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Europium(II) and Ytterbium(II) Cyclic Organohydroborates with Agostic Interactions

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The divalent lanthanide bis((cyclooctane-1,5-diyl)dihydroborate) complexes $\{K(THF)_4\}_2\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ (Ln = Eu, **3**; Yb, **4**) were prepared by a metathesis reaction between $(THF)_xLnCl_2$ and $K[H_2BC_8H_{14}]$ in THF in a 1:4 molar ratio. Although the reaction ratios were varied between 1:3 and 1:6, complexes **3** and **4** were the only lanthanide 9-BBN hydroborates produced. Because of disorder of THF in crystals of **3** and **4**, good single-crystal X-ray structural data could not be obtained. However, when the potassium cation was replaced by the tetramethylammonium cation or when MeTHF (2-methyltetrahydrofuran) was employed in place of THF, good quality crystals were obtained. Complexes $[NMe_4]_2[Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (Ln = Eu, **5**; Yb, **6**) were afforded by metathesis reactions of NMe_4Cl with **3** and **4** in situ. On the basis of the single-crystal X-ray diffraction analysis, the four 9-BBN tetrahydroborate ligands are tetrahedrally arranged around the lanthanide cation in **5** and **6**. The two structures differ in that one α-C–H bond from each of the four $\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ units exhibits an agostic interaction with Eu(II) in **5** but, in complex **6**, only two of the α-C–H bonds form agostic interactions with Yb(II). Complexes $\{K(MeTHF)_3\}_2\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ (Ln = Eu, **7**; Yb, **8**) were produced by employing MeTHF in place of THF. The structures of **7** and **8** display connectivity between the anion $\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}^{2-}$ and the cation $\{K(MeTHF)_3\}^+$, in which the potassium not only interacts directly with the hydrogens of the Ln–H–B bridged bonds but is also involved in agostic interactions with α-C–H bonds. By systematically examining the structures of complexes **3**–**8** and taking into account the previously reported complexes $(THF)_4Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ (Ln = Eu, **1**; Yb, **2**), it is concluded that Eu(II) appears to have a better ability to form agostic interactions than Yb(II) because of its larger size, even though Yb(II) has a higher positive charge density.

Introduction

The cyclic organohydroborate anions $[H_2BC_4H_8]^-$, $[H_2BC_5H_{10}]^-$, and $[H_2BC_8H_{14}]^-$ function as chelating ligands to form a variety of covalent complexes with transition-metal metallocenes.[1] Additionally, the actinide organohydroborate $Cp_3U\{(\mu\text{-}H)_2BC_8H_{14}\}$ has also been prepared and characterized.[2] Recently, the lanthanide Eu(II) and Yb(II) 9-BBN hydroborate complexes $(THF)_4Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ (Ln = Eu, **1**; Yb, **2**) have been reported (eq 1).[3] The $[H_2BC_8H_{14}]^-$ ligand offers the opportunity to form agostic interactions between the α-C−H hydrogens as well as the B−H hydrogens and the lanthanide.[3] Previously, we observed that there was a strong agostic interaction, visible in the X-ray structure (Figure 1) and indicated in the IR spectrum, between Eu(II) and the α-C−H bond in complex **1**, (THF)$_4$Eu-

$$(THF)_xLnCl_2 + 2K[H_2BC_8H_{14}] \xrightarrow[-2KCl]{THF} (THF)_4Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_2 \quad (1)$$

1, Ln = Eu
2, Ln = Yb

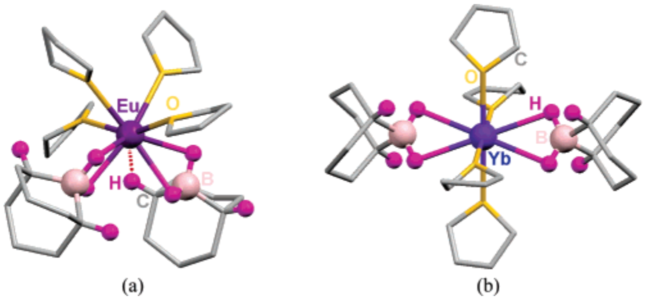

Figure 1. Molecular structures of **1** (a) and **2** (b), reported in ref 3.

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$\{(\mu\text{-H})_2BC_8H_{14}\}_2$, but such an interaction was not observed in its analogue, $(THF)_4Yb\{(\mu\text{-H})_2BC_8H_{14}\}_2$ (**2**).[3]

The study of lanthanide complexes with potential agostic interactions is of interest because of recent observations that suggest that strong α-H and β-H agostic interactions in efficient organolanthanide catalysts play a significant role in the stabilization of the reactive species in olefin polymerization. Thus, for example, a strong Sm···H−Si bis agostic interaction has been proposed as the early step for the oxidative addition of a Si−H bond to a metal center.[4] Identification of such interactions could permit a better understanding of the factors governing the stability and the reactivity of lanthanide complexes.[5] Although agostic interactions involving Ln(III) have been abundantly reported,[6] few reports concern Ln(II),[7] especially Eu(II).[3,8] It was of interest to prepare 9-BBN hydroborate derivatives of Eu(II) and Yb(II) to observe trends in the formation of agostic hydrogen bonds. Therefore, a series of complexes of $[Ln\{(\mu\text{-H})_2BC_8H_{14}\}_4]^{2-}$ (Ln = Eu, Yb) were prepared and their single-crystal X-ray structures were determined for comparison. Reported here is the preparation and the structural and spectroscopic characterization of Eu(II) and Yb(II) 9-BBN hydroborates.

Results and Discussion

A. Preparation and Molecular Structure of $\{K(THF)_4\}_2\{Ln\{(\mu\text{-H})_2BC_8H_{14}\}_4\}$ (Ln = Eu, 3; Yb, 4). The reaction of $(THF)_xLnCl_2$ (Ln = Eu, Yb) with $K[H_2BC_8H_{14}]$ in a 1:4 molar ratio at room temperature in THF produces the complexes $\{K(THF)_4\}_2\{Ln\{(\mu\text{-H})_2BC_8H_{14}\}_4\}$(Ln = Eu, **3**; Yb, **4**) (eq 2). Employing molar ratios of 1:3, 1:5, and 1:6 for the reaction in THF, **3** and **4** are the only organohydroborates produced, as demonstrated by IR spectra, elemental analysis, and single-crystal X-ray diffraction analysis. Complexes **3** and **4** are very soluble in THF and are soluble in toluene. They are stable in THF and toluene solution but are not stable in the solid state because of loss of the THF ligands. Complexes **3** and **4** are regenerated when the decomposition products are placed in THF. The solid-state IR spectra of **3** and **4** are similar with bands at 2162−2080 cm^{-1} for **3** and 2124−2078 cm^{-1} for **4** that are assigned to Ln−H−B stretches. Complex **4** possesses similar proton NMR spectra in d_8-THF and d_8-Tol. Assignments of proton signals are provided in the Experimental Section. Suitable NMR spectra of the Eu(II) complexes could not be obtained because of the paramagnetic property of europium.

$$(THF)_xLnCl_2 + 4K[H_2BC_8H_{14}] \xrightarrow[-2KCl]{THF} \{K(THF)_4\}_2\{Ln\{(\mu\text{-H})_2BC_8H_{14}\}_4\} \quad (2)$$
$$\mathbf{3},\ Ln = Eu$$
$$\mathbf{4},\ Ln = Yb$$

