Title
CYCLOOCTATETRAENEACTINIDE(IV) BIS-BOROHYDRIDES

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Although bis(η⁸-cyclooctatetraene)actinide(IV) (Figure 1a) complexes have been extensively studied (1) since the synthesis of uranocene in 1968 (2,3), mono-COT actinide "half-sandwiches" (Figure 1b) were unknown until recently (4,5). The proposed covalent bonding, involving overlap between filled ligand \( e_g \) orbitals with empty metal 5f orbitals (3), could also apply to the bonding in mono-ring complexes. Whereas uranocene has been compared to ferrocene, COT half-sandwiches could show the varied reactivity exhibited by mono-cyclopentadienyl transition metal complexes such as \( \text{CpFe(CO)}_2\text{Cl} \). Thus, reactions such as ligand substitution and reactions of coordinated ligands might be observed along with the usual reactions of uranocene. Mono-COT actinide complexes could also show chemistry similar to the \((\text{C}_5\text{Me}_5)_2\text{MX}_2\) compounds studied by Marks and coworkers (6).

The possibility of COT half-sandwich complexes was established by the observation of an intermediate COT signal in the nmr spectrum of the preparation of thorocene from \( \text{ThCl}_4 \) and \( \text{K}_2\text{BuCOT} \) (4). LeVanda and Streitwieser were able to isolate a white crystalline solid from the reaction of equimolar amounts of \( \text{ThCl}_4 \) and \( \text{K}_2\text{COT} \) (4) and an x-ray crystal structure determination (7) confirmed the product as \((\text{COT})\text{ThCl}_2(\text{THF})_2\). A better synthesis for 1a and complexes with substituents on the cyclooctatetraene ring is reaction of a thorocene and \( \text{ThCl}_4 \) in refluxing THF.

\[
\text{ThCl}_4 + \text{K}_2\text{COT} \xrightarrow{\Delta} (\text{COT})\text{ThCl}_2(\text{THF})_2 \tag{1}
\]

\[
\frac{1}{2}\text{ThCl}_4 + \frac{1}{2}\text{Th}((\text{RCOT})_2 \xrightarrow{\Delta} (\text{RCOT})\text{ThCl}_2(\text{THF})_2 \tag{2}
\]

Interestingly, disproportionation, e.g.,

\[
2((\text{RCOT})\text{ThCl}_2 \rightarrow (\text{RCOT})_2\text{Th} + \text{ThCl}_4 \tag{3}
\]
does not occur in this case or for \((\text{C}_5\text{Me}_5)_2\text{MCl}_2\) (8), whereas \((\text{C}_5\text{H}_5)_2\text{UCl}_2\) is apparently unstable (9). The increased stability of the pentamethylcyclopentadienyl system has been attributed to steric hindrance. The cyclooctatetraene complexes acquire two molecules of solvent (THF) to complete the coordination sphere.

In order to take advantage of the known volatility of actinide borohydride complexes (10), we sought to prepare half-sandwich borohydrides \((\text{RCOT})\text{M(BH}_4\text{)}_2\). Several routes have been developed for the synthesis of the thorium complexes in 65 to 90\% yield (5). \(\text{Th(BH}_4\text{)}_4(\text{THF})_2\) (11) has been found to react with an equimolar quantity of a cyclooctatetraene dianion in THF to give 2 as a microcrystalline white solid. In contrast to the preparation of 1, 2 is readily prepared at ambient temperature without prolonged reflux. 2 can also be prepared in a manner analogous to the synthesis of 1, using \(\text{Th(BH}_4\text{)}_4(\text{THF})_2\) and \(\text{Th(RCOT)}_2\).

\[
\text{Th(BH}_4\text{)}_4(\text{THF})_2 + \text{Th(RCOT)}_2 \xrightarrow{\Delta} 2(\text{RCOT})\text{Th(BH}_4\text{)}_2(\text{THF})_2 \quad (4)
\]

The preparation of 2 directly from \(\text{ThCl}_4\) is a modification of the recent synthesis of \(\text{Cp}_2\text{U(BH}_4\text{)}_2\) (12).

