text{PPh}_2]^-$ anion (Eq. (6)).

2.2.4. Production of **3** from **4** (or **1**)

The production of **3** from **4** or **1** implies the abstraction of BH_3 from a $\text{U}-\text{BH}_4$ group by a $\text{C}_5\text{H}_4\text{PPh}_2$ moiety. This was unexpected because the triscyclopentadienyl complex $[(\text{C}_5\text{H}_4\text{PPh}_2)_3\text{UBH}_4]$ is stable and easily isolated [14]. The formation of the corresponding borane adduct $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)_3\text{UBH}_4]$ needs a borane reagent. The basicity of the phosphorus in a $\text{C}_5\text{H}_4\text{PPh}_2$ moiety should be comparable to that of PPh_3 and it is known that $[\text{U}(\text{BH}_4)_4]$ is easily reduced by PET_3 , PET_2Ph or PPh_3 at room temperature [11], whereas the reduction of $[(\text{C}_5\text{H}_5)\text{U}(\text{BH}_4)_3]$ or $[(\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2]$ by PPh_3 requires a very long time at room temperature and some hours in refluxing benzene.



The facile formation of the borane adduct **3** from **4** or **1** suggests the presence of $[\text{U}(\text{BH}_4)_4]$ which acts as a

Scheme 4.

and are, nevertheless, implicated in multiple exchange reactions which strongly influence their reactivity.

4. Experimental part

All manipulations were carried out under purified dinitrogen in a Jacomex glove box or under argon using standard vacuum techniques. Solvents were distilled from appropriate drying agents, stored over Na–benzophenone and vacuum transferred to reaction vessels. ^1H and ^{31}P NMR spectra were recorded on an AC 200 Bruker spectrometer ($T^\phi = 297\text{ K}$). IR spectra were obtained using a 205 FT Nicolet spectrometer. Elemental analyses were performed by Service Central de Microanalyses of the CNRS. The U/P/B ratios are obtained by ICPAES on a JY70 Jobin-Yvon apparatus by the Valduc Center of the C.E.A.

$[\text{U}(\text{NEt}_2)_4]$ [17], $\text{TlC}_5\text{H}_4\text{PPh}_2$ [18], $[(\text{CO})_5\text{Mo}(\text{Ph}_2\text{-PC}_5\text{H}_4\text{Ti})]$ [19], UCl_4 [20], $[\text{U}(\text{BH}_4)_4]$ [21], $[\text{U}(\text{BH}_4)_3(\text{THF})_3]$ [22], and $[(\text{Mes})\text{U}(\text{BH}_4)_3]$ [23] were prepared as described. $\text{BH}_3 \cdot \text{SMe}_2$ solutions were purchased from Aldrich.

4.1. $[(\text{C}_5\text{H}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ **1**

(a) To 300 mg (1 mmol) of $[\text{U}(\text{BH}_4)_4]$ and 450 mg (1 mmol) of $\text{TlC}_5\text{H}_4\text{PPh}_2$, 20 ml of toluene were added and the solution was stirred for 20 h. After removal of the solvent, a crude orange solid containing **1** (80%) and **3** (20%) was obtained. All attempts at recrystallization from toluene–pentane mixtures afforded only yellow crystals of **3** mixed with some dark red-brown solid and a tan dusty powder.

(b) In an NMR tube containing 5 mg (16 μmol) of $[\text{U}(\text{BH}_4)_4]$ and 7.5 mg (16 μmol) of $\text{TlC}_5\text{H}_4\text{PPh}_2$, 0.4 ml of C_6D_6 was condensed. After 30 min stirring by ultrasound, only **1** was present.

(c) 5 mg (12.4 μmol) of $[(\text{Mes})\text{U}(\text{BH}_4)_3]$ and 5.6 mg (12.4 μmol) of $\text{TlC}_5\text{H}_4\text{PPh}_2$ were charged in an NMR tube and 0.4 ml of C_6D_6 were condensed. Black thallium immediately deposited and the NMR spectra of the solution showed the formation of **1** alone.

(d) $[\text{U}(\text{BH}_4)_4]$ (8 mg, 27 μmol) and **2** (20 mg, 27 μmol) were charged in an NMR tube, 0.4 ml of C_6D_6 were condensed and the mixture was stirred 30 min by ultrasound. The NMR spectra showed only **1**.