The structures of **3** and **4** are determined by single-crystal X-ray analyses. Because of disorder of the THF molecules, some bond distances appear to be unusually long or short. Nevertheless, the molecular structures clearly show that agostic interactions occur between Ln and α-C−H bonds and K$^+$ and α-C−H bonds. The bridging hydrogen of the Ln−H−B bonds also interacts with K$^+$ as a μ_3-H ligand to give a Ln−(μ_3-H)−K interaction. Details of the structure determination of **3** and **4** are given in the Supporting Information. The structural results from **3** and **4** were verified in good-quality structure determinations from crystals of **7** and **8** (Results and Discussion section C), in which the

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Table 1. Crystallographic Data for **5**−**8**

	5	**6**	**7**	**8**
empirical formula	$C_{48}H_{104}O_2N_2B_4Eu$	$C_{40}H_{88}N_2B_4Yb$	$C_{67}H_{134}O_7B_4EuK_2$	$C_{67}H_{134}O_7B_4YbK_2$
fw	936.53	813.40	1325.14	1346.22
space group	*Fdd*2 (No. 70)	*C*2/*c* (No. 63)	*C*2/*c* (No. 63)	*C*2/*c* (No. 63)
a (Å)	32.3315(3)	10.6239(1)	17.628(1)	17.624(1)
b (Å)	17.2577(2)	20.1448(1)	19.844(1)	19.953(1)
c (Å)	19.4755(2)	20.7248(2)	21.264(1)	21.284(1)
α (deg)	90	90	90	90
β (deg)	90	102.72	95.16(1)	95.56(1)
γ (deg)	90	90	90	90
V (Å^3)	10866.7(2)	4326.50(6)	7408.3(7)	7449.3(7)
Z	8	4	4	4
D_{calcd} (g·cm^{-3})	1.145	1.249	1.188	1.210
T (°C)	−33	−123	−123	−63
μ (mm^{-1})	1.189	2.189	1.005	1.413
R1 [$I > 2\sigma(I)$]^a	0.0225	0.0226	0.0433	0.0305
wR2 (all data)^b	0.0589	0.0809	0.1139	0.0874

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

disorder problem was eliminated by substituting MeTHF (2-methyltetrahydrofuran) for THF. The replacement of the potassium cation by the $[NMe_4]^+$ tetramethylammonium cation simplified the structures.

B. Preparation and Molecular Structure of $[NMe_4]_2$-$[Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (Ln = Eu, 5; Yb, 6). Complexes **5** and **6** are prepared by metathesis reactions of **3** and **4** with tetramethylammonium chloride at room temperature in THF (eq 3). They are yellow solids that are air-sensitive and very

$$\{K(THF)_4\}_2\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\} \xrightarrow[-2KCl]{2NMe_4Cl} [NMe_4]_2[Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4] \quad (3)$$

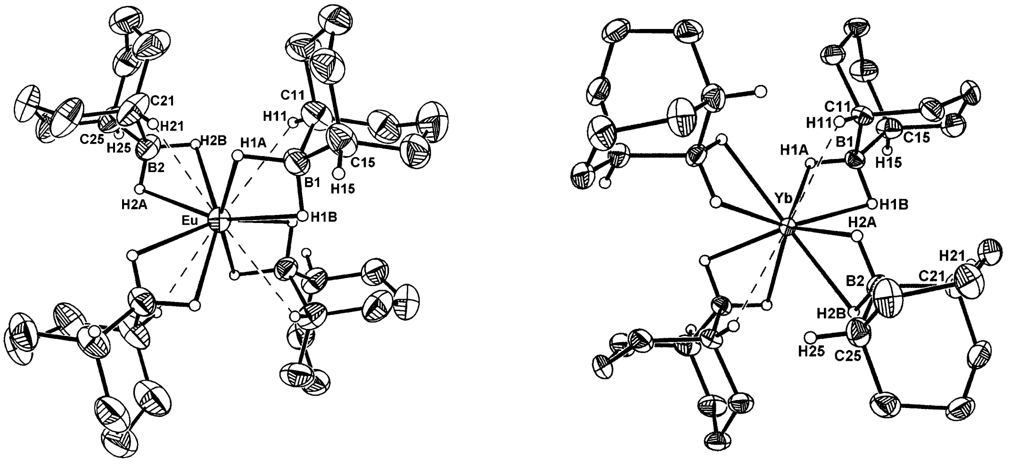
$$\mathbf{5},\ Ln = Eu$$
$$\mathbf{6},\ Ln = Yb$$

soluble in THF, soluble in toluene, and insoluble in hexane. Complexes **5** and **6** produce IR spectra that are similar to those of **3** and **4** with bands at 2078−2021 cm^{-1} for **5** and 2164−2045 cm^{-1} for **6** that are characteristic of Ln−H−B stretches. An absorption band is present at 2763 cm^{-1} in the IR spectrum of **5**, assigned to the α-C−H stretch involved in an agostic interaction with the Eu(II) cation. A similar band is not observed in the IR spectrum of **6**. The NMR spectrum of **6** displays signals assignable to the groups $[NMe_4]^+$ and $[(\mu\text{-}H)_2BC_8H_{14}]^{2-}$.

Table 2. Selected Bond Distances and Angles for $[NMe_4]_2[Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (Ln = Eu, **5**; Yb, **6**)

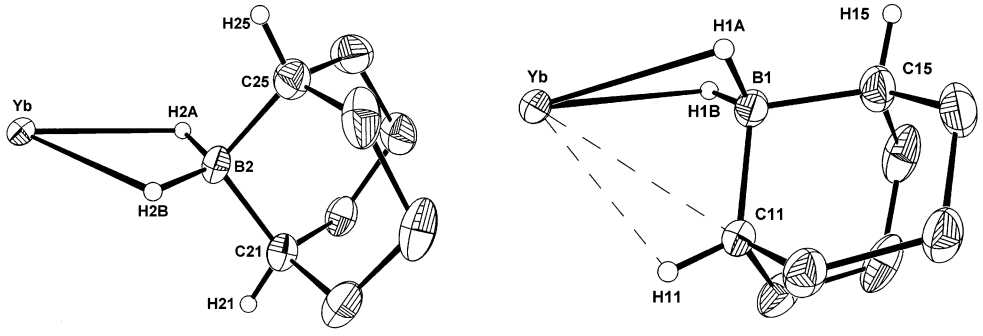
5		**6**	
	Bond Distances (Å)		
Eu···B(1)	2.806(3)	Yb···B(1)	2.630(3)
Eu···B(2)	2.856(4)	Yb···B(2)	2.777(3)
Eu···C(11)	3.242(3)	Yb···C(11)	2.940(3)
Eu···C(21)	3.184(3)	Yb···C(21)	4.049(3)
Eu···C(15)	4.396(3)	Yb···C(15)	4.231(3)
Eu···C(25)	4.446(3)	Yb···C(25)	3.872(3)
Eu−H(1A)	2.46(3)	Yb−H(1A)	2.43(4)
Eu−H(1B)	2.41(4)	Yb−H(1B)	2.42(4)
Eu−H(2B)	2.56(3)	Yb−H(2B)	2.39(4)
Eu−H(2A)	2.53(4)	Yb−H(2A)	2.30(4)
Eu−H(11)	2.76(3)	Yb−H(11)	2.57(4)
Eu−H(21)	2.65(3)	Yb···H(21)	4.08(4)
B(1)−C(11)	1.630(4)	B(1)−C(11)	1.641(4)
B(1)−C(15)	1.626(4)	B(1)−C(15)	1.615(4)
B(2)−C(21)	1.634(5)	B(2)−C(21)	1.619(4)
B(2)−C(25)	1.610(5)	B(2)−C(25)	1.617(4)
C(11)−H(11)	1.09(3)	C(11)−H(11)	0.97(4)
C(15)−H(15)	0.94(5)	C(15)−H(15)	1.02(4)
C(21)−H(21)	0.97(3)	C(21)−H(21)	0.98(4)
C(25)−H(25)	0.91(4)	C(25)−H(25)	0.94(4)
	Angles (deg)		
Eu−B(1)−C(11)	89.89(17)	Yb−B(1)−C(11)	83.59(15)
Eu−B(1)−C(15)	165.00(19)	Yb−B(1)−C(15)	170.8(2)
Eu−B(2)−C(21)	85.78(18)	Yb−B(2)−C(21)	132.35(19)
Eu−B(2)−C(25)	168.7(2)	Yb−B(2)−C(25)	121.35(18)
Eu−C(11)−H(11)	54.5(16)	Yb−C(11)−H(11)	58(2)
Eu−C(21)−H(21)	49.1(19)		

