Ca(BH₄)₂ as a Simple Tool for the Preparation of Thorium and Uranium Metallocene Borohydride Complexes: First Synthesis and Crystal Structure of (C₅Me₅)₂Th(η^3 -H₃BH)₂

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ABSTRACT

Dedicated to David E. Morris, for his many years of friendship and encouragement, on the occasion of his retirement from Los Alamos National Laboratory.

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Borohydride

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Pentamethylcyclopentadienyl

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Calcium borohydride allows for the high-yielding synthesis of (C₅Me₅)₂An(η^3 -H₃BH)₂ (An = Th, U) by reaction with (C₅Me₅)₂AnCl₂ (An = Th, U). While a preparative synthesis of (C₅Me₅)₂U(η^3 -H₃BH)₂ has been previously reported in the literature using K(C₅Me₅) and U(BH₄)₄, the use of Ca(BH₄)₂ is higher yielding and mild. Full characterization of the novel compound (C₅Me₅)₂Th(η^3 -H₃BH)₂ is presented.

Borohydride (BH₄⁻) can ligate through its bridging hydrogen atoms to access numerous coordination modes to metal centers and has been used in f-element chemistry to form a variety of stable, low coordination number metal complexes.[1, 2] In fact, the first f-element borohydride complexes were prepared during the Manhattan Project in search of volatile alternatives to UF₆ for uranium isotope separations. Since this time, borohydride compounds have become useful synthetic reagents in inorganic and organometallic uranium chemistry. For example, U(η^3 -H₃BH)₄,[1] (C₆Me₆)U(η^3 -H₃BH)₃,[3] and U(η^3 -H₃BH)₃(THF)₂,[4] have proved to be valuable precursors to new complexes resulting from reactions of the BH₄ groups with anionic and acidic reagents.

In contrast to uranium, there has been limited progress in the field of thorium borohydride chemistry over the past 80 years; to date, only a handful of structurally characterized examples, [N(SiMe₃)₂]₃Th(η^3 -H₃BH),[5] (C₉Me₇)₂Th(η^3 -H₃BH)₂,[6] (OTer^{Mes})₂Th(η^3 -H₃BH)₂(DME), (OTer^{Mes})₂Th(η^3 -H₃BH)₂, and [(OTer^{Mes})₂Th(η^3 -H₃BH)₂(4,4'-NC₅H₄C₅H₄N)]_∞ (OTer^{Mes} = O-2,6-(2,4,6-Me₃-C₆H₂)-C₆H₃),[7] have been reported.

Our group has been developing H₂-free routes to actinide hydride compounds.[8, 9] Since borohydride ligands can be viewed as a latent source of hydride,[10, 11] we were interested in preparing the metallocene complexes (C₅Me₅)₂An(η^3 -H₃BH)₂ (An = Th (**1**), U (**2**)) for use in multi-electron reduction chemistry.[12-17] Here we report the synthesis, characterization, and structure of the first pentamethylcyclopentadienyl thorium borohydride

complex, (C₅Me₅)₂Th(η^3 -H₃BH)₂ (**1**), as well as a new, straightforward, and high-yielding synthesis of (C₅Me₅)₂U(η^3 -H₃BH)₂ (**2**) using commercially available Ca(BH₄)₂ as a borohydride transfer reagent.

Actinide borohydride complexes have classically been synthesized by the reaction of lithium or sodium borohydrides with the corresponding actinide halide,[1] albeit in low yields. In our hands, reaction of 2.2 equivalents of NaBH₄ and (C₅Me₅)₂ThCl₂ in tetrahydrofuran did not result in the formation of a single product. Despite modifying reaction conditions, >50% conversion of starting material was never achieved.

There is precedent for using alkaline earth borohydrides as metathesis reagents to form metal borohydride complexes.[6, 7] As shown in Eq (1), quantitative conversion of (C₅Me₅)₂ThCl₂ into the corresponding bis(borohydride) complex (C₅Me₅)₂Th(η^3 -H₃BH)₂ (**1**) was conveniently achieved in 1 hour at room temperature by reaction with one equivalent of Ca(BH₄)₂ in tetrahydrofuran.

