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Homoleptic Uranium and Lanthanide Phosphinodiboranates

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Here we report a new class of homoleptic *f*-element borohydride complexes called phosphinodiboranates. Treating $UI_3(1,4\text{-dioxane})_{1.5}$, NdI_3, or ErI_3, with three equiv of $K(H_3BP^tBu_2BH_3)$ in Et_2O yielded $M_2(H_3BP^tBu_2BH_3)_6$, where M = U, Nd, and Er. All three complexes form solid-state dimers, but exist as mixtures of monomers and dimers in solution.

Homoleptic borohydride complexes are renowned for their high coordination numbers and inner coordination spheres comprised exclusively of hydrogen atoms.[1] Many are also highly volatile, which gave rise to early interest in their use for uranium enrichment for atomic weapons. The first actinide borohydride complexes $An(BH_4)_4$ and $An(MeBH_3)_4$ (where An = actinide) were discovered during the Manhattan project and reported after World War II in separate, but parallel efforts by Hoekstra and Katz for thorium (BH_4^{1-}),[2] and Schlesinger, Brown, and co-workers for uranium (BH_4^{1-} and $MeBH_3^{1-}$).[3] Several decades later, Edelstein and coworkers expanded this work to the more radiotoxic congeners Pa, Np, and Pu.[4,5] Since their initial discovery, the chemistry of borohydrides with actinides has remained limited to BH_4^{1-} and $MeBH_3^{1-}$ with few exceptions.[6]

In 2010, a new class of homoleptic *f*-element complexes containing chelating borohydrides known as aminodiboranates were reported.[7-12] Aminodiboranates are anionic ligands composed of two BH_3 groups bridged by an amido linker (Chart 1). *N*,*N*-Dimethylaminodiboranate ($H_3BNMe_2BH_3^{1-}$) in particular shows outstanding versatility as a ligand, forming coordination complexes with a diverse range of metals that include alkaline earth metals,[13] uranium,[7,8] thorium,[9] and lanthanides.[10-12] The larger size and chelating ability of $H_3BNMe_2BH_3^{1-}$ relative to BH_4^{1-} and $MeBH_3^{1-}$ allows it to saturate a larger portion of the metal coordination sphere so that discreet molecular complexes can be isolated with large metal ions in low oxidation states. However, $H_3BNMe_2BH_3^{1-}$ is not large enough to avoid forming coordination polymers with the largest trivalent *f*-metal ions. For example, $U(H_3BNMe_2BH_3)_3$, $Pr(H_3BNMe_2BH_3)_3$, and $Sm(H_3BNMe_2BH_3)_3$ form coordination polymers in the solid-state, whereas complexes with smaller lanthanide ions such as $Dy(H_3BNMe_2BH_3)_3$ and $Er(H_3BNMe_2BH_3)_3$ dimerize to form molecular species.[8,11]

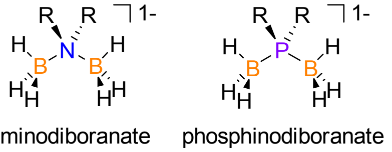

Chart 1. Comparison of aminodiboranate and phosphinodiboranate anions.

This observation raised the following question: can larger chelating borohydrides be prepared to form molecular complexes with the largest trivalent actinides and lanthanide ions? One possibility is to exchange the amido linker in aminodiboranates for a phosphido linker to increase the chelate size (Chart 1). The phosphinodiboranate anion, which was prepared as its parent ammonium salt as early as 1940 by Gamble and Gilmont,[14] has been reported as different alkali metal salts with a wide-variety of phosphorus substituents (R = H,[15] Me,[16] Et,[17] ^{t}Bu,[18] Ph,[19] imidazole-2-thione,[20] and others[21]). However, despite the large number of salts with Group I metals, the coordination chemistry of phosphinodiboranates is unexplored with transition metals and *f*-elements.[22] In this communication, we describe the first homoleptic actinide and lanthanide phosphinodiboranate complexes with the empirical formula $M(H_3BP^tBu_2BH_3)_3$.

