

Bora-Amidinate Complexes of Lanthanide(II) Metals

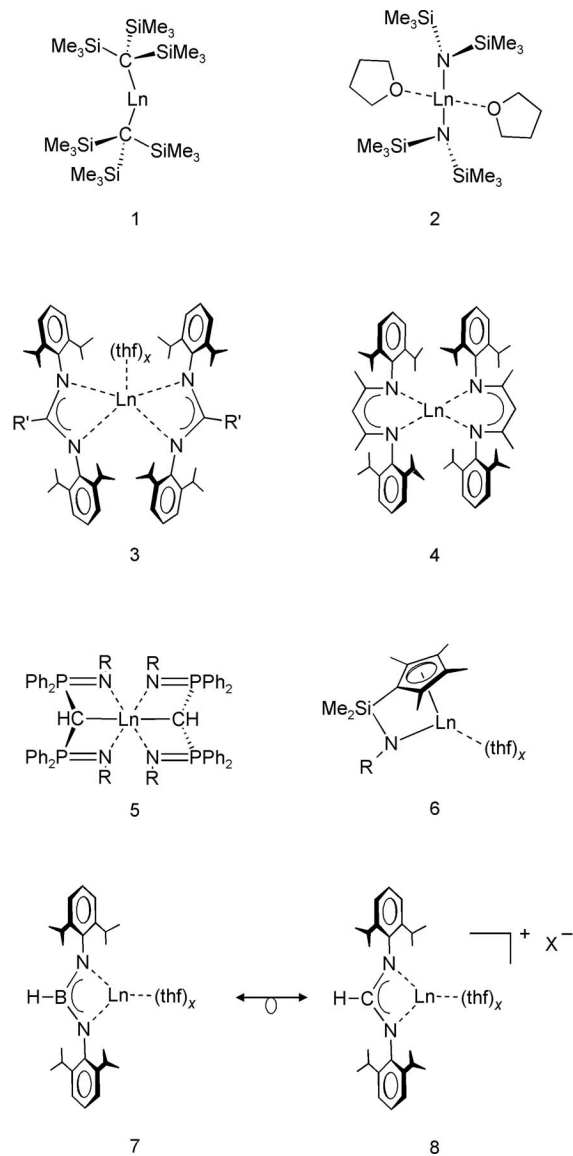
Sjoerd Harder^{*[a]} and Dominik Naglav^[a]**Keywords:** Lanthanides / Europium / Ytterbium / Samarium

Reaction of (2-Me₂N- α -Me₃Si-benzyl)₂Ln·(thf)₂ (Ln = Yb, Eu and Sm) with one equivalent of DIPP(H)N-BH-N(H)DIPP (^{DIPP}NBN-H₂, DIPP = 2,6-*i*Pr-phenyl) gave the first Ln^{II} bora-amidinate complexes which crystallized in the presence of THF as ^{DIPP}NBN-Ln·(thf)₄. Although only the Sm and Eu

complex crystallize isomorphous, all three show similar structures. The very small N–Ln–N' bite angles of 59.74(6)–63.28(9)° leave a large part of the metal coordination sphere available for neutral thf ligands.