\[
\text{ThCl}_4 + 2\text{LiBH}_4 \xrightarrow{\text{THF}} \text{K}_2\text{COT} \xrightarrow{\text{K}_2\text{COT}} (\text{COT})\text{Th(BH}_4\text{)}_2(\text{THF})_2 \quad (5)
\]

This synthesis is complicated, however, by the need to remove the \(\text{LiCl}\) formed in the reaction. In addition, metathesis of 1 with \(\text{LiBH}_4\) gives the borohydride half-sandwich.

\[
(\text{RCOT})\text{ThCl}_2(\text{THF})_2 \xrightarrow{\text{LiBH}_4, \text{THF}} (\text{RCOT})\text{Th(BH}_4\text{)}_2(\text{THF})_2
\]

A 1,2-dimethoxyethane complex of 2, \((\text{COT})\text{Th(BH}_4\text{)}_2(\text{DME})\), 3, was prepared by the reaction of \(\text{Th(BH}_4\text{)}_4(\text{THF})_2\) and \(\text{K}_2\text{COT}\) in DME. In contrast to the THF complex, the DME complex is only sparingly soluble in toluene.

Although satisfactory elemental analyses have not been obtained, spectroscopic characterization of 2 is straightforward. The \(^1\text{H}\) nmr spectrum of 2 in Table 1 contains signals from one cyclooctatetraene, two equivalent borohydride groups and two molecules of coordinated THF. The borohydride signal appears as a quartet due to coupling to the \(^{11}\text{B}\) nucleus and indicates that the terminal and bridging protons are rapidly exchanging. The borohydride signal of \(\text{Cp}_3\text{Th(BH}_4\text{)}\) also appears as a quartet, at \(\delta 3.30\) (13). At low temperature, the quartet of 2 collapses symmetrically to a broad singlet at \(\delta 3.0\). Marks and Shimp have observed this effect in the spectrum of \(\text{Zr(BH}_4\text{)}_4\) and have interpreted the process as a temperature-dependent loss of B-H
coupling rather than a slowing of the $H_6^\alpha - H_6^\beta$ exchange (14).

The infrared spectra of 2 (Table 2) provide information regarding the binding of the borohydride group to the metal (13). Both bidentate (A) and tridentate (B) forms are known for actinide borohydrides (13,15).

$$\begin{align*}
\text{M} & \quad \text{H} & \quad \text{B} & \quad \text{H} \\
\text{(A)} & & & & \\
\text{H} & \quad \text{H} & \quad \text{B} & \quad \text{H} \\
\text{(B)} & & & & \\
\end{align*}$$

The infrared spectra of 2 are in accord with that expected for a tridentate form (B) and are similar to that from Th[N(SiMe$_3$)$_2$]$_3$ (BH$_6$) for which tridentate bonding has been established by X-ray crystal structure determination (16).

The infrared spectra of 2 also contain a strong band at 714 cm$^{-1}$; 1 gives similar spectra in this region. In thorocene, a strong absorption at 698 cm$^{-1}$ has been assigned to a perpendicular C-H deformation (17) or, more recently, to an asymmetric ring-metal-ring vibration (18). Bands at 742 and 775 cm$^{-1}$ in thorocene have been interpreted as C-H or C-C-C perpendicular bending modes (18). The absence of an absorption at ca 700 cm$^{-1}$ and the presence of strong bands at 15-30 cm$^{-1}$ higher frequency appear to be characteristic of the half-sandwich complexes.