We focused our initial efforts on the phosphinodiboranate with bulky *tert*-butyl groups, $H_3BP^tBu_2BH_3^{1-}$ (^{t}Bu-PDB), which can be prepared as the potassium salt from commercially available starting materials using the method described by Dornhaus and Bolte.[18,19] Treating $UI_3(1,4\text{-dioxane})_{1.5}$ with three equivalents of $K(H_3BP^tBu_2BH_3)$ in Et_2O yielded a dark red solution with the expected precipitation of KI (Scheme 1). The reaction was filtered after 12 h and dark red needles were obtained by layering the Et_2O solution with pentane and cooling to -30 °C. IR data collected on the crystals revealed several B-H stretching modes, the most intense being assigned to terminal (2424 cm^{-1}) and metal-bound B-H bonds (2224 cm^{-1}).

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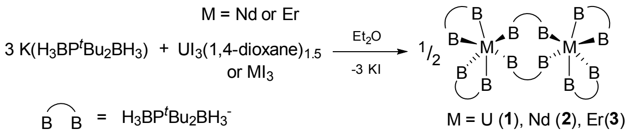


Scheme 1. Synthesis of $U_2(H_3BP^tBu_2BH_3)_6$ (**1**), $Nd_2(H_3BP^tBu_2BH_3)_6$ (**2**), and $Er_2(H_3BP^tBu_2BH_3)_6$ (**3**).

Single crystal X-ray diffraction (XRD) studies revealed the red needles to be the dimeric complex $U_2(H_3BP^tBu_2BH_3)_6$ (**1**; Figure 1). Each uranium ion in **1** is surrounded by two chelating and two bridging phosphinodiboranates that connect the two metal fragments. The coordination geometry around each metal is best described as distorted trigonal prismatic with the three largest B-U-B angles of 148.1(3)°, 150.3(3)°, and 154.7(3)°. The hydride positions were not located in the difference map, but the U-B distances provide an excellent estimate of the coordination number for each BH_3 unit. The U-B bond distances for the chelating ligands range between 2.89(1) and 2.96(1) Å, whereas those for the bridging ligands are ca. 0.2 Å shorter at 2.69(1) Å. The change in U-B distances reflect a change in BH_3 denticity from κ^3-H_3B to κ^2-H_3B, as reported previously for U(III) complexes with BH_4^{1-}, $MeBH_3^{1-}$, and $H_3BNMe_2BH_3^{1-}$ ligands.[7,8,23] Overall, this suggests that the uranium ions in **1** are 14-coordinate with an average U-H distance of 2.6(1) Å.

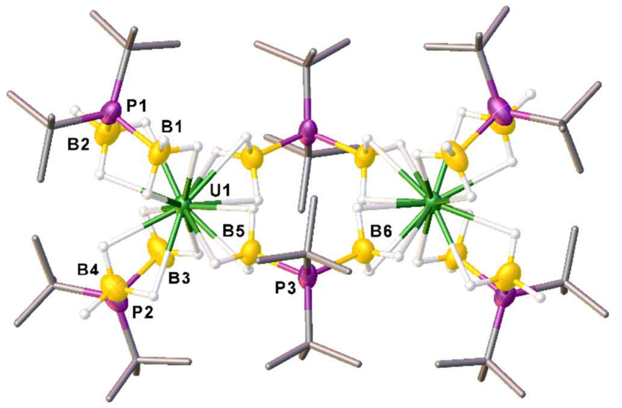


Figure 1. Molecular structure of $U_2(H_3BP^tBu_2BH_3)_6$ (**1**). Ellipsoids were drawn at the 50% probability level. Solvent and hydrogen atoms attached to carbon were omitted from the figure, and carbon atoms were drawn as tubes for easier viewing.

