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Synthesis of bulky hydride ligands: *m*-terphenylborohydride complexes with trivalent uranium and neodymium†

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Here we describe the first coordination complexes containing a bulky *m*-terphenyltrihydroborate ligand. Treating $[\text{U}(\text{thf})_4]$ and NdCl_3 with three equiv. of $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu}_4})(\text{Et}_2\text{O})$ (where $\text{Ar}^{\text{tBu}_4} = 2,6-(3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$) yielded $[\text{M}(\text{H}_3\text{BAR}^{\text{tBu}_4})_3(\text{thf})_2]$ ($\text{M} = \text{U}$ and Nd). $[\text{U}(\text{H}_3\text{BAR}^{\text{tBu}_4})_3(\text{dme})_2]$ is also described, and structural comparisons reveal the influence of the Lewis base on $\text{H}_3\text{BAR}^{\text{tBu}_4}$ positioning.

Actinide borohydride complexes have been known since the discovery of $[\text{U}(\text{BH}_4)_4]$ during the Manhattan Project.¹ The simplest borohydride, BH_4^{1-} , for example, forms molecular complexes with the general formula $[\text{M}(\text{BH}_4)_4]$ with $\text{M} = \text{Th}\text{--}\text{Pu}$,^{1a,2} and similar homoleptic complexes are known with methyltrihydroborate (MeBH_3^{1-}).³

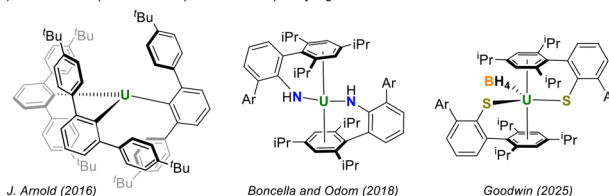
Despite the well-known examples of borohydride complexes with actinides in the +4 oxidation state,⁴ conventional borohydride ligands like BH_4^{1-} and MeBH_3^{1-} are too small to form neutral, mononuclear, and homoleptic complexes with trivalent actinides because of their larger ionic radius and reduced charge. The only homoleptic examples with borohydrides are those with chelating ligands like aminodiboranes and phosphinodiboranes.⁵ Even though these latter ligands saturate a larger percentage of the metal coordination sphere, their complexes with trivalent actinides are only known to exist as dimers or oligomers in the solid state. In this context, a mononuclear and homoleptic borohydride complex has yet to be isolated with a trivalent f-element.

We therefore set out to develop sterically bulky borohydride ligands for the isolation of homoleptic and mononuclear complexes with trivalent actinides. A structural scaffold that has proven effective at isolating low-coordinate transition metal, lanthanide, and actinide complexes is *m*-terphenyl. The demanding steric presence of *m*-terphenyl groups generally

serve to shield open coordination sites and stabilize metals and main group elements with low coordination numbers.⁶ Notable and recent examples with uranium are provided in Fig. 1a. Arnold and coworkers demonstrated how the bulky terphenyl ligand $(2,6\text{-(}4\text{-}^t\text{Bu-C}_6\text{H}_4)_2\text{C}_6\text{H}_3)^{1-}$ could be used to isolate the first structurally authenticated homoleptic tris(aryl)U(III) complex.⁷ Boncella and Odom used the *m*-terphenylamido ligand $(\text{NHAr}^{\text{iPr}_6})^{1-}$ where $\text{Ar}^{\text{iPr}_6} = 2,6\text{-(}2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$ to isolate a rare example of a formally U(II) complex.⁸ Though not a homoleptic example, Goodwin and coworkers recently described how the *m*-terphenylthiolate ligand $(\text{SAr}^{\text{iPr}_6})^{1-}$ can be used to isolate low coordinate U(III) complexes like $[\text{U}^{\text{III}}(\text{SAr}^{\text{iPr}_6})_2(\text{BH}_4)]$.⁹ These and other examples of coordinatively unsaturated *m*-terphenyl complexes led us to explore the development of *m*-terphenylborohydride ligands for low-valent actinide chemistry.¹⁰