The preparation of mono-COT complexes of uranium was also of interest. Marquette-Ellis has reported a $^1$H nmr spectroscopic study of the reaction between UCl$_4$, LiBH$_4$, and K$_2$COT (19). He observed signals from both uranocene and a second product assigned as (COT)U(BH$_4$)$_2$. We have studied this reaction and found that it is not straightforward. A high yield of uranocene was formed when cyclooctatetraene dianion, either solid or in THF solution, was added to a solution formed from the reaction of UCl$_4$ and two equivalents of LiBH$_4$. A mixture of equimolar amounts of U(BH$_4$)$_4$ and K$_2$COT also yielded uranocene upon addition of THF. However, a second product, 4, could be obtained by the slow dropwise addition of a THF solution of K$_2$COT to the UCl$_4$-2LiBH$_4$ reaction mixture. The brown product is soluble in benzene and was separated from the insoluble uranocene byproduct by filtration.

$$\text{UCl}_4 + 2\text{LiBH}_4 \xrightarrow{\text{THF}} \text{K}_2\text{COT} \rightarrow (\text{COT})\text{U(BH}_4)_2(\text{THF})_2 + \text{U(COT)}_2$$

4

The visible spectrum of 4 (Table 3) contains a strong band at 396 nm and tails off to longer wavelength with a series of shoulders much like a uranocene. The infrared spectrum of the compound is nearly identical to that of the thorium analog 2a and is consistent with tridentate bonding. We are, however, unable to reproduce the nmr spectrum reported by Marquette-Ellis.
Another route to mono-cyclooctatetraene compounds is cleavage of one ring from the bis-COT complexes by protonation. Kablitz and Wilke have prepared (COT)ZrCl₂ and its THF adduct in this manner (20).

\[
(COT)_2Zr + 2HCl (g) \xrightarrow{C_6H_5CH_3} [(COT)ZrCl_2]_n + C_6H_{10}
\]

\[
(COT)_2Zr + 2HCl (g) \xrightarrow{\text{THF}} (COT)ZrCl_2(THF)_2 + C_6H_{10}
\]

Although the decomposition of uranocene in the presence of aqueous acids has been noted (3), we have found that the reaction of (BuCOT)₂Th with two equivalents of dry HCl gives 1b.

1,1'-Dibutyluranocene also reacts with HCl. The product is a dark green powder that gives a red-brown solution in THF with a visible spectrum similar to that of 3.

\[
U(RCOT)_2 + 2HCl (g) \xrightarrow{\text{THF}} (RCOT)UCl_2(THF)_x
\]

5, R=n-Bu

The \(^1\)H nmr spectrum of 5 clearly shows a COT ring distinct from that of (BuCOT)₂U and, unlike a substituted uranocene, coupling is observed between the nonequivalent protons on the COT ring. Although the signals from 5 are strongly shifted by the paramagnetic uranium, the signals are much sharper than those of a uranocene. The infrared spectrum of 5 contains absorptions from the COT ring at 734 and 719 cm⁻¹, in the region expected for a half-sandwich complex. 5, however, is much less soluble than the thorium analog 2b, and unreacted uranocene can be removed by washing the mixture with benzene. LeVanda has also observed this product from the prolonged reflux of UC₁₄ and U(BuCOT)₂ (21).

Several other reactions of these complexes have been investigated. Although Cp₂Zr(BH₄)₂ reacts readily with tertiary amines, converting metal-BH₄ groups to metal hydrides by formation of BH₃-amine complexes (22), (COT)Th(BH₄)₂(THF)₂ was unchanged on treatment with excess NEt₃ at room temperature. 1a was observed to react slowly with excess BEt₃ in refluxing benzene.

\[
(COT)Th(BH₄)₂(THF)₂ + BEt_3 \xrightarrow{\Delta} (COT)Th(BH₃Et)₂(THF)_x
\]

6

Marks and Kolb have carried out the analogous reaction of Cp₃U(BH₄) and have observed complete substitution of the terminal proton in 36 hours. In contrast, 1a was only about 50% reacted after 40 hours and a trace remained after four additional days with a fresh charge of BEt₃. The infrared spectrum of 6 is much like that of 1a but the B-H terminal absorption is absent. Neither 1a nor 6 sublime on heating in vacuo and 6 is slowly
decomposed to thorocene (and other unidentified products) at ca. 100°C at 10⁻⁶ torr. Thorocene is also formed when Ia is allowed to react with K₂COT at room temperature in THF.

\[
\text{(COT)Th(BH₄)}_2(\text{THF})_2 + \text{K₂COT} \rightarrow \text{(COT)₂Th}
\]

Further studies of the synthesis and reactivity of these half-sandwich compounds are in progress.