The structures of complexes **5** and **6** are established by single-crystal X-ray diffraction analyses. Crystal data are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Complex **5** is an ionic compound that consists of the cation $[NMe_4]^+$ and the anion $[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}]^{2-}$. The structure of the anion is depicted in Figure 2a. Four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units occupy the four corners of a distorted tetrahedron, and these are bound to Eu(II) through two Eu−H−B three-centered, two-electron bonds and one Eu···α-C−H agostic interaction per 9-BBN hydroborate. The Eu−H distances in the Eu−H−B bridge system are 2.46(3), 2.41(4), 2.56(3), and 2.53(4) Å, respectively, compared with those distances, 2.30(6)−2.57(4) Å, in complex **1**.[3] The distance 2.76(3) Å of Eu−H(11) and 2.65(3) Å of Eu−H(21) in the Eu···α-C−H agostic interactions are, in general, within 3 esd's of the distance of Eu−H in Eu−H−B bridge bonds. In the EuH_2B bridge system of **5**, the dihedral angles between the planes EuH(1A)H(1B) and B(1)H(1A)H(1B) and the planes EuH(2A)H(2B) and B(2)H(2A)H(2B) are 133(2)° and 131(2)°, respectively. Without agostic interactions, the angle would be close to 180° in a MH_2B bridge system. Therefore, in each case, the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit is asymmetrically bound to Eu(II) by bringing one of the two α-C−H hydrogens sufficiently close to Eu(II) for an agostic interaction. The Eu···α-C(11) and Eu···α-C(21) distances, 3.242(3) and 3.184(3) Å, are much shorter than those of Eu···α-C(15) and Eu··α-C(25), 4.396(3) and 4.446(3) Å, for the 9-BBN hydroborate that is not connected to the Eu(II) through an agostic interaction. Consistent with the presence of agostic interactions, the IR spectrum contains a peak at 2763 cm^{-1} assigned to the α-C−H with agostic interactions.



(a) (b)

Figure 2. Molecular structures of the anions of **5** (a) and **6** (b), showing 50% probability thermal ellipsoids. The metal atoms Eu, in **5**, and Yb, in **6**, are situated on a 2-fold symmetric axis. Bridging hydrogens and α-hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms were omitted for clarity.



(a) (b)

Figure 3. Two coordination modes, symmetric mode (a) and asymmetric mode (b), in complex **6**, showing 50% probability thermal ellipsoids. Bridging hydrogens and α-hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms were omitted for clarity.

Complex **6** is also an ionic complex composed of the $[NMe_4]^+$ cation and the $[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]^{2-}$ anion. The structure of the anion of **6** is shown in Figure 2b. The coordination sphere of ytterbium is a distorted tetrahedron with four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units with two different coordination modes to ytterbium; one is symmetrically coordinated to Yb(II) (Figure 3a) and the other is asymmetrically coordinated to Yb(II) (Figure 3b) because of agostic interactions. As seen in Figure 3a, the two bridging hydrogens, H(2A) and H(2B), are located symmetrically on each side of the Yb···B vector and two bridging hydrogens and atoms Yb and B(2) lie in a plane (the sum of the internal angles in the four-membered ring defined by the atoms Yb, B(2), H(2A), and H(2B) is 50(2)° + 113(4)° + 93(4)° + 101(4)° = 357°, indicating a virtually planar arrangement, and the dihedral angle of the plane YbH(2A)H(2B) with the plane B(2)H(2A)H(2B) is 178(5)°, indicating the absence of an agostic interaction) close to 180°. The distances of Yb···α-C(21) (4.049(3) Å) and Yb···α-C(25) (3.872(3) Å) are too long to be considered as related to agostic interactions. But, the other $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units are asymmetrically coordinated (Figure 2b) because of agostic interactions between Yb and one of the α-C−H bonds from each 9-BBN hydroborate. The Yb···α-C(11) distance, 2.940(3) Å, is shorter by 1.3 Å than the Yb···α-C(15) distance (4.231(3) Å), and the Yb−H(11) distance, 2.57(4) Å, is shorter by 2.1 Å than the Yb···H(15) distance (4.64(4) Å). Also, the Yb−B(1)−C(11) angle of 83.6(2)° is much smaller than the related angle Yb−B(1)−C(15) of 170.8(2)°. Furthermore, the dihedral angle of the plane YbH(1A)H(1B) and the plane B(1)H(1A)H(1B), 119(2)°, is much smaller than the 178(5)° dihedral angle in the symmetrical system.

The Yb···B(1) distance of 2.630(3) Å for the asymmetrical coordination mode is noticeably shorter than the Yb···B(2) distance of 2.777(3) Å for the symmetrical coordination mode. The distance of Yb···B is 2.876(7) Å in the complex $(THF)_4Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, **2**, in which there is no agostic interaction.[3] It has been observed and discussed that the distance of M···B is dependent on the two distinct coordination modes of ligands for tetrahydroborates.[9] The M···B distance with a μ_2-BH_4 coordination mode is significantly shorter, 0.16−0.34 Å, than that with a μ_3-BH_4 coordination mode.[3,10] The Yb···B distance of 2.630(3) Å is consistent

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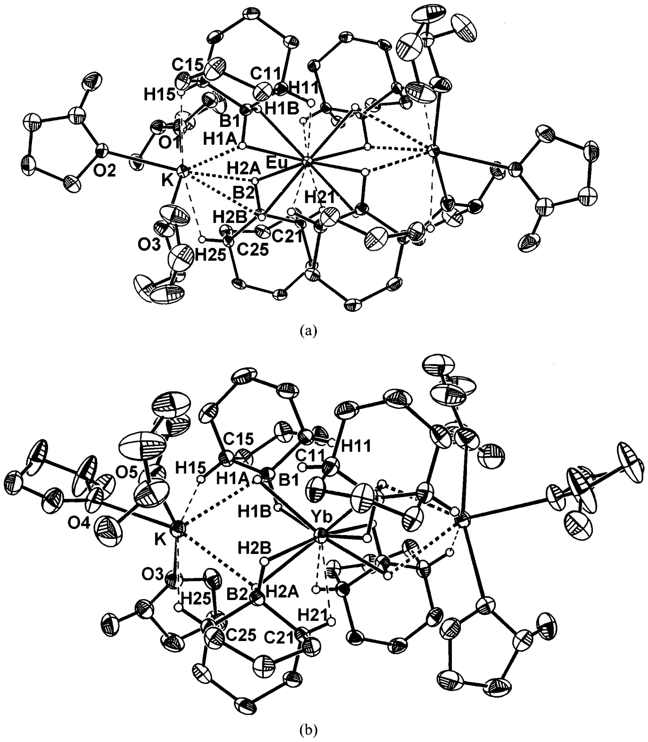

(a)

(b)

Figure 4. Molecular structures of **7** (a) and **8** (b), showing 25% probability thermal ellipsoids. The metal atoms Eu, in **7**, and Yb, in **8**, are situated on a 2-fold symmetric axis. Bridging hydrogens and α-hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms were omitted for clarity.

with the 2.666(6) and 2.692(5) Å lengths in $(CH_3CN)_4Yb\{(\mu\text{-}H)_3BH\}_2$ and $(C_5H_5N)_4Yb\{(\mu\text{-}H)_3BH\}_2$ in which the BH_4 is employed as a tridentate ligand.[11] Thus, the 9-BBN hydroborate can be considered to function as a psuedotridentate ligand because of the agostic interaction of an α-CH hydrogen.