Herein, we report the synthesis and characterization of the *m*-terphenyltrihydroborate ligand,¹¹ $(\text{H}_3\text{BAR}^{\text{tBu}_4})^{1-}$ where $\text{Ar}^{\text{tBu}_4} = 2,6\text{-(}3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$, and its use for the preparation

a) Recent examples of U complexes with terphenyl ligands



b) This work

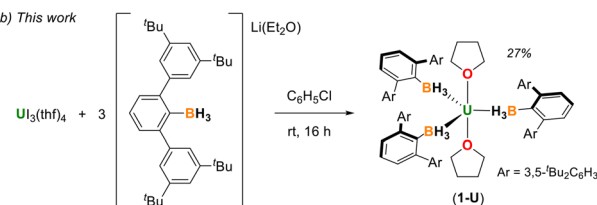


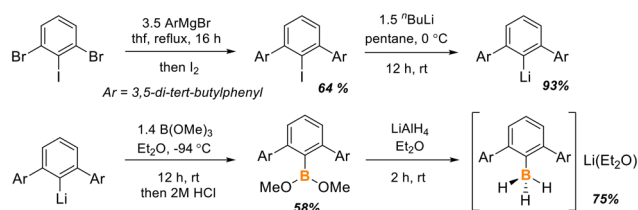
Fig. 1 (a) Notable examples of bulky *m*-terphenyl ligand scaffolds used to isolate mononuclear uranium complexes. (b) Synthesis of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu}_4})_3(\text{thf})_2]$ (**1-U**).

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of trivalent uranium and neodymium complexes (Fig. 1b). This ligand was targeted for our initial attempt because we anticipated that the 3,5-positioning of the *tert*-butyl substituents would provide greater steric protection as compared to more common *m*-terphenyl platforms like Ar^{IPr6} shown in Fig. 1. As we will show, despite its size, $(\text{H}_3\text{BAR}^{\text{tBu4}})^{1-}$ is still not large enough to prevent etherates like thf from coordinating to U^{3+} and Nd^{3+} .

The synthesis of $(\text{H}_3\text{BAR}^{\text{tBu4}})^{1-}$ is summarized in Scheme 1 (see ESI† for full details), and it followed the standard double benzyne reaction and I_2 quenching that is commonly used to prepare iodated *m*-terphenyl ligand precursors.¹² Subsequent lithiation of $\text{I-Ar}^{\text{tBu4}}$ with $n\text{-BuLi}$ to form $\text{Li-Ar}^{\text{tBu4}}$ followed by treatment with B(OMe)_3 in Et_2O afforded $(\text{MeO})_2\text{BAR}^{\text{tBu4}}$ in moderate yield (58%). Reduction of the borate with LiAlH_4 in Et_2O yielded the final terphenyl trihydroborate salt $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$ in 75% yield.¹³ The ^{11}B NMR spectrum revealed a diagnostic quartet at $\delta_{\text{B}} -29.1$ ppm with $^1J_{\text{BH}} = 75$ Hz due to coupling with the three hydrides.¹³ The ^1H and ^{13}C NMR spectra revealed the expected *m*-terphenyl resonances, as well as the presence of one Et_2O molecule based on ^1H integrations. X-ray diffraction (XRD) studies on transparent crystals isolated during a synthesis of **1-U** (*vide infra*) revealed the structure of unsolvated $[\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})]_2$. The structure is dinuclear with the Li cations bridged by BH_3 groups and coordinated in an η^3 fashion to a flanking aryl from the *m*-terphenyl group (Fig. 2).



Scheme 1 Synthesis of $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$.

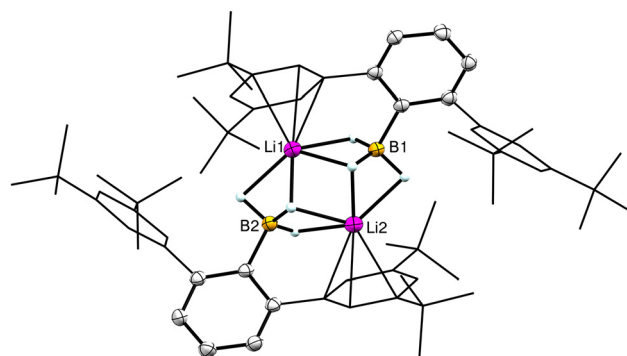


Fig. 2 Truncated molecular structure of unsolvated $[\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})]_2$. Ellipsoids are drawn at 50% probability, except hydrogens which are drawn as arbitrary sized spheres. The flanking aryl group carbon atoms are shown as wires and hydrogen atoms on carbon have been removed for clarity.

