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[Ln(BH$_4$)$_2$(THF)$_2$] (Ln = Eu, Yb)—A Highly Luminescent Material. Synthesis, Properties, Reactivity, and NMR Studies

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Supporting Information

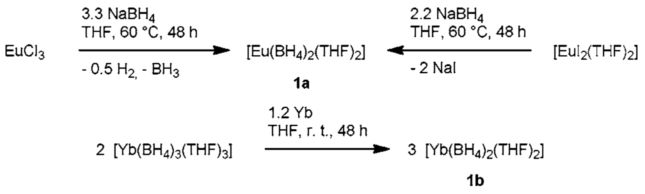
ABSTRACT: The divalent lanthanide borohydrides [Ln(BH$_4$)$_2$(THF)$_2$] (Ln = Eu, Yb) have been prepared in a straightforward approach. The europium compound shows blue luminescence in the solid state, having a quantum yield of 75%. Nonradiative deactivation of C−H and B−H oscillator groups could be excluded in the perdeuterated complex [Eu(BD$_4$)$_2$(d_8-THF)$_2$], which showed a quantum yield of 93%. The monocationic species [Ln(BH$_4$)(THF)$_5$][BPh$_4$] and the bis(phosphinimino)methanides [{(Me$_3$SiNPPh$_2$)$_2$CH}Ln(BH$_4$)(THF)$_2$] have been prepared from [Ln(BH$_4$)$_2$(THF)$_2$]. They show significantly lower or no luminescence. Using the diamagnetic compound [{(Me$_3$SiNPPh$_2$)$_2$CH}Yb(BH$_4$)(THF)$_2$], we performed a 2D ^{31}P/^{171}Yb HMQC experiment.

Lanthanide borohydrides [Ln(BH$_4$)$_3$(THF)$_3$] have attracted increasing research interest over the past two decades. They have been used as starting materials to prepare a large number of lanthanide borohydride coordination compounds and organometallic complexes.[1−4] Borohydride complexes exhibit some hydridic character through single or multiple Ln(μ-H)B bonds.[1−4] The hydridic character makes them useful as initiators for the ring-opening polymerization of cyclic esters and carbonates.[4−12] For the polymerization of nonpolar monomers, an alkylating agent as cocatalyst is required.[4,13,14] The developments of lanthanide borohydrides in synthesis and catalysis have been summarized in some comprehensive reviews.[1−4] The divalent bisborohydrides [Ln(BH$_4$)$_2$(THF)$_2$] (Ln = Sm, Eu, Yb) have been known since 1999.[15] They were originally prepared by thermal reduction of Na[Ln(BH$_4$)$_4$(DME)$_4$] (Ln = Sm, Eu, Yb) at 150−200 °C in a vacuum. Unfortunately, the characterization was poor. Recently, Nief and Visseaux reported a more convenient approach to [Sm(BH$_4$)$_2$(THF)$_2$], which was obtained from [Sm(BH$_4$)$_3$(THF)$_3$] and Sm metal.[16] The divalent thulium compound [Tm(BH$_4$)$_2$(DME)$_2$] was prepared recently by reduction of [Tm(BH$_4$)$_3$(THF)$_3$] with C$_8$K or via salt metathesis from TmI$_2$ and KBH$_4$ in DME.[17]

Herein we report an efficient synthesis of [Ln(BH$_4$)$_2$(THF)$_2$] (Ln = Eu (**1a**), Yb (**1b**)) as well as of the perdeuterated species [Eu(BD$_4$)$_2$(d_8-THF)$_2$] (**1a′**). We studied the luminescence properties of all three compounds. Moreover, some cationic species and some bis(phosphinimino)methanide derivatives were prepared to demonstrate the synthetic potential of **1a,b** and to apply, to the best of our knowledge, for the first time a ^{31}P/^{171}Yb HMQC NMR experiment.

The europium borohydride compound [Eu(BH$_4$)$_2$(THF)$_2$] (**1a**) is easily accessible by two synthetic pathways: either via a reductive pathway from EuCl$_3$ and NaBH$_4$ in high yield or by a salt metathesis from [EuI$_2$(THF)$_2$] and NaBH$_4$ (Scheme 1). In contrast, the corresponding ytterbium compound [Yb(BH$_4$)$_2$(THF)$_2$] (**1b**) was synthesized, analogous to [Sm(BH$_4$)$_2$(THF)$_2$], from [Yb(BH$_4$)$_3$(THF)$_3$] and Yb metal (Scheme 1).[16] **1b** could not be obtained directly from YbCl$_3$ and NaBH$_4$.