C. Preparation and Molecular Structure of $\{K(MeTHF)_3\}_2\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ (Ln = Eu, 7; Yb, 8). The arrangement of the ligands and associated agostic interactions in the 1:4 complexes is clear on the basis of the structures of **5** and **6**. But, a question remains concerning the interaction of the potassium cation with the $[(\mu\text{-}H)_2BC_8H_{14}]^{2-}$ anion in **3** and **4**. To resolve this question, 2-methyltetrahydrofuran (MeTHF) was chosen to replace THF to eliminate disorder of the ethers coordinated to potassium. The compounds **7** and **8** were prepared, and good quality crystals were obtained.

The structures and the molecular connectivities of **7** and **8** were elucidated by single-crystal X-ray analyses (Figure 4a and b). Complexes **7** and **8** are composed of two identical $\{K(MeTHF)_3\}$ units connected to the central anion $\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}^{2-}$ (Ln = Eu, Yb) (Figures 3 and 4). The central portion of the anion in **7** is similar to that of complex **5**. The europium is coordinated to four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units occupying the corners of a tetrahedron. The Eu−H distances in the Eu−H−B bridged bonds (2.46(4), 2.48(4), 2.43(4), and 2.38(4) Å) are consistent with those in **5**. One of the α-C−H bonds of each $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit is drawn close to Eu by an agostic interaction so that the Eu···α-C(11) distance of 3.248(4) Å and the Eu···α-C(21) distance of 3.154(4) Å are much shorter than those of Eu···α-C(15) (4.384(4) Å) and Eu···α-C(25) (4.418(4) Å) on the other side of the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit. Also, the Eu−H(11) distance of 2.86(4) Å and the Eu−H(21) distance of 2.70(4) Å are much shorter than those of Eu···H(15) (4.73(4) Å) and Eu···H(25) (4.78(4) Å).

The most striking feature of the molecular structure of **7** is the connectivity of potassium with the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit. Each potassium is bound to the anion by interacting with the bridge hydrogens of the Eu−H−B bond and by an agostic interaction with the α-C−H of the 9-BBN hydroborate. The bridged hydrogens in Eu−H−B are μ_3-H due to an interaction with potassium, and one of the α-hydrogens in the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit is bound to potassium by an agostic interaction. The distances of K−H(15) and K−H(25), with hydrogens coming from α-C−H bonds, are 2.74(4) and 2.85(4) Å. They are within the range of distances in which potassium interacts with hydrogen and come from the Eu−H−B bridge bond. The distances K−H(1A), K−H(2A), K···H(1B), and K−H(2B) are 2.63(4), 2.72(4), 3.23(4), and 3.02(4) Å, respectively. With the exception of the K···H(1B) distance, the K−H distances are comparable to those in complexes $K[\textit{fac}\text{-}RuH_3(dcypb)(CO)]KBH^{s}Bu_3 \cdot 0.5(toluene)$,[12a] $\{[(Me_3Si)_2N]_2V[N(SiMe_3)SiMe_2CH_2]\}\{K(THF)_2\}_2$,[12b] $[Et_8(C_4H_2NH)_3(3\text{-}EtC_5H_2N)]$,[12c] $[\{(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1\text{-}Et_8N_4)Zr\}_4\text{-}\{KH\}_8 \cdot (THF)_{10}]$,[12d] $K\{Al[CH_2CH(CH_3)_2]_4\}$,[12e] $[K(18\text{-}crown\text{-}6)][W(PMe_3)_3H_5]$,[12f,h] and $\{[(Ph_3P)_2ReH_3](\mu\text{-}H)[K(THF)_2]\}_2\text{-}(\mu_3\text{-}H)_4$[12g] in previous reports, and especially, the 2.714(6) Å average value of the K−H distance in complex $[K(18\text{-}crown\text{-}6)][W(PMe_3)_3H_5]$ is based on the neutron diffraction.[12f] Such short contacts between potassium and α-hydrogens and bridge hydrogens appear to be the only interatomic contacts present in the bonding range that keep potassium adhered to the anion to form a K···Eu···K backbone. The K···Eu···K arrangement is almost linear with an angle of 174.28(3)°. The metals are bridged by hydrogen that also bridges boron atoms. Thus, these hydrogens are three-coordinate (μ_3). Each potassium is involved in agostic interactions with two α-C−H hydrogens. Three 2-methyltetrahydrofurans complete the coordination sphere of each potassium atom with normal K−O distances (K−O1, 2.688(3) Å; K−O2, 2.696(3) Å; and K−O3, 2.738(4) Å).

The ytterbium analogue $\{K(MeTHF)_3\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **8**, forms crystals that are isomorphous with those of **7**. However, some structural differences still exist between **7** and **8**. Although each of the four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units possesses one α-C−H bond that strongly interacts with

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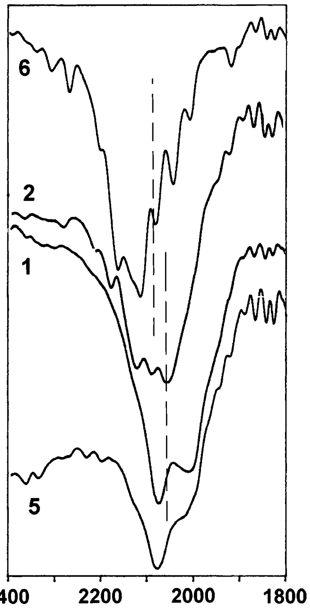

Figure 5. The comparison of the solid-state (KBr) IR spectra of the complexes $(THF)_4Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ (**1**), $(THF)_4Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ (**2**), $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**5**), and $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**6**) in the Ln−H−B stretching region.

europium in **7**, only two of the four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units show similar strong interactions in **8** and the other two seem to be involved in weaker agostic interactions. The Yb···α-C(21) distance of 3.079(4) Å and the Yb−H(21) distance of 2.59(3) Å in **8** reflect an agostic interaction. The Yb···α-C(11) distance of 3.294(4) Å and the Yb−H(11) distance of 2.92(3) Å are significantly long and are considered to be weak agostic interactions in this case.[13] The connectivity of potassium to the anion section in **8** is similar to, but not exactly the same as, that of **7**. For complex **8**, potassium is bound to bridging hydrogens H(1A) and H(2A) within distances of 2.68(3) and 2.79(3) Å. On the other hand, the K−H(1B) and K−H(2B) distances, 3.37(3) and 3.14(3) Å, are considered to be beyond the bonding range. However, in the case of **7**, there are three interactions between potassium and the bridging hydrogens K−H(1A), K−H(2A), and K−H(2B) that are considered to be within the bonding range.