The reaction of $[\text{U}(\text{thf})_4]$ with three equivalents of $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$ in chlorobenzene initially afforded a suspension of white and dark purple solids that slowly turned brown over the course of 16 hours. Evaporation of the reaction mixture, followed by extraction with benzene, afforded a deep red solution from which orange crystals of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{thf})_2]$ (**1-U**) were isolated by slow evaporation in low yield (27%). Despite the use of chlorobenzene as the solvent, **1-U** retains two thf ligands from the $[\text{U}(\text{thf})_4]$ starting material. Attempts to remove the thf by heating under vacuum at 50–70 °C yielded visual evidence of decomposition. **1-U** is appreciably soluble in aromatic solvents like benzene, toluene, fluorobenzene, and chlorobenzene, but is only sparingly soluble in Et_2O and pentane.

The solid-state structure of **1-U** from single-crystal XRD shows a monomeric trivalent uranium complex with three equatorial $(\text{H}_3\text{BAR}^{\text{tBu4}})^{1-}$ ligands and two axial thf molecules (Fig. 3). The three U–B distances ranged from 2.622(2)–2.646(3) Å, which is consistent with κ^3 coordination with three hydrides bound to the metal. These U–B distances are shorter than the $\kappa^3\text{-H}_3\text{B}$ distances reported previously for $[\text{U}^{\text{III}}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3]$ and $[\text{U}^{\text{III}}(\text{H}_3\text{BP}^t\text{Bu}_2\text{BH}_3)_3]_2$ at U–B = 2.665(6) and 2.69(1) Å respectively.^{5b,d} The U–O bond lengths of 2.4847(15) and 2.4873(15) Å are significantly shorter than those previously reported for $[\text{U}^{\text{III}}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3(\text{thf})]$ (U–O = 2.549(4) Å) and *trans* U–O distances in the oligomeric structure of $[\text{U}^{\text{III}}(\text{BH}_4)_3(\text{thf})_2]$ (2.519(5) Å).^{5a,14} The nine U–H and two U–O bonds indicate a total coordination number of 11 for the uranium center, which is lower than those observed for other $\text{U}(\text{III})$ borohydride complexes that range from 12–14.^{5,14} The B–U–B angles of 116.71(8)°, 119.33(8)°, and 123.93(8)° and the

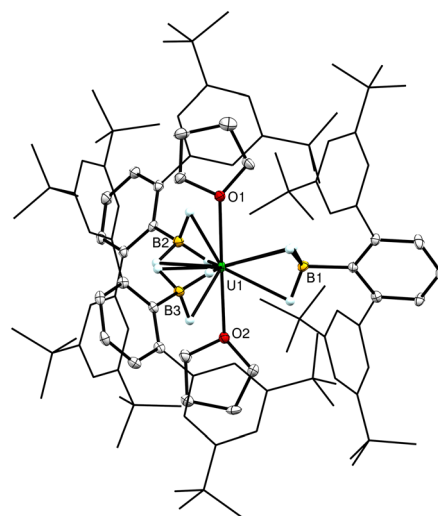


Fig. 3 Molecular structure of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{thf})_2]$ (**1-U**). Ellipsoids are drawn at 50% probability, except hydrogens which are drawn as arbitrary sized spheres. The flanking aryl group carbon atoms are shown as wires and hydrogen atoms on carbon have been omitted for clarity. Selected distances (Å): U(1)–B(1) = 2.638(3), U(1)–B(2) = 2.646(3), U(1)–B(3) = 2.622(2), U(1)–O(1) = 2.4573(15), U(1)–O(2) = 2.4848(15).



axial O–U–O bond angle of $178.96(6)^\circ$ indicate a distorted trigonal bipyramidal coordination geometry ($\tau_5 = 0.88$).¹⁵