Scheme 1. Syntheses of 1a,b



The new complexes were characterized by standard analytical/spectroscopic techniques, and the solid-state structure of **1a** was established by single crystal X-ray diffraction. Although the X-ray data collected from **1a** were poor, the connectivity of **1a** and its composition were deduced. Moreover, the lattice parameters of **1a** show that it is isostructural to [Sm(BH$_4$)$_2$(THF)$_2$][16] and [Sr(BH$_4$)$_2$(THF)$_2$].[18,19] In the solid state, **1a** forms an infinite one-dimensional chain in which each Eu atom is surrounded by four borohydrides and two THF molecules (Figure 1). If the BH$_4^-$

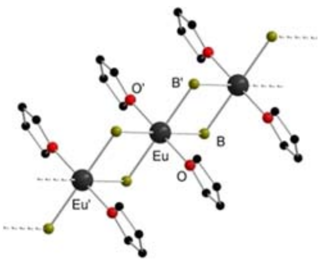


Figure 1. Cutout of the polymeric solid-state structure of **1a**, omitting hydrogen atoms.

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group is considered as one ligand, the Eu atoms are six-fold-coordinated in a distorted octahedral fashion. Although we could not localize the hydrogen atoms in the difference Fourier map, we anticipate that the bridging BH_4^- groups are tridendate, as observed in $[Sm(BH_4)_2(THF)_2]$[16] and $[Sr(BH_4)_2(THF)_2]$.[18,19] The NMR data of the diamagnetic compound **1b** show the expected signals. Thus, in the ^{11}B NMR spectrum we observe one quintet ($^1J_{B-H}$ = 83 Hz) of the BH_4^- groups at δ −34.6 ppm and in the $^{171}Yb\{^1H\}$ spectrum of **1b** a singlet at δ 319.2 ppm. Beside these analyses, we synthesized some derivatives of **1a,b** to prove indirectly their successful synthesis (see below).

The europium compound **1a** shows bright blue luminescence at room temperature (Figure 2). Interestingly, there is, to the best of our knowledge, only one report on the luminescence of Eu(II) hydrides addressing doped alkaline earth hydrides MH_2:Eu (M = Ca, Sr, Ba) with Eu^{2+} doping ranging from 5 to 10%.[20] These metal hydrides show comparably weak emission in the yellow to red spectral range (720−770 nm). The luminescence of complex hydrides such as $[Eu(BH_4)_2(THF)_2]$ is here first observed. Surprisingly, the title compound exhibits a very high quantum yield of about 75% (Table 1). Such a quantum yield is even more remarkable since compounds with >10% Eu^{2+} content typically are accompanied by significant concentration quenching.[21] Separation of the luminescent centers by BH_4^-, however, suppresses energy transfer between the Eu^{2+} sites and thereby allows an excellent quantum yield. Moreover, blue emission of Eu^{2+} is quite uncommon and typically only observed for highly ionic compounds such as $BaMgAl_{10}O_{17}$:Eu or CaF_2:Eu.[21,22] This finding therefore also reflects the predominately ionic binding situation of Eu^{2+} in the borohydride compounds that entails a small Stokes shift and d→f emission in the blue spectral range.

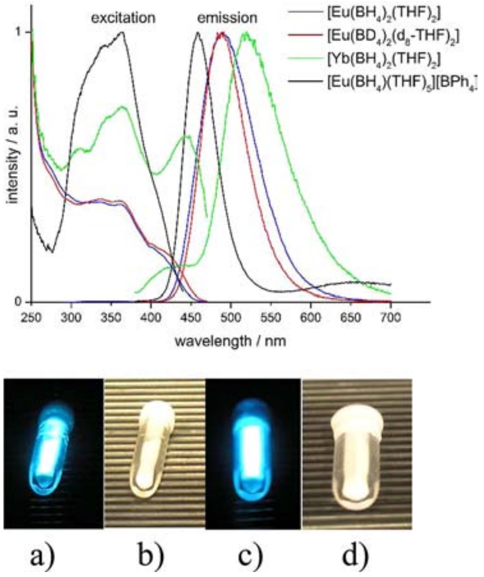


Figure 2. (Top) Excitation/emission spectra of complex hydrides. (Bottom) Photographs of **1a** (a,b) and **1a′** (c,d) under 366 nm excitation (a,c) and daylight (b,d).

