

Cyclopentadienyl and indenyl borohydride organoactinides: synthetic chemistry. Characterization and physical properties

S. Bettonville * and J. Goffart **

*Laboratory of Analytical Chemistry and Radiochemistry, University of Liège
 B-4000 Sart Tilman-Liège (Belgium)*

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Abstract

Dicyclopentadienylthorium bis(borohydride) and diindenylactinide bis(borohydride), (actinide = thorium or uranium), have been prepared and characterized by elemental analysis and mass spectrometry. The IR and ^1H , ^{13}C NMR spectra of the thorium compounds, and the IR, electronic, and ^1H NMR spectra and magnetic susceptibility of the uranium compound are described. The temperature dependence of the ^1H NMR spectra of $(\text{C}_9\text{H}_7)_3\text{ThBH}_4$ and $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$ between -85 and 110°C has been studied. Some $(\text{C}_9\text{H}_7)_3\text{UBH}_4$ was shown to be formed as a by-product in the $(\text{C}_9\text{H}_7)_2\text{U}(\text{BH}_4)_2$ preparation.

Introduction

The synthesis and characterization of transition metal, lanthanide and actinide organometallic borohydride compounds have been described in several reports [1–6]. One interesting aspect of those studies involves the geometry of the coordination of the borohydride anion BH_4^- to the metal, since the bonding can involve one, two, or three M–H–B bridges, and these bonding modes have been distinguished on the basis of infrared spectra [1].

Previous workers noted that use of the BH_4^- anion allowed the synthesis of $(\text{C}_5\text{H}_5)_2\text{U}(\text{BH}_4)_2$ [2], stable towards intermolecular rearrangement reactions, and $(\text{C}_5\text{H}_5)_3\text{U}(\text{BH}_4)_3$ [5], stable only as a solid or dissolved in non-coordinating solvents.

The present paper is concerned with $(\text{C}_5\text{H}_5)_2\text{Th}(\text{BH}_4)_2$ (**1a**), $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$ (**2a**), and $(\text{C}_9\text{H}_7)_2\text{U}(\text{BH}_4)_2$ (**3a**) compounds, and presents a comparison of these with the analogous species $(\text{C}_5\text{H}_5)_3\text{ThBH}_4$ (**1b**), $(\text{C}_9\text{H}_7)_3\text{ThBH}_4$ (**2b**) and $(\text{C}_9\text{H}_7)_3\text{UBH}_4$ (**3b**). The last compound and its BD_4^- analogue were observed by IR

* Research Assistant, National Fund for Scientific Research (Belgium).

** Research Associate, Inter-University Institute for Nuclear Sciences (Brussels).

and NMR spectroscopy but the compounds could not be isolated pure [3]. Attempts to make $(C_5H_5)Th(BH_4)_3$ and $(C_9H_7)Th(BH_4)_3$, in tetrahydrofuran (THF) solution, in both cases gave a mixture of derivatives **1a** or **2a** and $Th(BH_4)_4 \cdot 2THF$ (**4**), in accord with observations by Baudry et al. on the $(C_5H_5)U(BH_4)_3$ compound [5].

Experimental

General

Air- and moisture-sensitive compounds were handled in glove-box under purified nitrogen. Solvents were dried and distilled under argon immediately prior to use. Triindenylthorium borohydride (**2b**) was synthesized as previously described [3]. The tetrakis-borohydride of thorium was obtained from the reaction between stoichiometric amounts of $ThCl_4$ and $NaBH_4$ in THF. After vacuum evaporation of the solvent, the white solid residue was sublimed at $120^\circ C$ (10^{-3} torr), and the IR and 1H NMR spectra of the sublimate surprisingly showed the presence of two THF molecules (IR: THF bands at 3000–2900, 1000 and 850 cm^{-1} ; NMR: see Table 2) [7].

The $(C_9H_7)_2An(BH_4)_2$ compounds were synthesized by the routes as follows:

(i) A solution of C_9H_7Na (20 mmol) in THF (50 ml) was added to one of **4** (10 mmol) in THF (150 ml). After 2 d stirring at $20^\circ C$, a yellow solid was obtained upon vacuum evaporation of the solvent. This was purified by sublimation at $130^\circ C$ (10^{-3} torr; yield 20%).