Introduction

The chemistry of the lanthanide (Ln) metals in their hot oxidation +2 is surprisingly similar to that of the heavier alkaline-earth metal ions Ca²⁺ and Sr²⁺.^[1] This is not only due to equal oxidation states but also to very similar metal–ligand bond character: bonds to these metals should be considered highly ionic.^[2] In addition, the ionic radii for Sm²⁺ and Eu²⁺ compare well to that of Sr²⁺ whereas the size of Yb²⁺ is similar to that of Ca²⁺ (ionic radii for six-coordinate ions in Å: Ca²⁺ 1.00, Yb²⁺ 1.02, Sr²⁺ 1.18, Eu²⁺ 1.17, Sm²⁺ 1.22).^[3] For this reason Ln^{II} chemistry faces the same problems as the chemistry of the heavier alkaline-earth metals. E.g. the considerable size of the metal ions invokes the necessity to use large ligands that saturate the metal's coordination sphere in order to prevent formation of insoluble coordination polymers. From this point of view, it is not surprising that bulky cyclopentadienide (Cp) ligands are popular in the organometallic chemistry of Ln^{II}.^[4] The milestone synthesis of Cp^{*}₂Sm^[4a] (Cp^{*} = pentamethylcyclopentadienyl) initiated numerous investigations on its use as an one-electron reduction agent.^[5] Extensive developments in this field have led to many applications of Sm^{II} complexes in organic syntheses or in polymerization chemistry.^[6] Despite the versatility of Ln^{II} reagents only few homoleptic non-Cp complexes have been prepared. These complexes are generally based on bulky ligands: e.g. silylated alkyl anions (1),^[7] silylated amide anions (2),^[8] bulky amidinate (and guanidinate) anions (3),^[9] bulky β -diketiminate anions (4)^[11] or bis-(phosphoranoimino)methanide anions (5).^[10] While bulky ligands offer valuable protection for the Ln^{II} center, for catalytic application less demanding ligands would be favourable. This initiated investigations on heteroleptic complexes

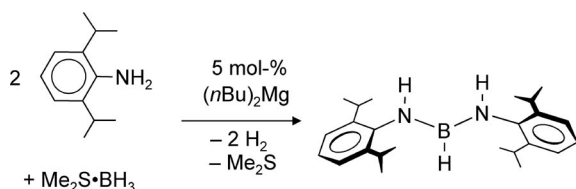


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of general formula Cp^*LnER ($\text{ER} = \text{OR}, \text{NR}_2, \text{SR}$).^[11] On account of the less demanding ER unit, these complexes are much more open for substrate coordination. At the same time, however, the strongly electron-donating Cp^* ligand warrants an electron-rich Ln^{II} center for efficient reduction chemistry. Even more open Ln^{II} complexes have been prepared by linking Cp^* and ER units (**6**),^[11] i.e., by making use of the constrained geometry ligand well-known in Ln^{III} and group 4 chemistry.^[12]

Serendipitously, we recently found a very convenient one-pot synthesis of a hitherto unknown bora-amidinate ligand (abbreviated as *bam* ligand).^[13] The ligand **DIPP**NBN- H_2 can be obtained quantitatively from the $(n\text{Bu})_2\text{Mg}$ -catalyzed reaction of two equivalents of 2,6-diisopropylaniline with one equivalent of $\text{Me}_2\text{S}\cdot\text{BH}_3$ (Scheme 1).^[14] This ligand can be deprotonated twofold to give **DIPP**NBN²⁻ which, by isolobal replacement of BH^- for CH^- , is iso-electronic to the corresponding amidinate anion $\text{HC}(\text{N-DIPP})_2^-$. However, on account of its double negative charge, it could substitute two amidinate ligands and should therefore be regarded as a very compact highly electron-donating ligand. Whereas this ligand would be optimally suited to stabilize complexes with metals in unusually high oxidation states, its use in low valent Ln chemistry could be equally rewarding. Complexes like **DIPP**NBN- Ln^{II} (**7**) would feature reactive Ln^{II} centers that are unusually exposed. At the same time, such compounds are isolobal to an (amidinate) $\text{Ln}^{\text{II}+}$ cation (**8**) which hitherto has not been prepared (**7** could be seen as a complex in which the non-coordinating anion is incorporated in the chelate ligand). The ambiguity of an electron-rich Ln^{II} metal in a complex that is isoelectronic with a cationic species could have interesting consequences in reduction chemistry. In here we describe our preliminary investigations and introduce syntheses and crystal structures of the first Ln^{II} bora-amidinate complexes **DIPP**NBN- Ln^{II} ($\text{Ln} = \text{Yb}, \text{Eu}, \text{and Sm}$).^[15]



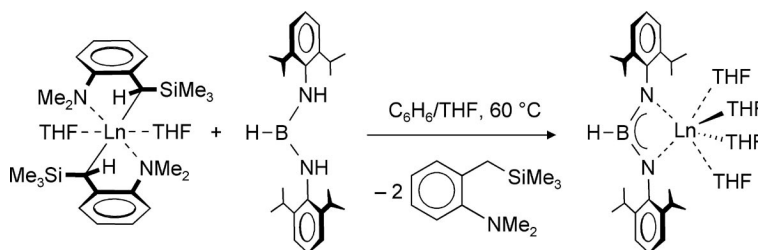
Scheme 1.