The three intra-ligand B···B distances in **1** range from 3.08(1) – 3.12(1) Å and can be used to quantify the chelate size of $H_3BP^tBu_2BH_3^{1-}$. For comparison, B···B distances previously reported for the aminodiboranate ligands in polymeric $U(H_3BNMe_2BH_3)_3$ were 0.5 Å shorter on average (ca. 2.6 Å) due to the smaller size of the bridging nitrogen in $H_3BNMe_2BH_3^{1-}$ vs. phosphorus in $H_3BP^tBu_2BH_3^{1-}$.[7] The B-P-B angles of 106.3(5)°, 106.9(5)°, and 108.3(4)° in **1** are slightly smaller than those reported for $U(H_3BNMe_2BH_3)_3$ at 108.4(4)°, 109.2(5)°, and 112.7(4)°.[7]

The lanthanide complexes $Nd_2(H_3BP^tBu_2BH_3)_6$ (**2**) and $Er_2(H_3BP^tBu_2BH_3)_6$ (**3**) can be prepared from NdI_3 and ErI_3, respectively, using similar methods used to synthesize **1** (Scheme 1). The IR spectrum of **2** was similar to **1**, revealing two intense absorptions assigned to terminal and bound B-H stretches at 2426 cm^{-1} and 2226 cm^{-1}, respectively. Single-crystal XRD analysis of lavender blocks of **2** obtained from Et_2O confirmed it to be isostructural with **1** despite the slight decrease in metal ionic radius (Nd^{3+} = 0.983 Å and U^{3+} = 1.025; CN = 6).[24] Both **1** and **2** crystallize in the same monoclinic space group $P2_1/n$ and have similar unit cell dimensions (Table S1; ESI), and bond distances and angles (Table 1).

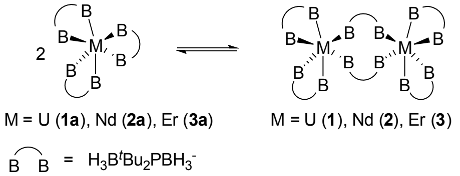
Table 1. Selected distances and angles from single-crystal XRD studies of $U_2(H_3BP^tBu_2BH_3)_6$ (**1**), $Nd_2(H_3BP^tBu_2BH_3)_6$ (**2**), and $Er_2(H_3BP^tBu_2BH_3)_6$ (**3**).

Compound	M-B (Å)	B···B (Å)	B-P-B (°)
$U_2(H_3BP^tBu_2BH_3)_6$ (**1**)	2.89(1)	3.08(1)	106.3(5)
	2.92(1)	3.09(2)	106.9(5)
	2.92(1)	3.12(1)[a]	108.3(4)[a]
	2.96(1)		
	2.69(1)[a]		
	2.69(1)[a]		
$Nd_2(H_3BP^tBu_2BH_3)_6$ (**2**)	2.939(9)	3.10(1)	105.9(4)
	2.848(9)	3.05(1)	104.4(4)
	2.89(1)	3.13(1)[a]	108.4(3)[a]
	2.866(8)		
	2.674(8)[a]		
	2.666(7)[a]		
$Er_2(H_3BP^tBu_2BH_3)_6$ (**3**)	2.74(1)	3.00(2)	100.8(5)
	2.75(1)	3.03(2)	104.7(6)
	2.77(1)	3.17(2)[a]	111.0(5)[a]
	3.19(1)		
	2.58(1)[a]		
	2.58(1)[a]		

[a] Indicates distances and angles associated with bridging ^{t}Bu-PDB ligands.