(ii) The method previously described for the synthesis of $(C_5H_5)_2U(BH_4)_2$ [2] was also used for both cyclopentadienyl and indenyl compounds. A yellow ($L = C_9H_7$) or white ($L = C_5H_5$) solid for thorium and a red brown solid ($L = C_9H_7$) for uranium were obtained after vacuum evaporation of the solvent.

In separate experiments, pentane or benzene extraction of the yellow residue gave a mixture of **2a** and **2b**, but sublimation at $120^\circ C$ (10^{-3} torr) gave the desired product **2a**. Pure **3a** was obtained by pentane extraction of the red brown solid.

Pentane extraction of the white solid for the C_5H_5 compound gave the complex **1b** (mass spectrum: peaks at $m/e = 442$, $(C_5H_5)_3Th(BH_4)^+$; $m/e = 427$, $(C_5H_5)_3Th^+$; $m/e = 377$, $(C_5H_5)_2Th(BH_4)^+$) and 1H NMR spectrum: singlet (15H); quartet (4H) [8]).

Attempts were made to synthesize $(C_5H_5)Th(BH_4)_3$ and $(C_9H_7)Th(BH_4)_3$ in THF solution by reaction between LNu , $ThCl_4$, and $NaBH_4$ in stoichiometric ratio. Sublimation (10^{-3} torr) of the solid residue left after vacuum evaporation of the

Table 1

Analytical data (%), with calculated values in parentheses

| | Th/U | C | H | B |
|------------------------|---------|---------|--------|--------|
| $(C_5H_5)_2Th(BH_4)_2$ | 59.48 | 30.56 | 4.56 | 5.40 |
| (1a) | (59.20) | (30.65) | (4.63) | (5.52) |
| $(C_9H_7)_2Th(BH_4)_2$ | 47.46 | 43.89 | 4.46 | 4.19 |
| (2a) | (47.16) | (43.94) | (4.51) | (4.39) |
| $(C_9H_7)_2U(BH_4)_2$ | 48.26 | 43.37 | 4.38 | 3.99 |
| (3a) | (47.79) | (43.42) | (4.45) | (4.34) |

Table 2

^1H and ^{13}C NMR chemical shifts ^a for $\text{Th}(\text{BH}_4)_4\cdot 2\text{THF}$ and $\text{L}_{4-x}\text{An}(\text{BH}_4)_x$ ($x = 1$ or 2 ; $\text{L} = \text{C}_5\text{H}_5$ or C_9H_7 ; $\text{An} = \text{Th}$ or U), in C_6D_6 solution

| | H(1)–H(3) C(1)–C(3) | H(2) C(2) | H(4)–H(7) C(4)–C(7) | H(5)–H(6) C(5)–C(6) | C(8)–C(9) | Others | H C |
|---|------------------------|----------------|------------------------|------------------------|-----------|----------------------|---|
| $\text{Th}(\text{BH}_4)_4\cdot 2\text{THF}$ (4) | | | | | | BH_4 THF | 4.05 0.91; 3.80; 25.32; 77.34 |
| $(\text{C}_9\text{H}_7)_3\text{ThBH}_4$ ^b (2b) | 5.79 105.42 | 6.27 127.65 | 7.45 (124.66) | 6.95 (123.16) | 132.61 | BH_4 | 2.35 |
| $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$ ^b (2a) | 6.07 106.73 | 6.33 126.24 | 7.41 (124.51) | 6.90 (124.27) | 132.74 | BH_4 | 2.85 |
| $(\text{C}_9\text{H}_7)_3\text{UBH}_4$ ^b (3b) | –4.76 | –19.80 | (1.96) | (6.08) | | BH_4 | –31.57 |
| $(\text{C}_9\text{H}_7)_2\text{U}(\text{BH}_4)_2$ (3a) | 12.54 | 6.72 | (3.41) | (–2.86) | | BH_4 | –0.94 |
| | C_5H_5 | H C | BH_4 | | | | |
| $(\text{C}_5\text{H}_5)_3\text{ThBH}_4$ ^c (1b) | | 6.05 118.85 | 3.38 | | | | |
| $(\text{C}_5\text{H}_5)_2\text{Th}(\text{BH}_4)_2$ (1a) | | 6.05 118.85 | 3.38 | | | | |