The volatiles were removed from the reaction mixture and the resulting residue was dissolved in toluene.

Separation of the insoluble salts was accomplished by filtration through a Celite-padded coarse-porosity fritted funnel. The filtrate was collected and the volatiles were removed to reproducibly afford $(\text{C}_5\text{Me}_5)_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$ (**1**) as an off-white solid in 93% yield.[18]

Complex **1** was fully characterized by a combination of NMR and ATR-FTIR spectroscopy, elemental analysis, and X-ray crystallography. The ^1H NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$ (**1**) is dominated by a resonance in both tetrahydrofuran- d_8 (2.20 ppm) and benzene- d_6 (2.07 ppm), corresponding to the C_5Me_5 protons. Although the BH_4 hydride resonances were not observed in tetrahydrofuran- d_8 , in benzene- d_6 they appeared as a broad quartet at 3.16 ppm.

The BH_4 groups were readily identified in the ^{11}B NMR spectra as a broad singlet at -12.11 ppm in tetrahydrofuran- d_8 and a pentet at -11.04 ppm in benzene- d_6 . These combined data are consistent with an averaged BH_4 hydride environment in the coordinating solvent tetrahydrofuran- d_8 and a static binding of the borohydride ligands in non-coordinating benzene- d_6 on the NMR time scale. ^{11}B NMR data for actinide borohydrides are exceedingly rare; however, for comparison, the two related heteroleptic aryloxy borohydride thorium complexes recently reported by Arnold and co-workers, $(\text{OTer}^{\text{Mes}})_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2(\text{DME})$ and $(\text{OTer}^{\text{Mes}})_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$, have comparable ^{11}B NMR chemical shifts in benzene- d_6 at -12.42 ppm (singlet) and -10.08 ppm (pentet), respectively.[7]

Evidence for tridentate coordination of the BH_4 ligands ($\eta^3\text{-H}_3\text{BH}$) in $(\text{C}_5\text{Me}_5)_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$ (**1**) is provided by ATR-FTIR spectroscopy, which reveals a terminal B–H stretch at 2360 cm^{-1} , a bridging B–H stretch at 2160 cm^{-1} , and a bridging B–H deformation at 1420 cm^{-1} . [1, 2]

Single crystals suitable for X-ray diffractometry were grown from concentrated toluene solutions of **1** at -35°C . Figure 1 shows the molecular structure of complex **1**. [19] The hydrogen atoms attached to boron were located on the Fourier difference map, which is rare among structurally characterized thorium compounds, and were refined with restraints. The molecular structure features a classic bent metallocene framework in the solid-state, with the borohydride ligands contained within the metallocene wedge ($\text{B–Th–B} = 101.4(2)^\circ$; $\text{Th–B} = 2.627(5)\text{ \AA}$). The average $\text{Th–C}_{\text{ring}}$ bond distance is $2.807(3)\text{ \AA}$, the $\text{Th–C}_{\text{cent}}$ (C_{cent} = cyclopentadienyl centroid) bond length is $2.534(3)\text{ \AA}$, and the $\text{C}_{\text{cent}}\text{–Th–C}_{\text{cent}}$ angle is $132.9(3)^\circ$. There are no structurally characterized bis(cyclopentadienyl) thorium borohydride complexes; for comparison, $(\text{C}_5\text{Me}_5)_2\text{U}(\eta^3\text{-H}_3\text{BH})_2$ (**2**) has comparable metrical parameters: $\text{B–U–B} = 101.46^\circ$; $\text{U–B} = 2.587\text{ \AA}$; average $\text{U–C}_{\text{ring}} = 2.699\text{ \AA}$; $\text{U–C}_{\text{cent}} = 2.756\text{ \AA}$; $\text{C}_{\text{cent}}\text{–U–C}_{\text{cent}} = 132.72^\circ$. [20, 21]