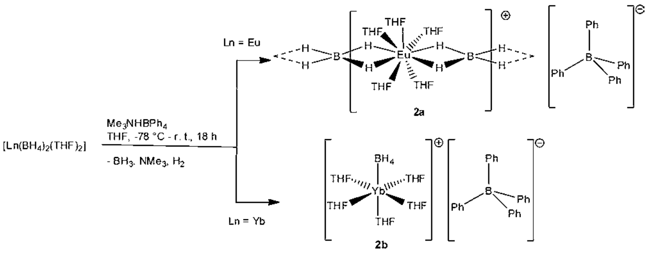
Table 1. Luminescence Properties of Complex Hydrides

compound	maximum of emission/ nm (λ_{exc} = 360 nm)	quantum yield/% (λ_{exc} = 360 nm)	
		absolute	relative
$[Eu(BH_4)_2(THF)_2]$	490	75(1)	79(3)
$[Eu(BD_4)_2(d_8\text{-}THF)_2]$	490	93(1)	88(3)
$[Yb(BH_4)_2(THF)_2]$	519	10(2)	11(3)
$[Eu(BH_4)(THF)_5]$ $[BPh_4]$	458	5(1)	11(2)

Since it is known that high-energy X−H oscillators close to the emissive metal center (X = O, N, C, B) efficiently quench lanthanide excited states,[23] deuteration is an efficient pathway to encourage the luminescence efficiency.[24,25] Whereas acid protons easily can be exchanged in D_2O by deuterium, the elimination of C−H oscillators is more difficult.[26,27] In contrast, a deuterated analogue of **1a**, $[Eu(BD_4)_2(d_8\text{-}THF)_2]$ (**1a′**), could easily be obtained by the reaction of $EuCl_3$ and $NaBD_4$ in d_8-THF. As a consequence of the deuteration, **1a′** with about 90% efficiency shows a significantly increased quantum yield as compared with **1a** (Table 1). Notably, the quantum yield is even higher than for $BaMgAl_{10}O_{17}$:Eu (i.e., 80% quantum yield with 10 mol% Eu^{2+})—a standard industrial blue-emitting phosphor utilized in fluorescent lamps.[21]

We then investigated the reactivity of compounds **1a,b**. Protonation of **1a,b** with 1 equiv of Me_3NHBPh_4 in THF gave the monocationic species $[Ln(BH_4)(THF)_5][BPh_4]$ (Ln = Eu (**2a**), Yb (**2b**)) (Scheme 2).[28]

Scheme 2. Syntheses of 2a,b



Both complexes have been characterized by standard analytical/spectroscopic techniques and their solid-state structures established by single crystal X-ray diffraction (Figure 3). Although both compounds have the same sum formula, their solid-state structures are significantly different. The cationic part of **2a** forms a linear infinite one-dimensional polymer, in which the hydrogen atoms of each BH_4^- group coordinate to two Eu atoms in a μ-(κ^2(H):κ^2(H)) mode. The BPh_4^- counterions are localized in between these chains. The Eu atom is seven-fold-coordinated if the BH_4^- groups are considered as one ligand. Thus, a pentagonal bipyramid is formed in which the five THF molecules are in equatorial

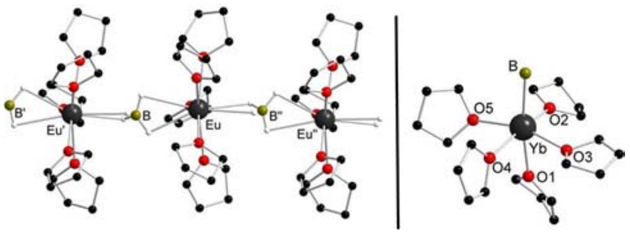


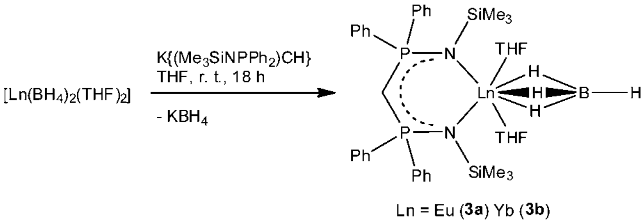
Figure 3. Cutout of the polymeric solid-state structure of $[Eu(\mu\text{-}BH_4)(THF)_5]^+$ (left) and the monomeric cation $[Yb(BH_4)(THF)_5]^+$ (right), omitting some hydrogen atoms.