^a Chemical shifts are in ppm, downfield from TMS. ^b Chemical shifts in parentheses may possibly be assigned the wrong way around. ^c Ref. 12 and our results.

solvent, gave **1a** at 100°C and **2a** at 150°C , both mixed with the THF adduct of $\text{Th}(\text{BH}_4)_4$ (**4**) as shown by ^1H NMR spectroscopy. Compounds **1a** and **2a** were separated from **4** respectively, by slow resublimation in sealed tube at 10^{-3} torr, **1a** at 60°C and **2a** at 80°C . Analytical data for the new compounds **1a**, **2a** and **3a** are shown in Table 1.

Physical measurements

IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer for CsI pellets sandwiched between KBr plates in an airtight holder sealed with an O-ring. Electronic spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. Mass spectra were obtained with a Varian MAT-112 or a VG7070E spectrometer. The magnetic susceptibility of the uranium compound was measured between 1.5 and 300 K with a Faraday balance.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer at 400.1 MHz and 100.6 MHz, respectively.

Results and discussion

The mass spectra of **1a**, **2a** and **3a** clearly indicate that the new complexes contain two borohydride and two cyclopentadienyl or indenyl groups (Table 3). The molecular peak was present in each case.

Table 3
Partial mass spectra (70 eV)

| $(C_5H_5)_2Th(BH_4)_2^a$ (1a) Inlet temperature 150 °C | | | $(C_9H_7)_2Th(BH_4)_2^a$ (2a) Inlet temperature: 60 °C to 260 °C | | | $(C_9H_7)_2U(BH_4)_2^a$ (3a) Inlet temperature: 60 °C to 260 °C | | |
|---|-------------------|--------------------------|---|-------------------|--------------------------|--|-------------------|-------------------------|
| m/e | R.I. ^b | Ion | m/e | R.I. ^b | Ion | m/e | R.I. ^b | Ion |
| 392 | 24 | $(C_5H_5)_2Th(BH_4)_2^+$ | 492 | 15 | $(C_9H_7)_2Th(BH_4)_2^+$ | 498 | 4 | $(C_9H_7)_2U(BH_4)_2^+$ |
| 377 | 57 | $(C_5H_5)_2Th(BH_4)^+$ | 477 | 20 | $(C_9H_7)_2Th(BH_4)^+$ | 483 | 27 | $(C_9H_7)_2U(BH_4)^+$ |
| 362 | 100 | $(C_5H_5)_2Th^+$ | 462 | 45 | $(C_9H_7)_2Th^+$ | 468 | 60 | $(C_9H_7)_2U^+$ |
| 327 | 22 | $(C_5H_5)Th(BH_4)_2^+$ | 377 | 100 | $(C_9H_7)Th(BH_4)_2^+$ | 383 | 41 | $(C_9H_7)U(BH_4)_2^+$ |
| 312 | 38 | $(C_5H_5)Th(BH_4)^+$ | 362 | 43 | $(C_9H_7)Th(BH_4)^+$ | 368 | 76 | $(C_9H_7)U(BH_4)^+$ |
| 297 | 13 | $(C_5H_5)Th^+$ | 347 | 30 | $(C_9H_7)Th^+$ | 353 | 100 | $(C_9H_7)U^+$ |

^a a 50 ≤ m/e ≤ 1000 range was investigated. ^b R.I. = relative intensity.