Summary

A. IR Spectra. The complexes **1**−**8** produce infrared bands between 2300 and 1900 cm^{-1} that are assigned to Ln−H−B stretches. The IR bands in this region reveal that Eu−H−B stretches in complexes **1** and **5** exhibit IR bands that are ca. 20 cm^{-1} lower than those in the corresponding complexes **2** and **6** that contain Yb−H−B bonds (Figure 5). This is not unexpected because of the dissimilarity in the radii of Eu(II) and Yb(II). Similar observations of IR spectra based on the metal radii have been previously reported for Sm(II), Eu(II), and Yb(II)[14] and also for alkaline earth metals.[15] The relatively larger ionic radii of Eu(II) compared to that of Yb(II) results in the weaker interaction in the Eu−H−B stretches as compared to the Yb−H−B stretches. However, this trend is not observed in complexes **3** and **4** and **7** and **8** in which some of the bridging hydrogens are μ_3, interacting with Ln, B, and K.

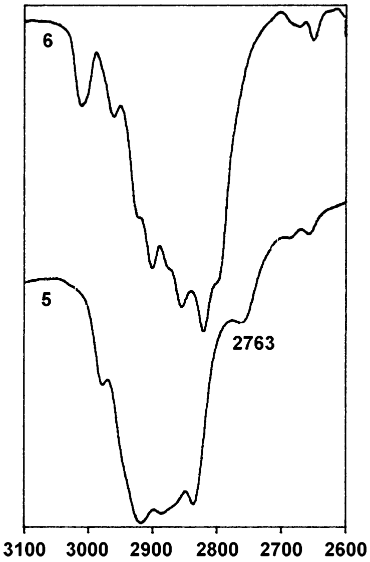

Figure 6. Solid-state (KBr) IR spectra of the complexes $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**5**) and $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (**6**) in the C−H stretching region.

In view of their molecular structures, an expected feature in the IR spectra of complexes **1**−**8** is that an additional C−H absorption band will appear because of the agostic interaction between Ln(II) and the α-C−H bond. Indeed, in all of the complexes containing europium, **1**, **3**, **5**, and **7**, such a C−H absorption occurs at ca. 2760 cm^{-1}, which is a shoulder peak in complexes **3** and **7** but is an isolated band in complexes **1**[3] and **5** (Figure 6). On the other hand, complexes **2**, **4**, **6**, and **8** containing ytterbium do not show this characteristic absorption band even though, on the basis of their molecular structures, there are agostic interactions in **6** and **8**.

B. Coordination Geometry of Ln(II). In complexes **5**−**8**, the Ln(II) is coordinated to eight bridge hydrogen atoms of the four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units.[16] Usually, lanthanide(II) bonding with hydride ligands is stabilized by binding to a bulky ligand[17] or donor solvent molecules, as in complexes **1** and **2**.[3,11] The presence of several agostic interactions between the Ln(II) and α-C−H bond is an additional stabilizing factor for complexes **3**−**8**.

Each metal center in complexes **5**−**8** is bound to the four $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units, and the coordination geometry, based on the peripheral boron atoms, can be described as a distorted

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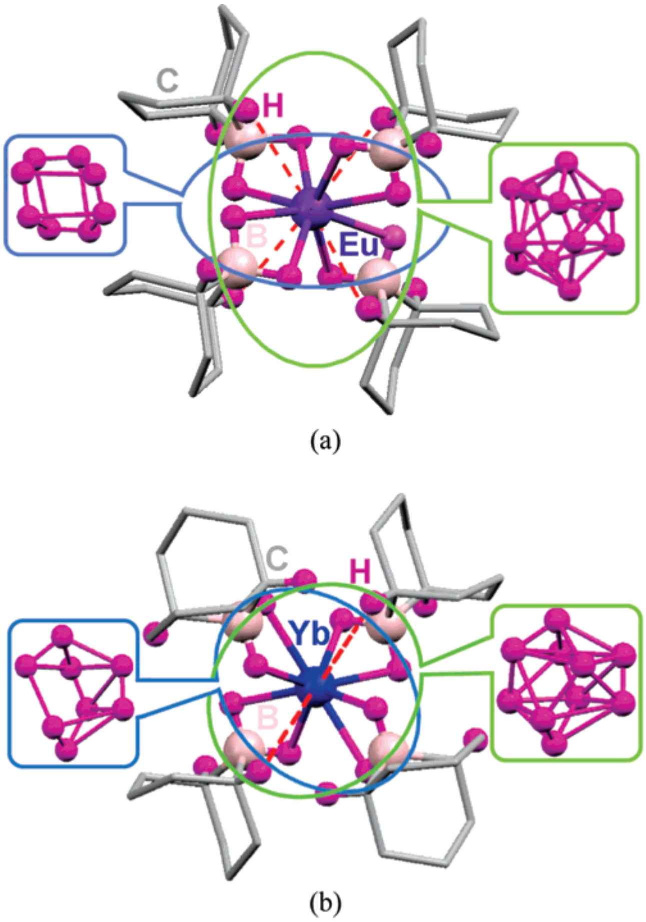

Figure 7. The bridge hydrogen arrangement (left) and the bridge and α-C−H hydrogen arrangement (right) around europium in complex **5** (a) and ytterbium in complex **6** (b).

tetrahedron. In complex **5**, the eight bridge hydrogens are arranged at the corners of a distorted cube (Figure 7a). Including the four α-C−H agostic interactions, Eu(II) in complex **5** is coordinated to 12 hydrogens that form a distorted icosahedron with the longest Eu−H distance being 2.76(3) Å and the shortest one being 2.41(3) Å (Figure 7a).

In complex **6**, the eight bridge hydrogens are arranged at the corners of a polyhedron, which is related to a distorted bicapped square antiprism with two corners, 2 and 7, that are unoccupied by B−H−Yb bridge hydrogens but are occupied by the two C−H agostic hydrogens, with the longest Yb−H bond distance being 2.57 Å and the shortest one being 2.30 Å. Thus, the Yb(II) in complex **6** is coordinated to ten hydrogens, and its coordination geometry is a distorted bicapped square antiprism (Figure 7b).

The bridge hydrogen arrangements in complexes **7** and **8** are similar to those in complex **5**. The coordination geometry of Ln(II) is a very distorted cube. By taking into account the agostic hydrogens in **7**, the total hydrogen arrangement is a distorted icosahedron. This is also the same situation in **8** if the α-C(11)−H(11) hydrogen, which is slightly out of the agostic interaction range, is considered. These hydrogen polyhedrons are more distorted than those in complex **5**. To our knowledge, this is the first example of Ln(II) surrounded by twelve hydrogens to produce, in a sense, a “hydrogen sphere”.