Results and Discussion

In a first series of experiments we attempted to deprotonate **DIPP**NBN- H_2 with an equimolar amount of the commonly used Ln^{II} base $\text{Ln}[(\text{NSiMe}_3)_2]_2\cdot(\text{thf})_2$ ($\text{Ln} = \text{Sm}, \text{Eu}$ or Yb)^[8] in benzene at 60 °C. Although distinct colour changes were indicative for conversion we have never been able to isolate well-defined products from these solutions. It is likely that the acid-base equilibrium is not fully at the product side. Although there is no information on the acidity of bora-amidine ligands we estimate the $\text{p}K_{\text{a}1}$ value of **DIPP**NBN- H_2 to be lower than that of $(\text{Me}_3\text{Si})_2\text{NH}$ ($\text{p}K_{\text{a}} = 25.8$).^[16] Relevant for the second deprotonation, however, is the $\text{p}K_{\text{a}2}$ value which might be in the same region. For that reason we decided to use benzylanthanide reagents for deprotonation: $(2\text{-Me}_2\text{N-}\alpha\text{-Me}_3\text{Si-benzyl})_2\text{Ln}\cdot(\text{thf})_2$ (Scheme 2). These reagents, which are known for all three lanthanide metals that generally occur in the 2+ oxidation state (Sm ,^[1] Eu ^[17] and Yb ^[1]), are easily accessible in good yields and crystalline purity. They are among the strongest bases hitherto known in Ln^{II} chemistry and should be considered as convenient precursors.

Addition of **DIPP**NBN- H_2 to a solution of $(2\text{-Me}_2\text{N-}\alpha\text{-Me}_3\text{Si-benzyl})_2\text{Yb}\cdot(\text{thf})_2$ in benzene resulted already at room temperature in an immediate colour change from orange to red. Soon after, yellow rectangular crystals of **DIPP**NBN- $\text{Yb}\cdot(\text{thf})_4$ started to grow. In order to complete the reaction, the mixture was heated overnight to 60 °C. After cooling a crop of large uniform crystals could be isolated (yield: 88%). A similar procedure also gave the Eu and Sm analogues in yields of 84% and 68%, respectively. The Sm complex is extremely sensitive towards oxidation and difficult to handle. The Yb and Eu complexes were found to be much less sensitive. Under vacuum, all complexes can lose part of the thf ligands.

Crystallographic studies revealed that all three complexes crystallize as **DIPP**NBN- $\text{Ln}\cdot(\text{thf})_4$: i.e. a monomer in which four thf ligands are needed to saturate the coordination sphere of the central metal (Figure 1, a). The crystal structures of **DIPP**NBN- $\text{Sm}\cdot(\text{thf})_4$ and **DIPP**NBN- $\text{Eu}\cdot(\text{thf})_4$ are isomorphous (crystal data are given in Table 1) and the asymmetric unit contains one molecule. The complex with the somewhat smaller metal, **DIPP**NBN- $\text{Yb}\cdot(\text{thf})_4$, crystallizes in a different crystal system with half a molecule in the asym-



Scheme 2.

Table 1. Crystal data.