**Experimental**

**General.** Due to the air-sensitive nature of the compounds in this study, all work was carried out in an argon atmosphere using a glove box or standard Schlenk techniques. Solvents were distilled under argon from sodium-benzophenone ketyl. LiBH₄ was purified by Soxhlet extraction with diethyl ether before use and other reagent grade chemicals were used as received. Uranocenes (2,23) and thorocenes (24) were prepared by published procedures. Th(BH₄)₄(THF)₂ was prepared by a modification of the method of Ehemann and Noth (11) using THF in place of diethyl ether and was shown by a powder pattern to be isostructural with U(BH₄)₄(THF)₂ (25). The synthesis (5) and X-ray crystal structure (7) of (RCOT)ThCl₂(THF)₂ have been published.

Infrared spectra were run of Nujol mulls prepared in a glove box and sealed between salt plates. Samples could then be transferred to a Perkin-Elmer Model 283 spectrometer without decomposition. Visible spectra were run in stoppered glass cells on a Cary 118 spectrometer. NMR spectra were run at 180 MHz on a FT instrument.

**Preparation of (RCOT)Th(BH₄)₂(THF)₂ (2).** (A) Th(BH₄)₄(THF)₂ (0.51 g, 1.2 mmole) and K₂COT (0.21 g, 1.2 mmole) were mixed and ca. 75 ml of THF was added. The solution was stirred in the glove box for 16 hrs until the yellow color faded. The white precipitate was removed by centrifugation and the solids were washed with 10 ml of THF. The solutions were combined and the solvent was pumped off to give 0.45 g (76%) of (COT)Th(BH₄)₂(THF)₂ (2a).

(B) Th(BH₄)₄(THF)₂ (0.37 g, 0.85 mmole) and Th(BuCOT)₂ (0.44 g, 0.80 mmole) were mixed and 50 ml of THF was transferred onto the solids in vacuo. The flask was refilled with argon and the solution was heated at reflux for 5 days. A visible spectrum indicated no further trace of the thorocene. Removal of the solvent in vacuo gave a light yellow solid. The residue was rinsed with hexane and dissolved in ca. 30 ml of benzene. A small amount of solid was removed by centrifuge and the solvent was removed to give 0.60 g (67%) of (BuCOT)Th(BH₄)₂(THF)₂ (2b) as a white solid.

(C) THF (60 ml) was added to a mixture of 1.25 g (3.3
(COT)ThCl₂ and 0.16 g (7.3 mmole) of LiBH₄ and the solution was stirred for 16 hrs in a glove box. A solution of 0.54 g (3.0 mmole) of K₂COT in 40 ml of THF was added and the mixture was stirred an additional 16 hrs. The precipitate was removed by centrifuge and washed with two 10 ml portions of THF. The solutions were combined and the solvent was removed. The residue was dissolved in benzene and the insoluble material was removed by centrifuge. Removal of the solvent gave an oily white product. Recrystallization from benzene-hexane gave 1.38 g (91%) of (COT)Th(BH₄)₂(THF)₂.

(D) (BuCOT)ThCl₂(THF)₂ (211 mg, 0.347 mmole) and LiBH₄ (36 mg, 1.6 mmole, excess) were mixed and 15 ml of THF was added. The solution was stirred in the glove box for 2 days. The solvent was removed and the residue was extracted with benzene. Removal of the solvent gave (BuCOT)Th(BH₄)₂(THF)₂ (2b), identified by its infrared spectrum.

Preparation of (RCOT)Th(BH₄)₂(DME) (3). Following synthesis A above, 0.326 g (0.725 mmole) of Th(BH₄)₂(THF)₂ was dissolved in 2 ml of DME and a solution of 0.13 g (0.71 mmole) of K₂COT in 20 ml of DME was added. The solution was stirred for 40 hrs in a glove box. The white solids were removed by centrifugation and washed with 10 ml of DME. The solutions were combined and the solvent was pumped off to give 0.26 g (67%) of (COT)Th(BH₄)₂(DME).