The IR spectrum of **3** yielded a slightly different profile in the B-H stretching region than **1** and **2** (Figure S17; ESI), which suggested a change in BH_3 coordination at the metal. This was subsequently confirmed by single-crystal XRD studies. The structure of **3** was dimeric like **1** and **2**, but one of the chelating Er-B distances was significantly longer than the others at 3.19(2) Å, which is close to the κ^1-BH_3 distance reported previously in $Tm(BH_3NMe_2BH_3)_3(thf)$ and $Lu(BH_3NMe_2BH_3)_3(thf)$ at 3.136(3) and 3.139(5) Å, respectively.[11] The remaining Er-B distances of 2.74(1) – 2.77(1) Å and 2.58(1) Å are consistent with those previously assigned to κ^2-BH_3 and κ^3-BH_3 groups, respectively. Hence, the coordination number appears to decrease from 14 in **1** and **2** to 13 in **3**. This change is attributed to the ~0.1 Å decrease in ionic radii of Er^{3+} (0.89 Å; CN = 6)[24] compared to U^{3+} and Nd^{3+}. The change in size is also reflected in the phosphinodiboranate ligand structure. The smaller metal radii in **3** results in a small, but significant contraction of the chelating $H_3BP^tBu_2BH_3^{1-}$ B···B distances and B-P-B angles, and a corresponding increase in the symmetric bridging B···B distance and B-P-B angle (Table 1).

^1H and ^{11}B NMR data collected for **1** and **2** revealed that both complexes exist as mixtures of monomer and the parent dimer in solution, whereas **3** with the smaller Er^{3+} exists primarily as monomer (Scheme 2). The ^1H NMR spectrum of **1** in toluene-d_8, for example, revealed two broad BH_3 resonances assigned to the dimer at δ 94.6 (chelating ^{t}Bu-PDB) and δ 72.7 (bridging ^{t}Bu-PDB) in a 2-to-1 ratio. A smaller peak at δ 100.4 was assigned to the monomer **1a** with chemically-equivalent ^{t}Bu-PDB ligands. Likewise, the ^{11}B NMR spectrum revealed two resonances at δ 301.3 and 120.8 in the same 2-to-1 ratio for the dimer **1**, and a third peak at δ 180.5 was assigned to **1a**. ^{1}H NMR resonances corresponding to the *tert*-butyl groups for **1** and **1a** were observed with the expected ratios and integrations. The Nd congener revealed similar sets of ^{1}H and ^{11}B NMR resonances assignable to **2** and **2a**. XRD analysis of **3** still revealed a dimer in the solid state like **1** and **2**, however ^{1}H and ^{11}B NMR data for **3** revealed almost exclusively monomer present in solution at 20 °C. The ^{1}H NMR spectrum showed only one peak for the BH_3 resonance of **3a**, which is shifted to δ –181.1. The ^{11}B data also only shows one resonance at δ -281.1. No resonances were observed in the ^{31}P NMR spectra for **1** – **3**, presumably due to a combination of paramagnetic broadening and ^{31}P coupling to quadrupolar ^{10}B/^{11}B and ^{1}H nuclei in BH_3.



Scheme 2. Monomer/dimer equilibrium observed in solution by NMR spectroscopy.

As observed with ^{t}Bu-PDB in **1** – **3**, borohydride ligands in uranium and lanthanide complexes are known to rearrange in solution. For example, polymeric uranium and lanthanide *N*,*N*-dimethylaminodiboranate complexes break-up into monomers with chemically equivalent ligands when dissolved in non-polar solvents such as benzene.[7,8,10,11] $U(BH_4)_4$ also forms a 14-coordinate solid-state coordination polymer that rearranges to a 12-coordinate monomeric structure upon sublimation with a ΔG = +2.6 kcal/mol.[5] However, the NMR results with **1** and **2** are unusual by way of comparison because the dimeric structure persists in solution on the NMR timescale. This is not observed with uranium and lanthanide *N*,*N*-dimethylaminodiboranates,[8,11] suggesting that more energy is required to rearrange the ^{t}Bu-PDB ligands in **1** and **2**. Indeed, variable-temperature (VT) ^{1}H and ^{11}B NMR studies of **1** and **2** revealed that the dimer/monomer ratio decreases with increasing temperature (Figure 2). The dimer/monomer ratio for **1**/**1a** of 10:1 at 20 °C decreases stepwise to 2:1 at 90 °C (Figures S12-S13; ESI). Likewise, the dimer/monomer ratio for **2**/**2a** of 3:1 at 20 °C decreases further to 0.6:1 at 90 °C so that the monomer is in higher abundance (Figures S14-S16; ESI).