Compound	DIPP ⁺ NBN ²⁻ -Yb ⁺ ·(thf) ₄	DIPP ⁺ NBN ²⁻ -Eu ⁺ ·(thf) ₄	DIPP ⁺ NBN ²⁻ -Sm ⁺ ·(thf) ₄
Formula	C ₄₀ H ₆₇ BN ₂ O ₄ Yb·C ₄ H ₈ O	C ₄₀ H ₆₇ BN ₂ O ₄ Eu	C ₄₀ H ₆₇ BN ₂ O ₄ Sm
MW	895.91	802.73	801.12
Size [mm]	0.2 × 0.05 × 0.05	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.1
Colour	yellow	yellow	black
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	C222 ₁	P2 ₁ /n	P2 ₁ /n
<i>a</i> [Å]	11.9023(8)	10.8223(5)	10.8185(4)
<i>b</i> [Å]	16.4066(8)	18.4564(8)	18.4750(4)
<i>c</i> [Å]	23.2940(14)	20.8239(9)	20.8417(8)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	90	97.968(2)	96.132(1)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	4548.8(5)	4119.2(3)	4125.3(3)
<i>Z</i>	4	4	4
<i>ρ</i> [g cm ⁻³]	1.308	1.294	1.290
<i>μ</i> (Mo- <i>Kα</i>) [mm ⁻¹]	2.098	1.561	1.462
<i>T</i> [°C]	−120	−100	−100
<i>θ</i> (max.) [°]	28.4	28.3	29.3
Number of total/unique reflections	27241/5668	75701/10231	79921/11077
<i>R</i> _{int}	0.042	0.033	0.053
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	4947	8510	8308
Parameters	247	445	445
<i>R</i> ₁	0.0275	0.0302	0.0362
<i>wR</i> ₂	0.0608	0.0688	0.0848
GOF	1.04	1.11	1.07
min./max. residual electron density [e Å ⁻³]	−0.45/1.19	−1.24/1.25	−1.14/1.08

metric unit (the complex is crystallographically C₂-symmetric). Selected bond lengths and angles are summarized in Table 2.

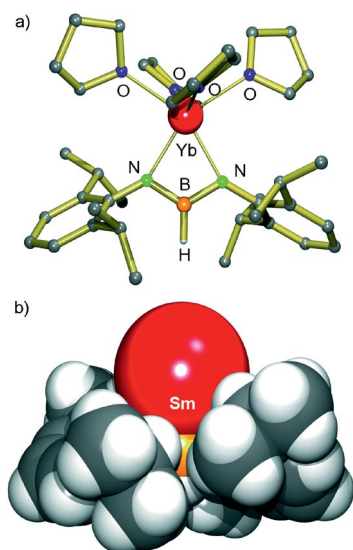


Figure 1. a) Crystal structure of DIPP⁺NBN²⁻-Yb⁺·(thf)₄; all hydrogen atoms, except that at B, have been omitted for clarity. The Sm and Eu complexes are isostructural. b) Spacefilling model for the Sm analogue, the complex with the largest metal and smallest N–Ln–N bite-angle. Neutral thf ligands have been omitted in order to show the space around the metal.

In all structures the DIPP⁺NBN ligands coordinate to the metal in a *N, N'*-chelating fashion. The metal is situated close to the plane spanned by the N–B–N backbone [the maximum out-of-plane deviation is 0.043(1) Å found in DIPP⁺NBN²⁻-Sm⁺·(thf)₄]. Least-squares planes defined for the