4.2. $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{U}(\text{BH}_4)_2]$ **2**

(a) 20 ml of THF were condensed on to 200 mg (0.52 mol) of UCl_4 and 41 mg (1.05 mol) of NaBH_4 , and the solution was stirred for 16 h. After filtration, $\text{TlC}_5\text{H}_4\text{PPh}_2$ 370 mg (0.81 mmol) was added and the mixture stirred for 2 h. The solvent was removed, affording a yellow brownish solid (220 mg) which was

identified as **2** containing 5% of **3**. A part of this crude product was dissolved in pentane, affording yellow crystals of **3** after several days and an unidentified tan powder.

(b) 20 ml of THF (or toluene) were condensed onto 179 mg (0.60 mmol) of $[\text{U}(\text{BH}_4)_4]$ and 540 mg (1.2 mmol) of $\text{TlC}_5\text{H}_4\text{PPh}_2$. After 1 h stirring, the solution was filtered, and the solvent removed affording 390 mg of a yellow powder. After extraction with 2×50 ml of pentane and concentration to about 10 ml, 275 mg (60%) of yellow-orange microcrystals of **2** containing about 5% of **3** were obtained. IR nujol: 2498, 2186, 2100 cm^{-1} , indicating tridentate BH_4^- .

(c) To an NMR tube charged with $[\text{U}(\text{BH}_4)_3(\text{THF})_3]$ 8 mg (16 μmol) and 0.4 ml C_6D_6 , $\text{TlC}_5\text{H}_4\text{PPh}_2$ 14.4 mg (32 μmol) was added. A black powder of thallium deposited immediately and the NMR spectra showed the sole formation of **2**.

(d) To a red solution of $[(\text{C}_5\text{H}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ **1** in 0.4 ml of C_6D_6 prepared in situ from $[\text{U}(\text{BH}_4)_4]$ and $\text{TlC}_5\text{H}_4\text{PPh}_2$, 1 equivalent (2.7 μl) of THF was added. After 30 min stirring, the NMR spectra were consistent with the formation of a 1:1 mixture of **2** and $[\text{U}(\text{BH}_4)_4(\text{THF})_n]$.

4.3. $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)_2\text{U}(\text{BH}_4)_2]$ **3**

(a) 13 μl of a 2 M solution of $\text{BH}_3 \cdot \text{SMe}_2$ in THF were added to 10 mg (13 μmol) of **2** in 0.5 ml of C_6D_6 . The orange solution turned yellow and the NMR spectra (^1H and ^{31}P) showed the sole formation of **3**.

(b) A crude toluene solution of **2** was concentrated to about 5 ml and 20 ml of pentane added. After 7 days, large amounts of yellow rhombohedral plates of **3** were hand-separated from a mixture also containing dark brown lumps of **2** contaminated by **3** and another unidentified uranium borohydride.

Anal. Found (Calc. for $\text{C}_{34}\text{H}_{42}\text{B}_4\text{P}_2$): C 49.88 (51.38); H 5.28 (5.28); B 4.53 (5.54); P 6.43 (7.8)%.

ICPAES analysis: ratio found (Calc.): B/U 3.66 (4); P/U 2.01 (2).

IR (Nujol): tridentate BH_4 : 2513, 2181, 2108 cm^{-1} ; BH_3 : 2362 cm^{-1} .

(c) To a solution of $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **4** (10 μmol) in 0.4 ml of C_6D_6 , 8 μl of THF were added. After 30 min, the NMR spectra (^1H and ^{31}P) showed the formation of a 1:1 mixture of **3** and $[\text{U}(\text{BH}_4)_4(\text{THF})_2]$.

(d) To a solution of $[(\text{C}_5\text{H}_4\text{PPh}_2)\text{U}(\text{BH}_4)_3]$ **1**, 1 equivalent of a 2 M solution of $\text{BH}_3 \cdot \text{SMe}_2$ in THF was added. After 30 min, the NMR spectra showed the formation of a 1:1 mixture of **3** and $[\text{U}(\text{BH}_4)_4(\text{THF})_2]$.

4.4. $[(\text{C}_5\text{H}_4\text{PPh}_2 \cdot \text{BH}_3)\text{U}(\text{BH}_4)_3]$ **4**

(a) An NMR tube was charged with 6 mg (20 μmol) of $[\text{U}(\text{BH}_4)_4]$ 16 mg (20 μmol) of **3** and 0.4 ml of

C_6D_6 . After 30 min of stirring by ultrasound, only **4** was present in the solution.