Other structurally characterized thorium bis(borohydride) complexes also feature similar $\text{Th–}(\eta^3\text{-H}_3\text{BH})$ metrics: $[\text{N}(\text{SiMe}_3)_2]_3\text{Th}(\eta^3\text{-H}_3\text{BH})$, $\text{Th–B} = 2.61(3)\text{ \AA}$; [5] $(\text{C}_9\text{Me}_7)_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$, $\text{Th–B} = 2.624(3)$, $2.618(7)\text{ \AA}$, $\text{B–Th–B} = 98.6(2)^\circ$; [6] $(\text{OTer}^{\text{Mes}})_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2(\text{DME})$, $\text{Th–B} = 2.670(2)\text{ \AA}$; $\text{B–Th–B} = 92.9(7)^\circ$; $(\text{OTer}^{\text{Mes}})_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$, $\text{Th–B} = 2.640(1)\text{ \AA}$, $\text{B–Th–B} = 96.00(2)^\circ$. [7]

Using $\text{Ca}(\text{BH}_4)_2$ as a metathesis reagent is an elegant, high-yielding, and effective route for obtaining thorium

borohydride complexes and also provides an improved method for the synthesis of $(\text{C}_5\text{Me}_5)_2\text{U}(\eta^3\text{-H}_3\text{BH})_2$ (**2**). Under similar reaction conditions as shown in Eq. (1), complex **2** was obtained in excellent yield, 90%. [22]

By contrast, the original preparation of $(\text{C}_5\text{Me}_5)_2\text{U}(\eta^3\text{-H}_3\text{BH})_2$ (**2**) reacts $\text{U}(\text{BH}_4)_4$ with two equivalents of $\text{K}(\text{C}_5\text{Me}_5)$ in toluene for 2 hours; following work-up, complex **2** was obtained in 58% isolated yield. [20] Both starting materials, $\text{U}(\text{BH}_4)_4$ and $\text{K}(\text{C}_5\text{Me}_5)$ must first be prepared, which requires the reaction of pentamethylcyclopentadiene with either KNH_2 or $\text{K}[\text{N}(\text{SiMe}_3)_2]$ in tetrahydrofuran. Alternatively, the synthesis of (**2**) was reported on an NMR scale reaction with NaBH_4 and $(\text{C}_5\text{Me}_5)_2\text{UCl}_2$ in tetrahydrofuran; however, this preparation was not scaled-up and **2** was not isolated. Thus, the use of $\text{Ca}(\text{BH}_4)_2$ provides a considerable synthetic improvement compared to existing literature procedures for the synthesis of $(\text{C}_5\text{Me}_5)_2\text{U}(\eta^3\text{-H}_3\text{BH})_2$ (**2**) since it reduces the reaction time and provides **2** in dramatically higher yields.

Figure 1. Molecular structure of $(\text{C}_5\text{Me}_5)_2\text{Th}(\eta^3\text{-H}_3\text{BH})_2$ (**1**) with thermal ellipsoids projected at the 50% probability level. The methyl groups on the pentamethylcyclopentadienyl ligands have been omitted for clarity. The hydrogen atoms attached to boron were located on the Fourier difference map and refined with restraints. Selected bond distances ($\text{\AA}$) and angles ($^\circ$): $\text{Th}(1)\text{–B}(1) = \text{Th}(1)\text{–B}(2) = 2.627(5)$; $\text{B}(1)\text{–Th–B}(2) = 98.6(2)$; $\text{C}_{\text{cent}}\text{–Th}(1)\text{–C}_{\text{cent}} = 132.9(3)$; $\text{Th}(1)\text{–C}_{\text{ring(ave)}} = 2.807(3)$.

In conclusion, this report broadens the synthetic application of $\text{Ca}(\text{BH}_4)_2$ as a useful borohydride transfer reagent to synthesize thorium and uranium borohydrides with shorter reaction times, mild reaction conditions, and higher yields. The protocol described in this work now allows us easier access to new thorium and uranium organometallic complexes. Given the increasing number of applications for f-element borohydride complexes in catalysis, [23–25] we anticipate that this result is general and will not be limited to the preparation of metallocene complexes. Work in this area is currently in progress.