aryl substituents make angles between 69.2(3)° and 87.2(3)° with the N–B–N plane. The Ln–N and Ln–O distances decrease along the row of lanthanide contraction (Sm > Eu > Yb), however, this decrease is less than expected. In going from Sm to Yb the Ln–N and Ln–O distances decrease by 0.109(3) and 0.148(3) Å, respectively, which is less than the 0.20 Å decrease for their ionic radii. All complexes display similar thf coordination: two of the thf ligands typically reside in the N–B–N plane. The average O–Ln–O' angles for neighbouring ligands (*cis*) are in the range of 79.69(8)–82.44(7)° whereas those in *trans* position display average O–Ln–O' angles between 128.58(8)° and 131.48(7)°. The B–N bond lengths are in the very narrow range of 1.420(3)–1.424(3) Å. The average value of 1.422(3) Å compares well to that of 1.429(1) Å in borazine (BHNH₃).^[18] Also the group 2 metal complex PhB(N-DIPP)₂Mg·(OEt)₂ shows a similar B–N bond length of 1.444(5) Å.^[19] There is not much variation in the N–B–N angles: 118.7(2)–119.5(3)°. The N–B–N angle in DIPP⁺NBN²⁻-Ln⁺·(thf)₄ [average: 119.1(3)°] is considerable wider than that in complexes containing the PhB(N-DIPP)₂ ligand [N–B–N range: 109.4(6)–112.5(3)°].^[13] This widening is due to the presence of a small H-substituent in the backbone of DIPP⁺NBN²⁻. Despite a rather wide N–B–N angle, the ligand bite angles in DIPP⁺NBN²⁻-Ln⁺·(thf)₄ are among the most acute reported so far. This is related to the long Ln–N bond lengths: hitherto the Sm–N bond length of 2.466(2) Å is the longest reported metal–N bond length to a *bam* ligand. The N–Ln–N' bite angle decreases with increasing metal size and in DIPP⁺NBN²⁻-Sm⁺·(thf)₄ an extremely small bite-angle of less than 60° is found. As exemplified in the space-filling model for the DIPP⁺NBN²⁻-Sm fragment (Figure 1, b), this leaves ample

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]. Average values are given between brackets.

Compound	Yb	Eu	Sm
M–N	2.346(3)	2.436(2)–2.462(2) <2.449(2)>	2.443(2)–2.466(2) <2.455(2)>
M–O	2.429(2)–2.505(3) <2.467(3)>	2.586(2)–2.636(2) <2.602(2)>	2.599(2)–2.647(2) <2.615(2)>
B–N	1.424(3)	1.416(3)–1.424(3) <1.420(3)>	1.416(3)–1.427(3) <1.422(3)>
N–B–N'	119.5(3)	119.0(2)	118.7(2)
N–M–N'	63.28(9)	59.97(7)	59.74(6)
O–Yb–O' <i>cis</i>	76.65(8)–82.72(8) <79.69(8)>	78.70(7)–88.64(7) <82.44(7)>	78.34(7)–82.31(7) <80.51(7)>
O–Yb–O' <i>trans</i>	117.49(8)–139.67(9) <128.58(8)>	123.65(7)–139.13(6) <131.39(7)>	124.42(7)–138.54(6) <131.48(7)>
Deviation M N–B–N plane [$\text{\AA}$]	0.000(1)	0.039(1)	0.043(1)
Dihedral angle DIPP/NBN [$^\circ$]	69.2(3)	77.7(3)–87.1(3) <82.4(3)>	77.4(3)–87.2(3) <82.3(3)>

space around the metal for coordination of four thf ligands. For comparison, the metal in the constrained geometry catalyst **6** (Ln = Yb, R = Ph) contains three thf ligands in its coordination sphere. Although there are examples for Ln^{II} complexes with even five thf ligands in its coordination sphere, LnI₂·(thf)₅ (Ln = Sm or Eu) and Eu(C₆F₅)₂·(thf)₅,^[20] the anionic ligands coordinated symmetrically around the metal. In contrast, the small bite angle of the N–B–N ligands in **DIPP**NBN–Ln·(thf)₄ is responsible for the very open nature of **DIPP**NBN–Ln·(thf)₄ complexes.