Table 3. Selected Bond Distances and Angles for $\{K(MeTHF)_3\}_2\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$ (Ln = Eu, **7**; Yb, **8**)

7		8	
Bond Distances (Å)			
Eu···B(1)	2.810(5)	Yb···B(1)	2.732(3)
Eu···B(2)	2.826(4)	Yb···B(2)	2.705(3)
Eu···C(11)	3.248(4)	Yb···C(11)	3.294(3)
Eu···C(21)	3.154(4)	Yb···C(21)	3.079(3)
Eu···C(15)	4.384(4)	Yb···C(15)	4.273(3)
Eu···C(25)	4.418(4)	Yb···C(25)	4.313(3)
Eu−H(1A)	2.48(4)	Yb−H(1A)	2.44(3)
Eu−H(1B)	2.38(4)	Yb−H(1B)	2.32(3)
Eu−H(2A)	2.46(4)	Yb−H(2A)	2.39(3)
Eu−H(2B)	2.43(4)	Yb−H(2B)	2.37(4)
Eu−H(11)	2.86(4)	Yb−H(11)	2.92(3)
Eu−H(21)	2.70(4)	Yb−H(21)	2.59(3)
B(1)−C(11)	1.628(6)	B(1)−C(11)	1.613(4)
B(1)−C(15)	1.623(6)	B(1)−C(15)	1.619(4)
B(2)−C(21)	1.631(6)	B(2)−C(21)	1.620(4)
B(2)−C(25)	1.614(6)	B(2)−C(25)	1.632(4)
C(11)−H(11)	1.01(5)	C(11)−H(11)	0.92(3)
C(15)−H(15)	1.03(5)	C(15)−H(15)	1.01(3)
C(21)−H(21)	0.94(4)	C(21)−H(21)	0.95(3)
C(25)−H(25)	0.97(4)	C(25)−H(25)	0.99(3)
K−O(1)	2.688(3)	K−O(3)	2.700(2)
K−O(2)	2.696(3)	K−O(4)	2.723(2)
K−O(3)	2.738(4)	K−O(5)	2.742(3)
K−H(1A)	2.63(4)	K−H(1A)	2.68(3)
K−H(1B)	3.23(4)	K−H(1B)	3.37(3)
K−H(2A)	2.72(4)	K−H(2A)	2.79(3)
K−H(2B)	3.02(4)	K−H(2B)	3.14(3)
K−H(15)	2.74(4)	K−H(15)	2.69(3)
K−H(25)	2.85(4)	K−H(25)	2.74(3)
Angles (deg)			
Eu−B(1)−C(11)	90.0(2)	Yb−B(1)−C(11)	95.08(16)
Eu−B(1)−C(15)	162.3(3)	Yb−B(1)−C(15)	157.4(2)
Eu−B(2)−C(21)	85.7(2)	Yb−B(2)−C(21)	86.97(14)
Eu−B(2)−C(25)	168.3(3)	Yb−B(2)−C(25)	167.44(19)
Eu−C(11)−H(11)	59(3)	Yb−C(21)−H(21)	51.3(17)
Eu−C(21)−H(21)	53(2)		

C. Criteria for Existence and Strengths of Agostic Interactions. From a practical point of view, when can the approach of a C−H hydrogen to a transition metal be considered to be an agostic interaction on the basis of structural evidence? Criteria for the existence of an agostic interaction are a short metal−hydrogen distance, a reduced bond angle for $MC_{\alpha}C_{\beta}$ (MBC_{α} for complexes **5**−**8**), and a reduced dihedral angle between the LnH_2 and H_2B planes that arise from the interaction of the C−H hydrogen with the unsaturated metal. From analyses of structural reports, Green and Brookhart[13a,c] suggested that a metal−hydrogen distance no larger than 1.2 times the distance of a normal M−H distance would be consistent with an agostic interaction. We suggested that a distance less than the sum of the metal covalent radius and the hydrogen van der Waals radius implys an agostic interaction.[1d] The Green−Brookhart approximation is difficult to apply because M−H bond distances are dependent upon their environment. However, in either approach, there is sufficient uncertainty in the distance criteria (uncertainty in the metal−hydrogen distance) that angular criteria, cited above, must also be taken into consideration to assess the existence of an agostic C−H···M interaction. Figure 3 illustrates the effect of nonagostic and agostic interactions on the dihedral angles in complex **6**. When no agostic interaction occurs, the dihedral angle between the YbH_2 and H_2B planes is

Table 4. Comparison of the Strengths of the Agostic Interactions by Distances of M−H, Angles of M···B−C, and Dihedral Angles of Plane LnH(A)H(B) and Plane BH(A)H(B) in Complexes **5**−**8**

	BBN unit involving B1			BBN unit involving B2		
	distances of M−H (Å)[a]	dihedral angles (deg)[b]	angles of M···B−C (deg)[c]	distances of M−H (Å)[a]	dihedral angles (deg)[b]	angles of M···B−C (deg)[c]
$[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]^{2-}$, **5**	2.76(3)	133(2)	89.9(2)	2.65(3)	131(1)	85.8(2)
$[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]^{2-}$, **6**	2.57(4)	119(2)	83.6(2)	3.80(4)	178(5)	121.4(2)
$\{K(MeTHF)_3\}\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **7**	2.86(4)	133(2)	90.0(2)	2.70(4)	131(2)	85.6(2)
$\{K(MeTHF)_3\}\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, **8**	2.92(3)	138(2)	95.0(2)	2.59(3)	133(2)	86.9(2)

[a] The closer distance of α-C−H and M in two sets of BBN units involving a B1 or B2 atom, respectively. [b] Dihedral angles of plane LnH(A)H(B) and BH(A)H(B) in two sets of BBN units involving a B1 or B2 atom in corresponding complexes, respectively. [c] The smaller angle of M···B−C in two sets of BBN units involving a B1 or B2 atom, respectively.

178(5)°, close to 180° (Figure 3a), but when an agostic interaction is present, the dihedral angle is markedly smaller, 119(2)° (Figure 3b). Table 4 summarizes the results for complexes **5**−**8**. Note that only half of the observed interactions are represented in the table; the other half are generated through a 2-fold operation. Employing the covalent radii Yb = 1.94 Å and Eu = 2.00 Å and the van der Waals radius H = 1.2 Å, our criteria for limiting agostic interactions are Yb···H = 3.1 Å and Eu···H = 3.2 Å. Note that in Table 4 there is only one M−H distance (complex **6**) that exceeds our criteria for an agostic interaction. This is also reflected in the angles that are significantly larger than those for situations in which the agostic interaction is present.

D. Ability to Form Agostic Interactions. In the compounds we are studying, europium complexes always contain more agostic interactions than ytterbium complexes. In the 1:2 ratio complexes **1** and **2**, an agostic interaction is present in **1** but is absent in **2**. Four agostic interactions are present in the europium complex **5**, and only two such interactions occur in the ytterbium complex **6**. For **7**, four agostic interactions are present, and only two agostic interactions are clearly involved in **8.** Two other Yb···C and Yb···H distances are considered to be weak agostic interactions. As discussed previously, ytterbium, with a smaller radius and higher positive charge density, would be expected to be more likely to interact with the α-C−H hydrogen. On the other hand, europium, with its larger size, can have a larger coordination number and this will also favor more agostic bonds.[3] Apparently, the larger size rather than the higher positive charge density appears to play a dominant role in the formation of agostic interactions of europium and ytterbium with the α-C−H hydrogen. Similar observations occur in the tetrahydroborate complexes of $U(BH_4)_4$, $Zr(BH_4)_4$, and $Hf(BH_4)_4$. Uranium, with a larger radius, is surrounded by 14 hydrogens,[18] but zirconium and hafnium only have coordination numbers of 12.[19,20]

Conclusions

The hydroborate complexes $\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}^{2-}$ (Ln = Eu, Yb), **3**−**8**, were prepared, and their structures were characterized by single-crystal X-ray analyses and IR spectroscopy. The structural results show that an agostic interaction exists between Ln(II) and an α-C−H bond of a 9-BBN hydroborate anion in europium and ytterbium complexes. The coordination environment of Ln(II) consists of eight bridging hydrogens and several α-C−H hydrogens through agostic interactions. Europium appears to have a greater ability to form agostic interactions; europium always forms more agostic interactions than ytterbium. Connectivity apparently occurs between the potassium cation and the $\{Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}^{2-}$ anion through interaction of potassium with bridge hydrogens and α-C−H hydrogens in complexes **7** and **8**.