(b) $[U(BH_4)_4]$ and a slight excess (5%) of $[(C_5H_4PPh_2 \cdot BH_3)_2U(BH_4)_2]$ **3** was stirred in toluene. After 30 min, an aliquot-part of the clear orange solution was analysed by ^{31}P NMR spectroscopy. It contained about 95% of **4** (signal at -76 ppm) and a very small amount of **3** (signal at -95 ppm).

4.5. $[(C_5Me_4PPh_2)U(BH_4)_3]$ **5**

(a) An NMR tube was charged with 6 mg (20 μ mol) of $[U(BH_4)_4]$ 6.3 mg (20 μ mol) of $LiC_5Me_4PPh_2$ and 0.5 ml of C_6D_6 . After stirring for 3 min by ultrasound and 30 min at room temperature, the NMR spectra of the orange solution showed the sole formation of **5**.

(b) Toluene (10 ml) was condensed onto 209 mg (0.70 mmol) of $[U(BH_4)_4]$ and 182 mg (0.53 mmol) of $KC_5Me_4PPh_2$; the mixture was stirred 20 min by ultrasound. The deep red solution was filtered, and toluene and the excess of $[U(BH_4)_4]$ were removed by pumping off at room temperature. The crude product was analysed by NMR spectroscopy **5** was present with small amounts of $[(C_5Me_4PPh_2)_2U(BH_4)_2]$ **7** (about 5%) and of $[(C_5Me_4PPh_2 \cdot BH_3)U(BH_4)_3]$ **6** (about 10%).

Attempts to recrystallize from toluene–pentane were unsuccessful. After removal of the solvents, the red-brown product was found to contain about 20% of $[(C_5Me_4PPh_2 \cdot BH_3)U(BH_4)_3]$ **6** and insoluble material.

4.6. $[(C_5Me_4PPh_2 \cdot BH_3)U(BH_4)_3]$ **6**

A 2 M solution of $Me_2S \cdot BH_3$ (0.27 ml, mmol) was added with a syringe to a toluene solution of **5** (prepared as described). The solution became immediately orange. Toluene was removed at room temperature and the crude orange solid was washed twice with pentane affording analytically pure **6** (65% yield). Calc. for $C_{21}H_{37}B_4PU$: C, 41.8; H, 6.14; Found: C, 41.72; H, 5.63%.

4.7. $[(C_5Me_4PPh_2)_2U(BH_4)_2]$ **7**

An NMR tube was charged with 3 mg (10 μ mol) of $[U(BH_4)_4]$ 6.9 mg (20 μ mol) of $KC_5Me_4PPh_2$ and 0.5 ml of C_6D_6 . After stirring for 3 min by ultrasound and 30 min at room temperature, a white solid deposited and the NMR spectra of the orange solution show the sole formation of **7**.

4.8. $[(C_5Me_4PPh_2 \cdot BH_3)_2U(BH_4)_2]$ **8**

A 2 M THF solution of $Me_2S \cdot BH_3$ (10 μ l, 20 μ mol) was added with a syringe to a solution of **7** (prepared as described). The solution became immedi-

ately orange-red. After removal of the solvents, C_6D_6 (0.4 ml) was condensed. The NMR spectra of the solution showed the formation of **8**.

4.9. $[(C_5H_4PPh_2)U(NEt_2)_3]$ **9**

To a Schlenk tube containing $[U(NEt_2)_4]$ (11.8 μ mol) in diethylether at $-78^\circ C$, cyclopentadienyldiphenylphosphine, $HC_5H_4PPh_2$ (2.8 mg, 11.2 μ mol) was added. After warming to room temperature, the solvent was removed and the resultant oil pumped on for 2 h. The brown powder was dissolved in 0.4 ml of C_6D_6 . The NMR spectrum showed the formation of **9** and of a small amount of $[(C_5H_4PPh_2)_2U(NEt_2)_2]$.

4.10. $[(C_5H_4PPh_2)Mo(CO)_5U(BH_4)_3]$ **10**

In an NMR tube, $[U(BH_4)_4]$ (13 mg, 43 μ mol) and $[(CO)_5Mo\{(PPh_2C_5H_4Ti)\}]$ (30 mg, 43 μ mol) were dissolved in 0.4 ml of C_6D_6 . After stirring by ultrasound for 3 h, only **10** was present in the solution.

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