The Sm and Eu complexes are paramagnetic but diamagnetic **DIPP**NBN–Yb·(thf)₄ could be completely characterized by ¹H, ¹³C and ¹¹B NMR spectroscopy. The ¹H NMR spectrum of the complex dissolved in C₆D₆ shows only one doublet for the *i*Pr–Me groups and one septet for the *i*Pr–CH groups. Also in ¹³C NMR spectrum single resonances are observed for the *i*Pr–Me and *i*Pr–CH groups. This indicates that the DIPP substituents can rotate freely around the N–DIPP axis and is due to the small hydride substituent in the boron backbone. In complexes with the PhB(N–DIPP)₂ ligand rotation of the DIPP substituent is blocked by the Ph group and the *i*Pr substituents give various NMR signals.^[19] The ¹¹B NMR resonance for **DIPP**NBN–Yb·(thf)₄ is a broad signal at $\delta = 32.0$ ppm [cf. for complexes containing the ligand PhB(N–DIPP)₂ chemical shifts in the range of 28–30 ppm are observed].^[19]

Conclusions

The first bora-amidinate complexes of Ln^{II} metals have been prepared. Successful twofold deprotonation of **DIPP**NBN–H₂ could only be achieved by use of strongly basic Ln^{II} precursors: (2–Me₂N– α –Me₃Si–benzyl)₂Ln·(thf)₂. The products all crystallize as complexes of composition **DIPP**NBN–Ln·(thf)₄ (Ln = Yb, Eu, Sm) and, although only two of these complexes crystallize isomorphically, all three show a similar structure. The very small bite angle of the twofold negatively charged ligand **DIPP**NBN^{2–} [range: 59.74(6)–63.28(9) $^\circ$] leaves a large part of the metal cation exposed for coordination of neutral ligands. The open na-

ture of these complexes could lead to interesting redox chemistry and/or catalytic activity. We are currently exploring the redox-chemistry and catalytic potential of these novel systems.

Experimental Section

General: All manipulations were performed under a dry and oxygen-free argon atmosphere using Schlenk line and glove box techniques and freshly dried solvents. Following complexes have been prepared according to literature procedures: **DIPP**NBN–H₂,^[14] (2–Me₂N– α –Me₃Si–benzyl)₂Ln·(thf)₂ (Ln = Sm,^[1] Eu,^[17] Yb^[11]).

General Synthetic Route: Equimolar quantities of **DIPP**NBN–H₂ (0.32 mmol) and (2–Me₂N– α –Me₃Si–benzyl)₂Ln·(thf)₂ (0.32 mmol) were dissolved in a mixture of 1.9 mL of benzene and 0.05 mL of THF and heated for 16 h at 60 $^\circ\text{C}$. Slowly cooling to 5 $^\circ\text{C}$ gave crystals of the product in the following yields: Ln = Yb 232 mg (88%, yellow), Ln = Eu 216 mg (84%, yellow) and Ln = Sm 175 mg (68%, black). The complexes **DIPP**NBN–Eu·(thf)₄ and **DIPP**NBN–Sm·(thf)₄ are paramagnetic but **DIPP**NBN–Yb·(thf)₄ has been fully characterized by NMR spectroscopy. ¹H NMR (300 MHz, [D₆]–benzene, 25 $^\circ\text{C}$): $\delta = 1.29$ [d, ³J_{(H,H)}} = 5.8 Hz, 24 H, CHMe₂], 1.31 (b, 16 H, thf), 3.45 (b, 16 H, thf), 3.59 [sept, ³J_{(H,H)}} = 5.8 Hz, 4 H, CHMe₂], 5.39 (b, 1 H, BH), 6.95 [t, ⁴J_{(H,H)}} = 6.9 Hz, 2 H, Ar], 7.15 [d, ⁴J_{(H,H)}} = 6.9 Hz, 4 H, Ar] ppm. ¹³C{¹H} NMR (75 MHz, [D₆]–benzene, 25 $^\circ\text{C}$): $\delta = 25.6$ (CHMe₂), 26.1 (thf), 29.0 (CHMe₂), 68.3 (thf), 119.1 (Ar), 123.6 (Ar), 141.2 (Ar), 154.6 (Ar) ppm. ¹¹B{¹H} NMR (160.5 MHz, [D₆]benzene, 25 $^\circ\text{C}$): $\delta = 32.0$ (s, BH) ppm. Elemental analysis for **DIPP**NBN–Eu·(thf)₄: calcd. (%) for C₄₀H₆₇BEuN₂O₄ (802.76): calcd. C 59.85, H 8.41, N 3.49; found C 59.34, H 8.21, N 3.22. Elemental analysis for **DIPP**NBN–Yb·(thf)₄: calcd. for C₄₀H₆₇BN₂O₄Yb (823.84): calcd. C 58.32, H 8.20, N 3.40; found C 58.30, H 8.41, N 3.38. The extreme sensitivity of **DIPP**NBN–Sm·(thf)₄ towards oxidation disabled a satisfying elemental analysis. Crystals of **DIPP**NBN–Sm·(thf)₄ were quenched in CD₃OD. The colourless solution was freed from Sm traces by filtering through Al₂O₃. ¹H NMR analysis gave a ligand/thf ratio of 1/3.8. The following melting points have been determined: **DIPP**NBN–Sm·(thf)₄ 141 $^\circ\text{C}$; **DIPP**NBN–Eu·(thf)₄ 143 $^\circ\text{C}$; **DIPP**NBN–Yb·(thf)₄ 160 $^\circ\text{C}$ (dec).