Experimental Section

General Comments. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen or argon. Tetrahydrofuran and 2-methyltetrahydrofuran were dried over sodium/benzophenone and freshly distilled prior to use. Hexane was stirred over concentrated sulfuric acid for 2 days and then decanted and washed with water. Next, the hexane was stirred over sodium/benzophenone for 1 week, followed by distillation into a storage bulb containing sodium/benzophenone. Celite was dried by heating at 150 °C under dynamic vacuum for 5 h. Ammonia (Matheson) was distilled from sodium immediately prior to use. Ammonium chloride (Fisher) was recrystallized from anhydrous methanol and vacuum-dried at 120 °C prior to use. Europium (ingot, Strem) was packaged under mineral oil, washed with hexane, and vacuum-dried. The metal was cut into small pieces before use. Ytterbium metal (40 mesh, Strem) was used as received. Tetrahydrofuran-free $K[H_2BC_8H_{14}]$ was prepared according to the literature procedure.[21] Potassium hydride (Aldrich) was received as an oil slurry, washed with hexane, vacuum-dried, and stored in the drybox. 9-Borabicyclo[3.3.1]nonane dimer (Aldrich) was used as received. Solvated lanthanide dichlorides were synthesized according to the published method[22] with the modifications listed below. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN. NMR spectra were recorded on a Bruker AM-250 spectrometer. ^1H NMR spectra were obtained at 250.1 MHz and referenced to residual solvent protons. ^{11}B NMR spectra were obtained at 80.3 MHz and externally referenced to

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BF_3·OEt_2 in C_6D_6 ($\delta = 0.00$ ppm). Infrared spectra were recorded on a Mattson-Polaris FT-IR spectrometer with 2 cm^{-1} resolution.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffraction system, which employs graphite-monochromated Mo Kα radiation ($\mu = 0.710\,73$). A single crystal of **3**−**8** was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package (Nonius BV, 1999).[23] The empirical absorption correction was applied with the SORTAV program[24] provided by MaXus software.[25] The structures were refined using the SHELXTL-97 (difference electron density calculations and full-matrix least-squares refinements) structure solution package.[26] Data merging was perfomed using the data preparation program supplied by SHELXTL-97. After all non-hydrogen atoms were located and refined anisotropically, hydrogen atom positions were calculated assuming standard geometries. Bridge hydrogens and the α-hydrogens of the organohydroborate ring in all complexes of **3**−**8** were located and refined isotropically.

Preparation of $\{K(THF)_4\}_2\{Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, 3. In a drybox, a 50-mL flask containing a Teflon-coated magnetic stir bar was charged with 76 mg (0.50 mmol) of Eu metal and 54 mg (1.00 mmol) of NH_4Cl. The flask was connected to a vacuum line and evacuated. Ammonia (25 mL, liquid) was condensed into the flask at −78 °C and stirred at that temperature. A reaction occurred immediately with evolution of H_2 and formation of a golden-yellow suspension. After 40 min of stirring, the NH_3 was removed in vacuo and a light gray-colored solid, $(NH_3)_xEuCl_2$, remained. $(THF)_xEuCl_2$ was prepared by stirring the NH_3-solvated complex in THF, pumping off the solvent, and repeating this procedure two more times to ensure that all of the ammonia was replaced. The flask was then charged with 324 mg (2.00 mmol) of $K[H_2BC_8H_{14}]$ in the drybox and evacuated. Next, 25 mL of THF was condensed into the flask at −78 °C, and the mixture was warmed to room temperature and stirred overnight. During this time, the color of the solution changed to an orange-brown with the formation of a precipitate. Filtration of the reaction mixture yielded a yellow-brown colored filtrate. The filtrate was cooled to 0 °C, and slow removal of the THF solvent under vacuum provided yellow X-ray quality crystals of **3**. Complete removal of the solvent at room temperature gave a yellow solid, which became faint yellow after washing with hexane and vacuum-drying. As determined by elemental analysis, this procedure promoted the loss of a total of eight THF ligands to form $K_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$. Anal. Calcd for $C_{32}H_{64}EuB_4K_2$ (loss of 8 THF solvent ligands): C, 53.48; H, 8.77. Found: C, 53.21; H, 8.93. A yield of 288 mg of $K_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (79.8% based on Eu) was obtained. IR (KBr): 3016(w), 2970(sh), 2908(vs), 2857(vs), 2822(vs), 2682(w), 2652(w), 2162(sh), 2110(s), 2080(sh), 2016(sh), 1939(w), 1922(w), 1481(vs), 1452(w), 1415(w), 1338(m), 1238(s), 1200(m), 1147(m), 1104(w), 1076(m), 1040(m), 945(s), 897(w), 823(w), 802(w), 743(w), 687(w) cm^{-1}.

Preparation of $\{(THF)_4K\}_2\{Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4\}$, 4. In a procedure similar to the one described above for **3**, 87 mg (0.50 mmol) of Yb metal and 54 mg (1.00 mmol) of NH_4Cl were reacted in 25 mL of liquid NH_3 to produce $(NH_3)_xYbCl_2$. The light green colored solid $(NH_3)_xYbCl_2$ was converted to $(THF)_xEuCl_2$, which was combined with 324 mg (2.00 mmol) of $K[H_2BC_8H_{14}]$ in 25 mL of THF. The mixture was stirred overnight, during which time the color of the solution changed to orange-brown with formation of a precipitate. Filtration of the reaction mixture yielded a yellow-brown colored filtrate. The filtrate was cooled to 0 °C, and slow removal of the THF solvent under vacuum provided yellow X-ray quality crystals of **4**. As determined by elemental analysis, this procedure promoted the loss of seven THF ligands to give $[K(THF)_{0.5}]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$. Anal. Calcd for $C_{36}H_{72}OYbB_4K_2$ (loss of 7 THF solvent ligands): C, 53.02; H, 8.90; B, 5.30; Yb, 21.22; K, 9.59. Found: C, 52.25; H, 8.45; B, 5.02; Yb, 20.79; K, 9.16. A yield of 367 mg of $[(THF)_{0.5}K]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (90% based on Yb) was obtained. IR (KBr): 2977(s), 2915(vs), 2864(vs), 2832(vs), 2684(w), 2657(w), 2124(m), 2078(m), 1960(w), 1447(m), 1410(m), 1335(m), 1289(m), 1205(m), 1166(w), 1107(w), 1075(m), 1043(s), 985(w), 893(m), 824(w), 801(w), 728(w), 689(w) cm^{-1}. ^{11}B NMR (80 MHz, d_8-THF): δ −13.6 (t, $^1J_{BH} = 60$ Hz). ^1H NMR (250 MHz, d_8-THF): δ 1.75−1.41 (m, β- and γ-H of $\{(\mu\text{-}H)_2BC_8H_{14}\}$, β-H of THF), 0.68 (s, α-H of $\{(\mu\text{-}H)_2BC_8H_{14}\}$). $^1H\{^{11}B\}$ NMR (250 MHz, d_8-THF): δ 1.06 (s, μ-H). ^{11}B NMR (80 MHz, d_8-Tol): δ −13.7 (t). ^1H NMR (250 MHz, d_8-Tol): δ 3.69 (br s, α-H of THF), 2.26−1.50 (m, β- and γ-H of $\{(\mu\text{-}H)_2BC_8H_{14}\}$, β-H of THF), 0.69 (s, α-H of $\{(\mu\text{-}H)_2BC_8H_{14}\}$). $^1H\{^{11}B\}$ NMR (250 MHz, d_8-Tol): δ 1.02 (s, μ-H).