Preparation of (COT)U(BH₄)ₓ(THF)ₓ. A solution of 0.22 g (10 mmole) of LiBH₄ in 10 ml of THF was added to a solution of 1.63 g (4.3 mmole) of UC₁₄ in 25 ml of THF. The solution was stirred for 24 hrs in a glove box. K₂COT (0.75 g, 4.1 mmole) was dissolved in 100 ml of THF and added dropwise to the UC₁₄-LiBH₄ solution. The resultant brown solution was stirred for 16 hrs and the solvent was pumped off. The residue was extracted with benzene and the insoluble material was removed by centrifuge. The solvent was removed in vacuo leaving a brown tacky residue. Infrared and visible spectra indicated the product to be (COT)U(BH₄)₂THFₓ. Recrystallization from benzene-hexane gave a tacky brown solid.

Preparation of (COT)Th(BH₄)₂(THF)₂ with BEt₃. (COT)Th(BH₄)₂(THF)₂ (0.34 g, 0.67 mmole) was dissolved in benzene and 1.7 ml (1.7 mmole of 1 M BEt₃ in THF was added by syringe. The solution was heated at reflux for 40 hrs. The solvent was removed and an infrared spectrum indicated that the reaction was ca. 50% complete. Benzene and 3.0 ml of BEt₃ in THF were again added and the solution was heated at reflux for 4 days. The solvent was removed to give a tacky residue of (COT)Th(BH₃Et)₂(THF)₂.
Reaction of \((\text{COT})\text{Th(BH}_4\text{)}_2(\text{THF})_2\) with \(\text{K}_2\text{COT}\). \((\text{COT})\text{Th(BH}_4\text{)}_2(\text{THF})_2\) (0.253 g, 0.496 mmole) and \(\text{K}_2\text{COT}\) (0.089 g, 0.49 mmole) were mixed and 50 ml of THF was added. The solution was stirred for 3 days and the solids were removed by centrifuge. The solids were washed with additional THF (ca. 25 ml) until no further yellow color was extracted. The solutions were combined and the solvent was removed to give 0.178 g (83\%) of \(\text{Th(COT)}_2\). 

Acknowledgments

We thank Rodney Banks for a sample of \(\text{U(BH}_4\text{)}_4\), and Wayne Luke for assistance with the nmr spectra. This work was supported in part by The Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng 48.

Literature Cited

Table 1. Infrared Spectra (Nujol, cm\(^{-1}\))

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<th>Compound</th>
<th>B-H(_a)</th>
<th>B-H(_b)</th>
<th>COT</th>
<th>Other</th>
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<td>2482(s)</td>
<td>2282(ω)</td>
<td>2220(s)</td>
<td>2150(m)</td>
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<td>2215(s)</td>
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<td>2339(ω)</td>
<td>2210(s)</td>
<td>2142(m)</td>
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<td>5 (COT)UC(_2)(THF)(_x)</td>
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<td>6 (COT)Th(BH(_3)Et)(THF)(_2)</td>
<td>2310(s)</td>
<td>2185(s)</td>
<td>2128(s)</td>
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Table 2. NMR Spectra (δ vs TMS)

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<td>6.69(s,8H)</td>
<td>3.11(q,J=85Hz,8H)</td>
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<td>3.1 (q,J=85Hz)</td>
<td>3.0, 2.8(DME)</td>
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<td>THF-d₈</td>
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<td>-29.0(t,2H),</td>
<td>-33.0(d,2H),</td>
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<td>-44.7(t,broad 2H)</td>
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Table 3. Visible Spectra (λ<sub>max</sub>,nm)

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<th>λ&lt;sub&gt;max&lt;/sub&gt;,nm</th>
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<td>4 (COT)U(BH₄)₂(THF)₂</td>
<td>396, 457, 492, 525</td>
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<tr>
<td>5 (BuCOT)UCl₂(THF)ₓ</td>
<td>402, 456, 499, 541</td>
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