Crystal Structure Determinations: All data were collected on a Siemens SMART CCD APEX II diffractometer (Table 2). The struc-

tures have been solved by direct methods (SHELXS-97)^[21] and were refined with SHELXL-97.^[22] The geometry calculations and graphics have been performed with PLATON.^[23]

DIPP⁺NBN-Yb(thf)₄: The asymmetric unit contains half a molecule of non-coordinated THF in a void. This solvent molecule shows slight disorder which was treated by refinement with large anisotropic displacement parameter. The BH hydrogen atom has been located in the difference Fourier map and was refined isotropically. All other hydrogen atoms have been placed on calculated positions and were refined in a riding mode.

DIPP⁺NBN-Eu(thf)₄: The BH hydrogen atom has been located in the difference Fourier map and was refined isotropically. All other hydrogen atoms have been placed on calculated positions and were refined in a riding mode.

DIPP⁺NBN-Yb(thf)₄: The thf ligands show a slight ring-puckering disorder typical for this ligand. This has been treated by refinement with large anisotropic displacement parameter. The BH hydrogen atom has been located in the difference Fourier map and was refined isotropically. All other hydrogen atoms have been placed on calculated positions and were refined in a riding mode.

CCDC-761675 (for Eu), -761676 (for Sm), -761677 (for Yb) contain the Crystallographic data (excluding structure factors) of this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Checkcif files for the X-ray structure determinations (including ORTEP plots of all products).