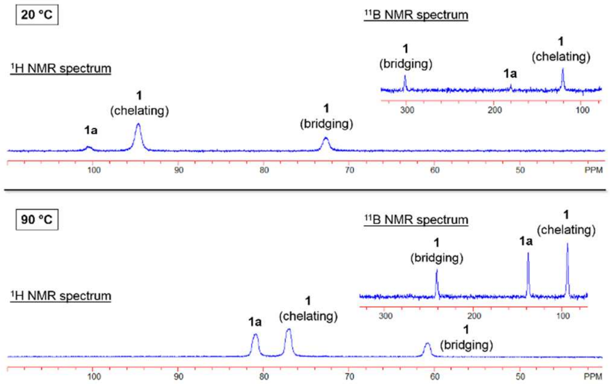


Figure 2. ^{1}H (BH_3 region) and ^{11}B NMR spectra of $U_2(H_3BP^tBu_2BH_3)_6$ (**1**) in toluene-d_8 at 20 °C (*top*) and 90 °C (*bottom*).

Density functional theory (DFT) calculations were performed on **1a** – **3a** and **1** – **3** to quantify the difference in free energy between the monomers and dimers as a function of the metal ion. Gas-phase calculations were performed with the TPSS-D3 functional and the def2-TZVP basis set in the Turbomole software package.[25] The def-TZVP was used for uranium as described previously.[26] The resolution of the identity (RI) approximation was used when computing the integrals.[27]

Calculated structures of **1** – **3** were in excellent agreement with the single-crystal XRD data (Table S2; ESI). Most notably, the calculated structure of **3** reproduced the long Er-B distance observed in the single-crystal XRD data (3.201 vs. 3.19(2) Å). The calculated ΔG values for the dimerization reaction at 298 K (2 monomer → dimer; Scheme 2) were slightly exergonic for U and Nd (-1.5 and -2.0 kcal/mol, respectively) and endergonic for Er (+1.0 kcal/mol). These values are in agreement with our NMR results that show **3** (Er) depolymerizes in solution to form monomeric **3a** whereas **1** (U) and **2** (Nd) maintain the dimeric structure at RT. DFT optimized structures and selected geometric parameters are presented as supporting information.

In conclusion, we have described the first examples of a new class of homoleptic *f*-element complexes with borohydride ligands called phosphinodiboranates. XRD, NMR, and DFT studies on **1** – **3** suggest that subtle differences in solid-state structures and monomer/dimer equilibria in solution depend primarily on the size of the trivalent *f*-metal cation. This observation is reminiscent of cation size-dependent dimerization equilibria with lanthanides and TriNOx ligands reported by Schelter and coworkers, and is notable because they showed it can be used as an effective means to perform lanthanide/lanthanide separations.[28] We are currently investigating if the monomer/dimer equilibria for lanthanide and uranium phosphinodiboranates can be exploited in a similar way. Furthermore, given the large number of phosphinodiboranate anions known with s-block metals, we anticipate that these studies will open the door to a rich area of coordination chemistry with actinides, lanthanides, and transition metals.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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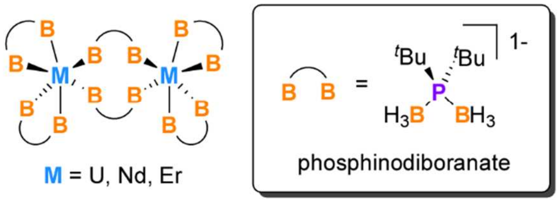
TOC Figure and Text



The synthesis and structures of new class of homoleptic *f*-metal borohydride complexes (phosphinodiboranates) are described with U, Nd, and Er.