Table 4

BH₄ and actinide-rings vibration frequencies (cm⁻¹) in solid state infrared spectra, (s = strong)

| | | (C ₅ H ₅) ₂ Th(BH ₄) ₂ (1a) | (C ₉ H ₇) ₂ Th(BH ₄) ₂ (2a) | (C ₉ H ₇) ₂ U(BH ₄) ₂ (3a) |
|-----------------|---|---|---|--|
| BH ₄ | | 2480s | 2490s | 2490s |
| | | 2220s | 2218s | 2200s |
| | | 2152s | 2140s | 2120s |
| | | 1182s | 1181s | 1178s |
| An-rings | $\left\{ \begin{array}{l} \nu_{\text{exp}} \\ \nu_{\text{cal}}^a \end{array} \right.$ | 260s | 246s | 244s |
| | | 258s | 244s | 244s |
| | | (C ₅ H ₅) ₃ ThBH ₄ (1b) | (C ₉ H ₇) ₃ ThBH ₄ (2b) | (C ₉ H ₇) ₃ UBH ₄ (3b) |
| An-rings | ν_{exp} | 230s | 255s | 225s |

^a The experimental vibration frequencies (ν_{exp}) for 1b, 2b, and 3b were used for calculating those (ν_{cal}) of 1a, 2a and 3a.

Infrared spectroscopy

Solid state infrared spectra of the new borohydride derivatives are essentially similar to those of other indenyl-actinide compounds [3,9]. The BH₄ vibration frequencies, (see Table 4) are characteristic of a tridentate coordination configuration. The infrared spectra of 1a, 2a and 3a in C₆H₆ solution showed the same features.

The presence of L₃AnBH₄ (L = C₅H₅, C₉H₇; An = Th, U) as an impurity in 1a, 2a and 3a can be unambiguously detected by use of a sensitive band found near 225 cm⁻¹. This band, which can be assigned to the actinide-ring stretching vibrations

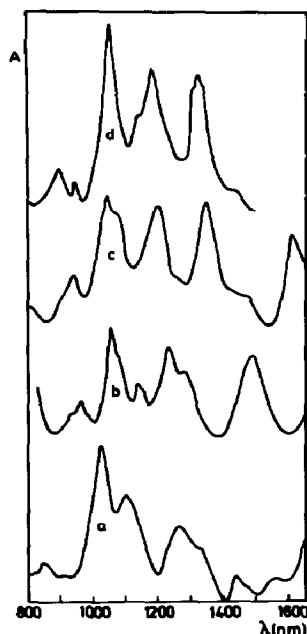


Fig. 1. Electronic spectra (THF solution). a: (C₉H₇)₂U(BH₄)₂; b: (1.4.7-(CH₃)₃-C₉H₄)₃UCl; c: (1-C₂H₅-C₉H₆)₃UCl; d: (C₉H₇)₃UBr.

[9,10], is considerably shifted, by ca. 25 cm^{-1} , on going to corresponding $L_2An(BH_4)_2$ compounds. This band shift can be accounted for in terms of a simple oscillator model involving cyclopentadienyl or indenyl entities (L_2 or L_3) and the remaining group ($An(BH_4)_2$ or $AnBH_4$). Table 4 summarizes the experimental and calculated positions of the band for the complexes studied.

Electronic spectra

Figure 1 shows the near infrared spectra in the 800–1650 nm region of **3a** and a series of indenyl compounds in THF solution [9]. A group of three bands with low extinction coefficients ($\epsilon < 100$) characteristic of pseudo-tetrahedral geometry is observed in the 940–1400 nm region [11–13].

Magnetic susceptibility

The magnetic susceptibility of the uranium compound **3a** was measured between 1.5 and 300 K by use of a Faraday balance. The susceptibility (2.46 ± 0.02 BM at 295 K), corrected for the diamagnetic contribution of the constituents, corresponds to the magnetic behaviour expected for a pseudo-tetrahedral compound (Fig. 2) [9].

NMR spectra

$(C_5H_5)_3ThBH_4$ (**1b**) and $(C_5H_5)_2Th(BH_4)_2$ (**1a**). The 1H and ^{13}C NMR spectral data for the title compounds are given in Table 2. The chemical shifts of the derivative (**1a**) are similar to those previously reported for **1b** [8], and so comparison of the integrals for the C_5H_5 and BH_4 protons had to be used for characterization of the two complexes. The integration ratio was 10/8 for **1a** and 15/4 for **1b**.