positions. In contrast, the cation of **2b** is a monomer. As a result of the smaller ionic radius of Yb(II), only the five THF and the BH_4^- group are coordinated around the ytterbium atom, forming a distorted octahedral coordination polyhedron. In the ^{11}B NMR spectrum we see a singlet for the BPh_4^- group (δ 5.1 ppm) and a quintet for the BH_4^- group ($\delta = -32.9$ ppm; $^1J_{B-H} = 83$ Hz). In the $^{171}Yb\{^1H\}$ spectrum, a significant upfield shift (δ 271.7 ppm) is observed in comparison with **1a** (δ 319.2 ppm).

The transformation of **1a**,**b** to **2a**,**b** has a dramatic influence on the luminescence properties. Thus, $[Eu(BH_4)_2(THF)_2]$ shows a quantum yield of 75%, whereas $[Eu(BH_4)(THF)_5][BPh_4]$ exhibits an absolute quantum yield of only 5% (Table 1). This dramatic decrease can be rationalized on the basis of three aspects: (1) The higher number of THF coordination leads to increased vibronic quenching. (2) The higher coordination is accompanied by lengthening of the Eu−H and Eu−O bond distances, which also favors vibronic quenching. (3) The BPh_4^- anion shows a certain absorption at 360 nm as well that does not lead to any emissive energy transfer to Eu^{2+}.

Beside the formation of a cationic species, we were also interested in attaching an organic ligand to study the reactivity of **1a**,**b** and the luminescence properties of the resulting product. As ligand we chose the bis(phosphinimino)methanide, $\{(Me_3SiNPPh_2)_2CH\}^-$, which is well established in lanthanide chemistry.[29,30] The ligand has several NMR-active nuclei, which are useful for studying the behavior of the resulting complexes in solution. Reaction of **1a**,**b** with $K\{(Me_3SiNPPh_2)_2CH\}$[31] resulted in the corresponding heteroleptic monoborohydride derivatives $[\{(Me_3SiNPPh_2)_2CH\}Ln(BH_4)(THF)_2]$ (Ln = Eu (**3a**), Yb (**3b**)) (Scheme 3).

Scheme 3. Synthesis of 3a,b



The BH_4^- group behaves like a pseudo-halide; thus, KBH_4 was formed as byproduct. The solid-state structures of both compounds could be established by single-crystal X-ray diffraction (Figure 4); they are isostructural to each other. The bis(phosphinimino)methanide ligand forms a six-membered metallacycle (N1−P1−C1−P2−N2−Ln) upon chelation of the two trimethylsilylimine groups to the metal atom. The ligand is almost symmetrically coordinated to the metal center. As observed earlier for bis(phosphinimino)methanides of the lanthanides, the metallacycle adopts a twist boat conformation in which both the central carbon and lanthanide atoms are displaced from the N_2P_2 least-squares plane. The interaction between the methine carbon atom (C1) and the lanthanide atom (2.8664(7) Å (**3a**), 2.7403(7) Å (**3b**)), which is longer than common Ln−C distances,[32] is shorter than in the dimeric iodine complex $[\{(Me_3SiNPPh_2)_2CH\}EuI(THF)]_2$ (2.945(2) Å) but longer than in the monomeric compound $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ (2.700(4) Å).[33] The BH_4^- group binds in a terminal κ^3(H)-coordination mode to the metal center.

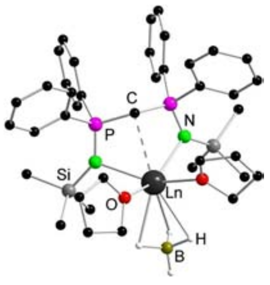


Figure 4. Solid-state structures of **3a**,**b**, omitting some hydrogen atoms.