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- [1] S. Harder, *Angew. Chem.* **2004**, *116*, 2768; *Angew. Chem. Int. Ed.* **2004**, *43*, 2714, and references cited therein.
- [2] C. Lambert, P. von R. Schleyer, *Angew. Chem.* **1994**, *106*, 1187–1199; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129–1140.
- [3] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.
- [4] a) W. J. Evans, L. A. Hughes, T. P. Hanusa, *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272; b) M. Visseaux, D. Barbier-Baudry, O. Blacque, A. Hafid, P. Richard, F. Weber, *New J. Chem.* **2000**, *24*, 939–942; c) M. Schultz, C. J. Burns, D. J. Schwartz, R. A. Andersen, *Organometallics* **2000**, *19*, 781–789; d) H. Sitzmann, T. Dezember, O. Schmitt, F. Weber, G. Wolmershäuser, M. Ruck, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2241–2244.
- [5] See for a recent review: W. J. Evans, *Inorg. Chem.* **2007**, *46*, 3435–3449.
- [6] a) H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 4908–4910; b) H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, *Macromolecules* **1993**, *26*, 7134–7143; c) Z. Hou, Y. Zhang, M. Nishiura, Y. Wakatsuki, *Organometallics* **2003**, *22*, 129–135; d) K. Mikami, M. Terada, H. Matsuzawa, *Angew. Chem.* **2002**, *114*, 3704–3722; *Angew. Chem. Int. Ed.* **2002**, *41*, 3554–3571.
- [7] a) C. Eaborn, P. B. Hitchcock, K. Izod, J. P. Smith, *J. Am. Chem. Soc.* **1994**, *116*, 12071–12072; b) C. Eaborn, P. B. Hitchcock, K. Izod, Z.-R. Lu, J. P. Smith, *Organometallics* **1996**, *15*, 4783–4790; c) G. Qi, Y. Nitto, A. Saiki, T. Tomohiro, Y. Nakayama, H. Yasuda, *Tetrahedron* **2003**, *59*, 10409–10418.
- [8] a) D. T. Tilley, A. Zalkin, R. A. Andersen, D. H. Templeton, *Inorg. Chem.* **1981**, *20*, 551–554; b) G. B. Deacon, G. D. Fallon, C. M. Forsyth, H. Schumann, R. Weimann, *Chem. Ber./Recueil* **1997**, *130*, 409–415; c) P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, A. V. Protchenko, *J. Organomet. Chem.* **2002**, *647*, 198–204.
- [9] a) M. L. Cole, P. C. Junk, *Chem. Commun.* **2005**, *21*, 2695–2697; b) D. Heitmann, C. Jones, P. C. Junk, K.-A. Lippert, A. Stasch, *Dalton Trans.* **2007**, 187–189.
- [10] a) M. S. Hill, P. B. Hitchcock, *Dalton Trans.* **2003**, 4570–4571; b) M. Wiecko, P. W. Roesky, V. V. Burlakov, A. Spannenberg, *Eur. J. Inorg. Chem.* **2007**, 876–881.
- [11] See for a review article: Z. Hou, Y. Wakatsuki, *J. Organomet. Chem.* **2002**, *647*, 61–70.
- [12] a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) P. S. Chum, W. J. Kruper, M. J. Guest, *Adv. Mater.* **2000**, *12*, 1759–1767; c) J. Okuda, *Dalton Trans.* **2003**, 2367–2378.
- [13] C. Fedorchuk, M. Copsey, T. Chivers, *Coord. Chem. Rev.* **2007**, *251*, 897–924.
- [14] J. Spielmann, M. Bolte, S. Harder, *Chem. Commun.* **2009**, 6934–6936.
- [15] a) Prof. Tristram Chivers kindly informed us of his concurrent work on (bora-amidinate)Ln^{III} complexes which was published during the revision of this manuscript: A. M. Corrente, T. Chivers, *Inorg. Chem.* **2010**, *49*, 2457–2463; b) Other ongoing work from our own research group deals with bora-amidinate Ln^{III} complexes of type **DIPP⁺NBN-LnR** (R = amide or benzylide): S. Harder, *Dalton Trans.* **2010** DOI: 10.1039/c001966f.
- [16] R. R. Fraser, T. S. Mansour, S. Savard, *J. Org. Chem.* **1985**, *50*, 3232–3234.
- [17] S. Harder, C. Ruspic, N. Ni Bhriain, F. Berkermann, M. Schürmann, *Z. Naturforsch., Teil B* **2008**, *63*, 267–274.
- [18] R. Boese, A. H. Maulitz, P. Stellberg, *Chem. Ber.* **1994**, *127*, 1887–1889.
- [19] T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen, R. T. Boeré, *Inorg. Chem.* **2006**, *45*, 2119–2131.
- [20] a) W. J. Evans, T. S. Gammersheimer, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 8999–9002; b) G. Heckmann, M. Niemeyer, *J. Am. Chem. Soc.* **2000**, *122*, 4227–4228; c) C. Forsyth, G. B. Deacon, *Organometallics* **2000**, *19*, 1205–1207.
- [21] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, **1997**, University of Göttingen, Germany.
- [22] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, **1997**, University of Göttingen, Germany.
- [23] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool* **2000**, Utrecht University, Utrecht, The Netherlands.

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