$(C_9H_7)_3ThBH_4$ (**2b**) and $(C_9H_7)_2Th(BH_4)_2$ (**2a**). Figure 3 shows the 1H NMR spectra of **2b** and **2a** in C_6D_6 solution. The assignment of the 1H NMR peaks is based on their relative integrals and splitting patterns. The signals for the five and six-membered rings show A_2B and $AA'BB'$ patterns, respectively [14–17]. The four protons of the BH_4 group exhibit a typical broad quartet ($J(^{11}B-H)$ 85 Hz).

The proton-decoupled ^{13}C NMR spectrum shows five peaks (Table 2). The assignment is based on a comparison with data for indenyl salts [17–19], heptamethylindenyl compounds of lanthanum [20], and alkyindenyl compounds [21]. The peak near 132 ppm was assigned to C(8)–C(9) by use of the DEPT method [22].

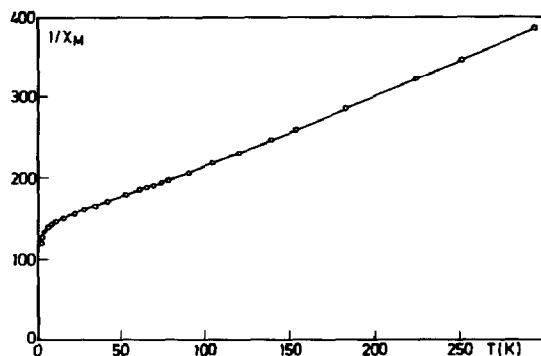


Fig. 2. Magnetic susceptibility of $(C_9H_7)_2U(BH_4)_2$.

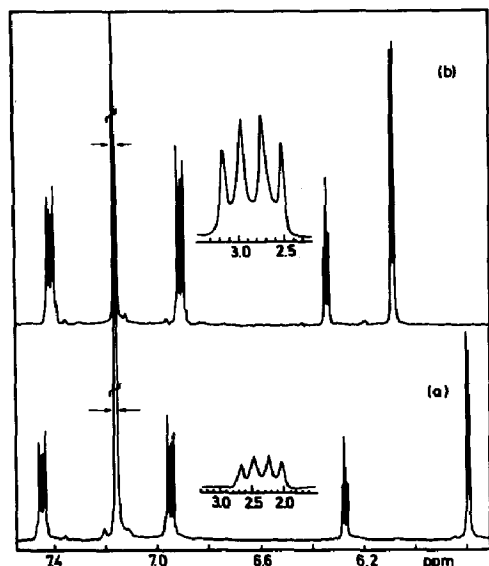


Fig. 3. ^1H NMR spectra of (a) $(\text{C}_9\text{H}_7)_3\text{ThBH}_4$, (b) $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$. The solvent peak (C_6D_6) is indicated by arrows. The BH_4 quartet intensity is enhanced by a factor 3.

Temperature dependence of the ^1H NMR spectra of 2a and 2b. The ^1H NMR spectra of $(\text{C}_9\text{H}_7)_3\text{BH}_4$ (**2b**) and $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$ (**2a**) were recorded between -85 and 110°C . Figure 4 shows the effect of temperature on the chemical shifts of the indenyl group. The C_5 ring protons undergo the most important change. For **2a**, the change in the chemical shift is similar to that observed for the ligand $(\text{C}_9\text{H}_7)\text{M}$ ($\text{M} = \text{Li}, \text{Na}$) [14]. A deshielding of ca. 0.15 ppm is noted over the full range of temperature. For **2b**, the change for the H(1) and H(3) signals corresponds to that of the **2a** protons but the H(2) signal shows a shielding of ca. 0.3 ppm.