Preparation of $[NMe_4]_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, 5. A procedure similar to the one described above produced a THF solution of **3** (0.5 mmol). Addition of $(NMe_4)Cl$ (110 mg, 1.0 mmol) and stirring overnight formed **5** and KCl precipitate. Filtration removed the precipitate, and the filtrate was cooled to 0 °C. Slow removal of the THF solvent under vacuum provided yellow X-ray quality crystals of **5**. Anal. Calcd for $C_{40}H_{88}N_2EuB_4$: C, 60.63; H, 11.11; N, 3.54; B, 5.46; Eu, 19.18. Found: C, 59.81; H, 10.76; N, 3.34; B, 5.44; Eu, 18.32. A yield of 342 mg of $(NMe_4)_2[Eu\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$ (86% based on Eu) was obtained. IR (KBr): 2979(m), 2919(vs), 2886(vs), 2837(vs), 2763(m), 2688(w), 2657(w), 2268(w), 2232(w), 2199(w), 2078(m), 2021(sh), 1557(w), 1539(w), 1508(m), 1465(s), 1452(s), 1405(s), 1334(s), 1314(m), 1283(s), 1262(sh), 1234(m), 1205(m), 1160(m), 1104(m), 1077(m), 1039(s), 968(m), 892(w), 823(w), 800(w), 741(w), 685(w) cm^{-1}.

Preparation of $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$, 6. A procedure similar to the one described above produced a THF solution of **4** (0.5 mmol). Addition of $(NMe_4)Cl$ (110 mg, 1.0 mmol) and stirring overnight formed **6** and KCl precipitate. Filtration removed the precipitate, and the filtrate was cooled to 0 °C. Slow removal of the THF solvent under vacuum provided yellow X-ray quality crystals of **6**. Elemental analysis indicated that there were three $[NMe_4][H_2BC_8H_{14}]$ crystallized with **6** as $(NMe_4)_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$·$3\{[NMe_4][H_2BC_8H_{14}]\}$.[27] Anal. Calcd for $C_{76}H_{172}N_5YbB_7$: C, 64.97; H, 12.34; N, 4.99; Yb, 12.32. Found: C, 64.86; H, 12.28; N, 5.02; Yb, 12.61. A yield of 237 mg of $[NMe_4]_2[Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_4]$·$3\{[NMe_4][H_2BC_8H_{14}]\}$(34% based on Yb) was

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obtained. IR (KBr): 3011(s), 2961(m), 2901(vs), 2855(vs), 2821(vs), 2672(w), 2650(w), 2601(w), 2339(w), 2307(w), 2268(m), 2201(sh), 2164((s), 2116(s), 2083(s), 2045(s), 2009(m), 1920(w), 1487(s), 1452(m), 1419(m), 1397(w), 1338(w), 1261(w), 1185(s), 1151(s), 1131(m), 1079(m), 1029(s), 950(s), 921(m), 827(w), 775(w), 723(w), 682(w) cm^{-1}. ^{11}B NMR (80 MHz, d_8-THF): δ −14.5 (t, $^1J_{BH}$ = 74 Hz). ^{1}H NMR (250 MHz, d_8-THF): δ 3.34 (s, 4Me−H), 1.81−1.45 (m, β- and γ-H of $\{(\mu\text{-H})_2BC_8H_{14}\}$, β-H of THF), 0.76 (s, α-H of $\{(\mu\text{-H})_2BC_8H_{14}\}$). ^{1}H{^{11}B} NMR (250 MHz, d_8-THF): δ 1.22 (s, μ-H).

Preparation of $\{(\mathrm{MeTHF})_3\mathrm{K}\}_2\{\mathrm{Eu}\{(\mu\text{-H})_2\mathrm{BC_8H_{14}}\}_4\}$, 7. A procedure similar to the one described above produced a THF solution of **3**. Removal of THF under vacuum and addition of MeTHF (2-methyltetrahydrofuran) as solvent replaced the THF. Repeating this procedure two more times ensured that all of the THF was replaced by MeTHF to afford a MeTHF solution of **7**. The solution was cooled to 0 °C, and slow removal of the MeTHF solvent under vacuum provided yellow X-ray quality crystals of **7**. Complete removal of the solvent at room temperature gave a yellow solid, which became faint yellow after washing with hexane and vacuum-drying. As determined by elemental analysis, this procedure promoted the loss of four MeTHF ligands to produce $\{\mathrm{K(MeTHF)}\}_2\{\mathrm{Eu}\{(\mu\text{-H})_2\mathrm{BC_8H_{14}}\}_4\}$. Anal. Calcd for $C_{42}H_{84}O_2EuB_4K_2$: C, 56.87; H, 9.42. Found: C, 56.39; H, 9.47. IR (KBr): 2974(vs), 2915(vs), 2867(vs), 2828(vs), 2687(w), 2656(w), 2257(sh,m), 2123(sh,s), 2082(s), 1967(sh,m), 1450(m), 1383(m), 1341(w), 1286(s), 1234(s), 1220(s), 1174(m), 1078(s), 1050(s), 1016(w), 989(m), 952(w), 926(w), 891(m), 826(m), 804(m), 743(w), 689(w), 616(w), 517(w), 475(w), 458(w) cm^{-1}.

Preparation of $\{(\mathrm{MeTHF})_3\mathrm{K}\}_2\{\mathrm{Yb}\{(\mu\text{-H})_2\mathrm{BC_8H_{14}}\}_4\}$, 8. A procedure similar to the one described above produced a THF solution of **4**. Removal of THF under vacuum and addition of MeTHF (2-methyltetrahydrofuran) as solvent replaced the THF. Repeating this procedure two more times ensured that all of the THF was replaced by MeTHF to afford a MeTHF solution of **8**. The solution was cooled to 0 °C, and slow removal of the MeTHF solvent under vacuum provided yellow X-ray quality crystals of **8**. Complete removal of the solvent at room temperature gave a yellow solid, which became faint yellow after washing with hexane and vacuum-drying. As determined by elemental analysis, this procedure promoted the loss of some MeTHF ligands to form $\{\mathrm{K(MeTHF)_{0.8}}\}_2\{\mathrm{Yb}\{(\mu\text{-H})_2\mathrm{BC_8H_{14}}\}_4\}$. Anal. Calcd for $C_{40}H_{80}O_{1.6}YbB_4K_2$: C, 54.71; H, 9.11. Found: C, 54.70; H, 8.81. IR (KBr): 2974(vs), 2913(vs), 2862(vs), 2827(vs), 2681(w), 2653(w), 2154(m), 2123(s), 2077(s), 1959(m), 1556(w), 1538(w), 1446(s), 1410(s), 1381(s), 1334(s), 1311(m), 1282(m), 1258(m), 1226(s), 1166(m), 1102(sh), 1074(s), 1044(sh), 1014(m), 988(m), 937(w), 917(w), 892(m), 826(w), 798(m), 729(w), 687(w), 613(w) cm^{-1}. ^{11}B NMR (80 MHz, d_8-THF): δ −13.9 (t). ^{1}H NMR (250 MHz, d_8-THF): δ 3.84−3.72 (m, H of α-THF), 1.93−1.25 (m, β- and γ-H of $\{(\mu\text{-H})_2BC_8H_{14}\}$, β-H of THF), 1.13 (d, CH_3), 0.65 (s, α-H of $\{(\mu\text{-H})_2BC_8H_{14}\}$). ^{1}H{^{11}B} NMR (250 MHz, d_8-THF): δ 0.91 (s, μ-H).

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Supporting Information Available: Six X-ray crystallographic files in CIF format and molecular structures and IR spectra of complexes **3**−**8** in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

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