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References

- [1] M. Ephritikhine, Chem. Rev., 97 (1997) 2193-2242.
- [2] T.J. Marks, J.R. Kolb, Chem. Rev., 77 (1977) 263-293.
- [3] D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, J. Organomet. Chem., 371 (1989) 155-162.
- [4] P.L. Arnold, C.J. Stevens, J.H. Farnaby, M.G. Gardiner, G.S. Nichol, J.B. Love, J. Am. Chem. Soc., 136 (2014) 10218-10221.
- [5] H.W. Turner, R.A. Andersen, A. Zalkin, D.H. Templeton, Inorg. Chem., 18 (1979) 1221-1224.
- [6] T.M. Trnka, J.B. Bonanno, B.M. Bridgewater, G. Parkin, Organometallics, 20 (2001) 3255-3264.
- [7] J. McKinven, G.S. Nichol, P.L. Arnold, Dalton Trans., 43 (2014) 17416-17421.
- [8] J.K. Pagano, J.M. Dorhout, K.R. Czerwinski, D.E. Morris, B.L. Scott, R. Waterman, J.L. Kiplinger, Organometallics, 35 (2016) 617-620.
- [9] J.K. Pagano, J.M. Dorhout, R. Waterman, K.R. Czerwinski, J.L. Kiplinger, Chem Commun (Camb), 51 (2015) 17379-17381.
- [10] J. Brennan, R. Shinomoto, A. Zalkin, N. Edelstein, Inorg. Chem., 23 (1984) 4143-4146.
- [11] S.M. Cendrowski-Guillaume, M. Lance, M. Nierlich, M. Ephritikhine, Organometallics, 19 (2000) 3257-3259.
- [12] D.J. Grant, T.J. Stewart, R. Bau, K.A. Miller, S.A. Mason, M. Gutmann, G.J. McIntyre, L. Gagliardi, W.J. Evans, Inorg. Chem., 51 (2012) 3613-3624.
- [13] E. Montalvo, K.A. Miller, J.W. Ziller, W.J. Evans, Organometallics, 29 (2010) 4159-4170.
- [14] W.J. Evans, S.A. Kozimor, J.W. Ziller, Chem. Commun., (2005) 4681-4683.
- [15] W.J. Evans, E. Montalvo, S.A. Kozimor, K.A. Miller, J. Am. Chem. Soc., 130 (2008) 12258-12259.
- [16] W.J. Evans, G.W. Nyce, J.W. Ziller, Angew. Chem., Int. Ed., 39 (2000) 240-242.
- [17] W.J. Evans, K.A. Miller, J.W. Ziller, Angew. Chem., Int. Ed., 47 (2008) 589-592.
- [18] *Synthesis of $(C_5Me_5)_2Th(BH_4)_2$ (1)*: A 20 mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2ThCl_2$ (0.189 g, 0.3290 mmol), $Ca(BH_4)_2$ (0.0291 g, 0.4171 mmol) and tetrahydrofuran (10 mL). The reaction was stirred at ambient temperature for 1 h. Volatiles were removed under reduced pressure and the resultant residue was extracted with toluene (2 x 10 mL) and filtered through a Celite-packed coarse-porosity frit. Upon removal of all volatiles from the filtrate, **1** was collected as an off-white crystalline powder (0.162 g, 0.03051 mmol, 93%). 1H NMR (298 K, benzene- d_6 , 400 MHz): δ 2.07 (s, 30H, $-C_5Me_5$), 3.16 (quartet ($J = 173.2, 85.5$ Hz), 8H, $-BH_4$); (298 K, tetrahydrofuran- d_8 , 400 MHz): δ 2.20 (s, 30H, $-C_5Me_5$), B-H not observed. ^{11}B NMR (298 K, benzene- d_6 , 128 MHz): δ -11.04 (p, $J = 87.1$ Hz); (298 K, tetrahydrofuran- d_8 , 128 MHz): δ -12.11 (br s). ^{13}C NMR (298 K, benzene- d_6 , 101 MHz): δ 11.23. ATR-IR (Neat, 296 K, cm^{-1}): 2960, 2880, 2360, 2160, 2030, 1970, 1590, 1420, 1260, 1100. Anal. Calcd for $C_{20}H_{38}B_2Th$ (mol. wt. 532.2 g mol^{-1}): C, 45.14; H, 7.20. Found: C, 45.32; H, 7.19.
- [19] *Crystal data for 1*: $C_{20}H_{38}B_2Th$, $M = 532.16$ g mol^{-1} , crystal dimensions $0.34 \times 0.19 \times 0.15$ mm^3 , $T = 100(1)$ K, orthorhombic, Fmm2, $a = 14.9952(16)$, $b = 17.752(3)$, $c = 8.1291(9)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 2163.9(5)$ Å 3 , $Z = 4$, $\rho_{calcd} = 1.634$ Mg m^{-3} , $\mu = 6.889$ mm^{-1} , θ range = 3.073 – 35.040° , reflections collected: 2442, independent: 1315 ($R_{int} = 0.0136$), $R1 = 0.0153$, $wR2 = 0.0334$ ($I > 2\sigma(I)$). Single crystals of **1** suitable for X-ray crystallography were obtained by recrystallization from a toluene solution. A crystal of **1** was mounted in a nylon cryoloop using Paratone-N oil under an argon gas flow. The data were collected on a Bruker D8 Quest diffractometer, with CMOS detector in shutterless mode. The crystals were cooled to 100 K using an Oxford Cryostream liquid nitrogen cryostat. The instrument was equipped with a graphite monochromatized Mo K α X-ray source ($\lambda = 0.71073$ Å), with TriumphTM X-ray source optics. A hemisphere of data was collected using ω scans. Data collection and initial indexing and cell refinement were handled using APEX II software.[26] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[27] The data were corrected for absorption