The diamagnetic compound **3b** was also fully characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{11}B, and $^{171}Yb\{^1H\}$ NMR. In the ^{11}B NMR the expected quintet at δ −32.2 ppm is observed. In the $^{31}P\{^1H\}$ NMR a coupling of the ^{171}Yb nucleus could be seen at δ 14.6 (t, $^2J_{P-Yb} = 58.5$ Hz) ppm (Figure S1). As expected, the $^2J_{P-Yb}$ coupling is significantly smaller than the $^1J_{P-Yb}$ coupling observed in $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2Yb]$ (680 Hz).[34] The ^{171}Yb chemical shift was determined by direct method, $^{171}Yb\{^1H\}$ NMR (Figure S2),[35] and indirect methods, $^1H/^{171}Yb$ gHMQC (Figure S3)[36] and $^{31}P/^{171}Yb$ HMQC (Figure 5). To the best of our knowledge, we have performed the first 2D $^{31}P/^{171}Yb$ HMQC experiment. The resonance of the phosphorus atoms was unambiguously correlated to the ^{171}Yb NMR resonance at δ 744.2 ppm. The ^{171}Yb NMR signal is shifted significantly downfield compared with those of compounds **1b** and **2b**. This method allows the determination of ^{171}Yb NMR data in a short time, together with connectivity between both nuclei. The $^1H/^{171}Yb$ gHMQC 2D map of **3b** shows scalar interactions with the methine group of the bis(phosphinimino)methanide ligand (Figure S3). Unfortunately, no coupling was observed to the BH_4^- hydrogen atoms due to the influence of the quadrupole moment of the boron atom.

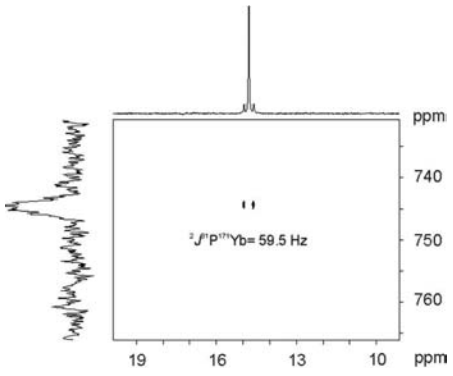


Figure 5. $^{31}P/^{171}Yb$ HMQC spectrum of complex **3b** in d_8-THF at 293 K.

Neither **3a** nor **3b** show any luminescence. Obviously the coordination of the bis(phoshinimino)methanide ligand leads to complete quenching. The strong difference in the luminescence properties of compounds **1a**,**b** and **3a**,**b** inspired us to follow the reaction of **1a** to **3a** by measuring the decay of the luminescence. In a THF solution, **1a** shows a yellow emission at 561 nm upon exitation at 423 nm. To this solution we added a THF solution of K{($Me_3SiNPPh_2$)$_2$CH} to form **3a**. As can be seen from Figure 6, we observed an immediate quenching of the luminescence.

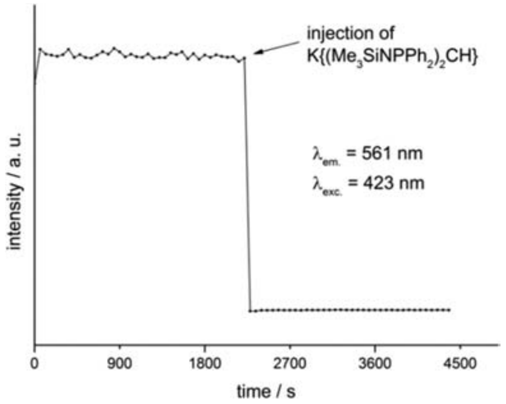


Figure 6. Treatment of **1a** with K{($Me_3SiNPPh_2$)$_2$CH} to form **3a** resulted in an immediate quenching of the luminescence.

In conclusion, we obtained, via a simple synthetic protocol, the divalent lanthanide borohydrides [Ln(BH_4)$_2$(THF)$_2$] (Ln = Eu, Yb) in high yields. The europium compound shows a very bright blue luminescence, which inspired us to prepare the perdeuterated species [Eu(BD_4)$_2$(d_8-THF)$_2$]. This compound gave quantum yields of 93%. To probe the application of [Ln(BH_4)$_2$(THF)$_2$] in synthesis and to study the luminescence properties of monoborohydride derivatives, the ionic compounds [Ln(BH_4)(THF)$_5$][BPh_4] and [{($Me_3SiNPPh_2$)$_2$CH}-Ln(BH_4)(THF)$_2$] were synthesized. For [{($Me_3SiNPPh_2$)$_2$-CH}Yb(BH_4)(THF)$_2$], a 2D ^{31}P/^{171}Yb HMQC experiment was performed, resulting in a scalar ^{31}P/^{171}Yb interaction. The monoborohydride derivatives showed a significantly lower luminescence compared with the bisborohydride.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, NMR spectra, and CIF files for **2a,b** and **3a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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