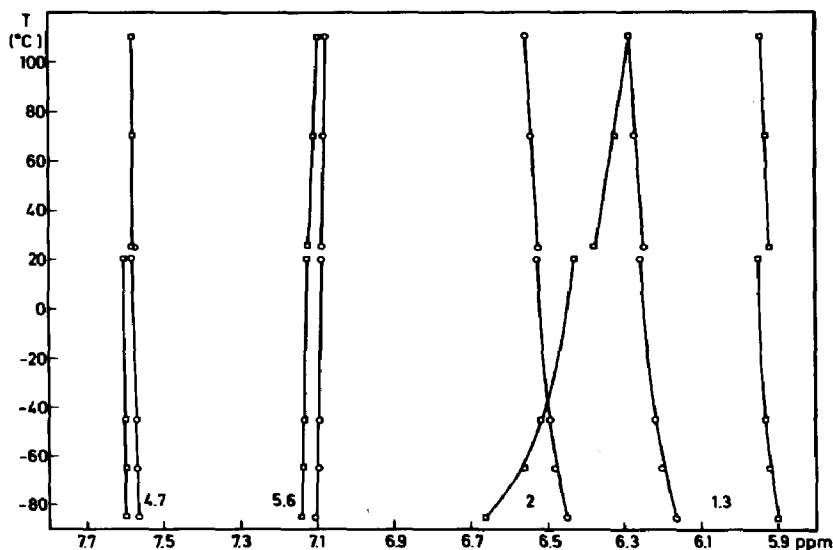


Fig. 4. The temperature dependence of the indenyl ^1H chemical shifts (in ppm from TMS) of $(\text{C}_9\text{H}_7)_3\text{ThBH}_4$ (\square) and $(\text{C}_9\text{H}_7)_2\text{Th}(\text{BH}_4)_2$ (\circ) in xylene- d_{10} ($T \geq 25^\circ\text{C}$) and toluene- d_8 ($T \leq 20^\circ\text{C}$).

The results can be tentatively accounted for in terms of the greater steric congestion in **2b** than in **2a**.

The intramolecular interactions in $(C_9H_7)_3ThBH_4$ would increase with temperature and this would favour a slight reduction of hapticity from η^5 to η^3 . Consequently the magnetic anisotropy that induces protons deshielding would be weakened. This effect would not be seen for **2a** since it is less congested.

A structural feature observed for indenyl compounds involves the differences in the C–C bond lengths, which are shorter for C(1)–C(2)–C(3) than for C(8)–C(9) [12,23–26]. By comparison with data for cyclopentadienyl compounds, this can be accounted for mainly in terms of steric effects and considered to arise from hapticity reduction [18].

At room temperature there was no difference in the 1H and ^{13}C chemical shifts for the cyclopentadienyl compounds **1a** and **1b**, in contrast with the behaviour observed for the more hindered indenyl derivatives **2a** and **2b**. The effects of electronic factors [23] and interligand ring currents can also act to different extents on the chemical shifts for **2a** and **2b**. This phenomenon has been discussed previously [9] for $(1,4,7-(CH_3)_3C_9H_4)_3ThCl$, for which the abnormal shift for H(2) was attributed to the proximity of a benzene ring of another ligand.

The effects of lowering the temperature in the spectra on the borohydride groups in $(C_9H_7)_3ThBH_4$ and $(C_9H_7)_2Th(BH_4)_2$ compounds are identical and near $-70^\circ C$ the B–H coupling can no longer be seen [1].

$(C_9H_7)_3UBH_4$ (**3b**) and $(C_9H_7)_2U(BH_4)_2$ (**3a**). The 1H NMR spectra are given in Table 2. The paramagnetism of uranium causes the peaks to spread over a large range of chemical shifts, and no coupling is observed for the C_5 ring protons [16,27].

Conclusions

Infrared and NMR spectroscopy has enabled unambiguous identification of the complexes $L_2An(BH_4)_2$ and L_3AnBH_4 . The IR data show that there is tridentate ligation of the borohydride ligand in all the compounds, in solution and in the solid state.

The variable-temperature 1H NMR spectra of $(C_9H_7)_3ThBH_4$ and $(C_9H_7)_2Th(BH_4)_2$ suggest that the more sterically hindered compound shows a greater tendency towards η^3 -indenyl–metal bonding. No slowing of the BH_4 fluxional process is detected even at $-85^\circ C$ for $(C_9H_7)_3ThBH_4$ and $(C_9H_7)_2Th(BH_4)_2$.

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