using the SADABS program.[28] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically, and non-borohydride atoms were treated as idealized contributions. Structure solution and refinement were performed with SHELXTL.[29]

- [20] P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, J. Organomet. Chem., 466 (1994) 107-118.
- [21] R.E. Marsh, M. Kapon, S. Hu, F.H. Herstein, Acta Crystallographica Section B, 58 (2002) 62-77.
- [22] *Synthesis of $(C_5Me_5)_2U(BH_4)_2$ (2)*: A 20 mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UCl_2$ (0.219 g, 0.3784 mmol), $Ca(BH_4)_2$ (0.027 g, 0.386 mmol) and tetrahydrofuran (10 mL). The reaction was allowed to stir at room temperature for 1 h. Volatiles were removed under reduced pressure and the resultant residue was extracted with toluene (2 x 5 mL) and filtered through a Celite-packed coarse porosity frit. Upon removal of all volatiles from the filtrate, **2** was isolated as a red crystalline powder (0.184 g, 0.3420 mmol, 91%). 1H NMR (298 K, benzene- d_6 , 400 MHz) data agreed with literature values:[20] δ 12.5 (s, 30H, $-C_5Me_5$), -68.1 (q, 8H, $-BH_4$). ^{11}B NMR (298 K, benzene- d_6 , 128 MHz): δ 37.87 (br s). ATR-IR (Neat, 296 K, cm^{-1}): 2970, 2880, 2470, 2350, 2230, 2110, 1590, 1430, 1380, 1160, 1020, 802.
- [23] C. Villiers, M. Ephritikhine, J. Chem. Soc., Chem. Commun., (1995) 979-980.
- [24] C. Villiers, P. Thuéry, M. Ephritikhine, Inorg. Chem. Commun., 10 (2007) 891-893.
- [25] S.M. Mansell, F. Bonnet, M. Visseaux, P.L. Arnold, Dalton Trans., 42 (2013) 9033-9039.
- [26] APEX2, v. 2014.7-1; Bruker AXS: Madison, WI, 2014
- [27] SAINT, v. 8.34A; Bruker AXS: Madison, WI, 2013
- [28] SADABS, v. 2014/3; Bruker AXS: Madison, WI, 2013
- [29] SHELXTL, v. 6.14; Bruker AXS: Madison, WI, 2000.