The IR spectrum of ground samples of **1-U** revealed bridging U–H–B stretches at 2173 cm^{-1} and a shoulder at 2072 cm^{-1} , consistent with the $\kappa^3\text{-BH}_3$ binding with uranium. The ^{11}B NMR spectrum for **1-U** in C_6D_6 showed a single resonance at δ_{B} 181.5 ppm, which is shifted more downfield compared to $[\text{U}^{\text{III}}(\text{BH}_4)_3(\text{thf})_2]$ at δ_{B} 152.9 ppm.¹⁶ The ^1H NMR spectrum of **1-U** in C_6D_6 revealed a complex set of resonances between δ_{H} –8 and 18 ppm due to the paramagnetic U^{III} ($5f^3$) metal center, with a characteristically downfield shifted resonance at δ_{H} 134.2 ppm assigned to BH_3 . The UV-vis/NIR electronic absorption spectrum of **1-U** in thf (Fig. S26; ESI†) displays features at 408 nm, 471 nm, and 529 nm with $\epsilon = 940$, 670, and $405\text{ M}^{-1}\text{ cm}^{-1}$ respectively. These absorptions are consistent with the orange color of the complex, and similar colors spanning yellow to red have been observed for other U^{III} borohydride complexes.^{5a,16b,17} Between 700 and 1500 nm there are weak absorptions ($\epsilon = 25\text{--}90\text{ M}^{-1}\text{ cm}^{-1}$) characteristic of f–f transitions.

Stirring solid samples of **1-U** in dimethoxyethane (dme) quickly leads to its dissolution and conversion to $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{dme})_2]$ (**2-U**). Evaporation of this solution, followed by crystallization from pentane afforded orange crystals suitable for single-crystal XRD studies. Unlike **1-U**, **2-U** is highly soluble in aromatic, as well as etherate and hydrocarbon solvents.

The molecular structure of **2-U** reveals a distorted pentagonal bipyramidal geometry based on O and B positioning with two dme molecules and one borohydride in the equatorial plane (Fig. 4). The U–B distances of $2.695(3)\text{ \AA}$, and $2.712(4)\text{ \AA}$ indicate the $(\text{H}_3\text{BAR}^{\text{tBu4}})^{1-}$ ligands retain the κ^3 binding mode upon coordination of dme. The B1–U–B2 angle decreases to $102.03(7)^\circ$, while the B1–U–B1' angle increases to $155.95(13)^\circ$ breaking the pseudo trigonal arrangement observed in **1-U** to

create coordination sites for two dme molecules to bind (Fig. S2†). The O1–U–O1' angle is also slightly decreased to $171.98(10)^\circ$. The two crystallographically unique U–O bond lengths of $2.596(2)\text{ \AA}$ and $2.788(2)\text{ \AA}$ reflect the steric crowding around the metal and are significantly longer than those observed in **1-U** and the starting material $[\text{U}(\text{thf})_4]$.^{16a,18} The nine U–H and four U–O bonds yield a total coordination number of 13 for **2-U**. The ^{11}B NMR spectrum of a crystalline sample of **2-U** in C_6D_6 shows a single dominant feature at δ_{B} 271 ppm, as well as several minor species that may be attributed to different coordination isomers of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{dme})_2]$ in solution.

In an attempt to prepare a lanthanide analog for a point of comparison to **1-U**, we initially conducted salt metathesis reactions under the same conditions employed for **1-U**. Interestingly, no evidence of reaction was observed after stirring NdI_3 or $\text{NdI}_3(\text{thf})_{3.5}$ with three equivalents of $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$ in chlorobenzene for 16 hours. The lack of reactivity with $\text{NdI}_3(\text{thf})_{3.5}$, as compared to $[\text{U}(\text{thf})_4]$, is possibly because this species can exist as the $[\text{NdI}_2(\text{thf})_5][\text{NdI}_4(\text{thf})_2]$ ion pair, which tends to be less soluble.¹⁹ Metathesis reactions conducted with the same Nd starting materials in Et_2O , toluene, or thf also yielded no evidence of reaction. Given the divergence in reactivity between the U and Nd iodide starting materials, we instead tried metathesis reactions with NdCl_3 . Gratifyingly, stirring NdCl_3 and three equivalents of $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$ in thf, followed by extraction with benzene and slow concentration of the solution, yielded very light blue blocky crystals of $[\text{Nd}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{thf})_2]$ (**1-Nd**) in 31% yield.

XRD studies revealed a trigonal bipyramidal arrangement of $(\text{H}_3\text{BAR}^{\text{tBu4}})^{1-}$ and thf ligands identical to **1-U** (Fig. S1; ESI†). The Nd–B distances of $2.628(2)\text{ \AA}$, $2.623(2)\text{ \AA}$, and $2.604(2)\text{ \AA}$ are consistent with a κ^3 binding mode of the BH_3^- units and are on average $\sim 0.017\text{ \AA}$ shorter than those observed for **1-U**, consistent with the decrease in ionic radius from U^{III} ($1.025\text{ \AA}$; CN = 6) to Nd^{III} ($0.983\text{ \AA}$; CN = 6).²⁰ The B–Nd–B angles that comprise the trigonal arrangement of B atoms are $123.80(6)^\circ$, $116.85(6)^\circ$, and $119.32(7)^\circ$, which is also very similar to those observed in **1-U**. Accounting for these angles and the axial O–Nd–O angle of $179.10(4)^\circ$ yields a τ_5 value of 0.92.¹⁵

The ^{11}B NMR spectrum of **1-Nd** in C_6D_6 depicts a single resonance at δ_{B} 197 ppm consistent with the equivalence of the boron atoms in the solid-state structure. The room temperature ^1H NMR spectrum of **1-Nd** in C_6D_6 unsurprisingly reveals a similarly complex set of paramagnetically shifted resonances to those in **1-U**. The IR spectrum of **1-Nd** (Nujol) features a B–H stretch at 2191 cm^{-1} with a shoulder at 2081 cm^{-1} . The profile of these absorptions are nearly identical to those for **1-U**, but they occur at slightly higher wavenumbers.

In summary, we have described the synthesis and characterization of the *m*-terphenyltrihydroborate salt $\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})(\text{Et}_2\text{O})$, and several complexes with trivalent U and Nd. The structures of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{thf})_2]$ (**1-U**) and $[\text{Nd}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{thf})_2]$ (**1-Nd**) demonstrate that despite the

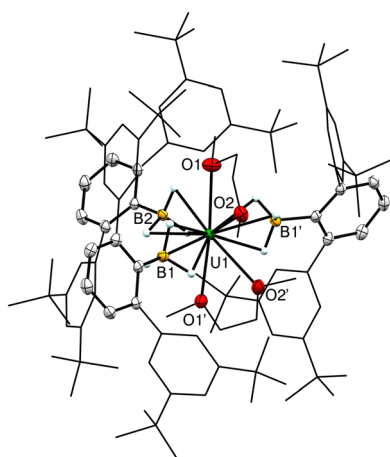


Fig. 4 Molecular structure of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{dme})_2]$ (**2-U**). Ellipsoids are drawn at 50% probability, except hydrogens which are drawn as arbitrary sized spheres. The flanking aryl groups and dme carbon atoms are shown as wires. Hydrogen atoms on carbon and co-crystallized pentane have been omitted for clarity. Selected distances ($\text{\AA}$): U(1)–B(1) = $2.695(3)$, U(1)–B(2) = $2.712(4)$, U(1)–O(1) = $2.596(2)$, U(1)–O(2) = $2.788(2)$.



increased steric profile of the *m*-terphenyl scaffold, it is not sufficient to completely suppress coordination of Lewis bases like thf. Moreover, the formation of $[\text{U}^{\text{III}}(\text{H}_3\text{BAR}^{\text{tBu4}})_3(\text{dme})_2]$ (2-U) shows how these complexes can distort to increase their coordination numbers and accommodate binding of additional Lewis-base donors. We are continuing to investigate other *m*-terphenyl scaffolds to identify the steric criteria and experimental conditions that will allow mononuclear borohydride complexes to be isolated with trivalent actinides without Lewis bases.

Author contributions

Peter A. Zacher III: writing – original draft, data curation, formal analysis. Daniel K. Unruh: data curation (crystal structures). Scott R. Daly: writing – original draft, formal analysis, supervision, funding acquisition, conceptualization.

Data availability

Crystallographic data for 1-U, 2-U, 1-Nd, and $[\text{Li}(\text{H}_3\text{BAR}^{\text{tBu4}})]_2$ have been deposited into the Cambridge Structural Database (CSD) and have been assigned the CCDC numbers 2439982–2439985.† All other data are available in the manuscript and ESI.†

Conflicts of interest

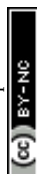
There are no conflicts to declare.

Acknowledgements

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