# Syntheses and Characterization of Samarium and Erbium Borohydrido Complexes Supported by N-Aryliminopyrrole Ligand

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Dedicated to Dr. Arogya Varam Saha on the Occasion of His 60th Birthday

Keywords: Iminopyrrole; Samarium; Erbium; Borohydrides; Steric crowding; Metallacyle

Abstract. Reaction of potassium salt of N-aryliminopyrrole ligand [2-(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)–C<sub>4</sub>H<sub>3</sub>NK] (1) with samarium tris-boro-hydride [Sm(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>] gave a samarium ate complex [ $\eta^2$ -{2-(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)–C<sub>4</sub>H<sub>3</sub>N}<sub>3</sub>Sm( $\eta^1$ -BH<sub>4</sub>){K(THF)<sub>6</sub>] (2); whereas similar treatment with erbium borohydride [Er(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>] afforded

## Introduction

In the last 20 years, organolanthanide complexes are used as catalysts extensively, especially in favor of polymerization.<sup>[1,2]</sup> Even though the lanthanide hydrides have already been proved to be powerful catalysts for many interesting chemical transformations, the challenging problem remains for their access, since they are mostly reactive.<sup>[3]</sup> In recent time, the search for alternatives to the ubiquitous [Ln]-H or [Ln]-R functions, i.e. the in situ alkylation of a pre-catalyst, or the use of borane supported hydrides [Ln]-HBR<sub>3</sub> or borohydrides [Ln]-BH<sub>4</sub> have appeared as new trends.<sup>[4,5]</sup> In these alternative methods, complexes bearing a [Ln]-BH<sub>4</sub> function are easily accessible and more robust in contrast to [Ln]-H compounds.<sup>[6]</sup> In general borohydride compounds of various metals have been recently proved their merits as potential hydrogen storage material.<sup>[7]</sup> The lanthanide trisborohydrides were first prepared in the early 1950s by reaction of rare earth metal alkoxides with diborane B<sub>2</sub>H<sub>6</sub>.<sup>[8]</sup> In the 1980s *Mirsaidov* et al. reported a more straight forward approach to access,  $[Ln(BH_4)_3(THF)_3]$  from the starting materials  $LnCl_2$  (Ln = La, Ce, Pr, Nd, Sm) and NaBH<sub>4</sub>.<sup>[9-11]</sup> Today in preparative chemistry, the use of lanthanide trisborohydrides  $[Ln(BH_4)_3(THF)_n]$  are restricted mainly in two fields.<sup>[6]</sup> Firstly, they are widely applied as efficient catalysts for the polymerization of isoprene,[12-15] styrene,<sup>[14,16]</sup> and some polar monomers such as  $\varepsilon$ -caprolactone (CL),<sup>[17-19]</sup> methyl methacrylate (MMA),<sup>[20-22]</sup> and trimethyl-

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 [a] Department of Chemistry Indian Institute of Technology Hyderabad Ordnance Factory Estate Yeddumailaram 502205, Andhra Pradesh, India the mono(iminopyrrolyl) complex  $[\eta^2-\{2-(2,6-\mathit{i}Pr_2C_6H_3N=CH)-C_4H_3N\}Er(\eta^3-BH_4)_2(THF)_2]$  (3). In the solid-state structures, the samarium complex 2 shows a rarely observed  $\eta^1$  and the erbium complex 3 shows a usual  $\eta^3$  coordination mode of the borohydrido ligand.

ene carbonate (TMC).<sup>[23]</sup> Secondly, a large number of lanthanide borohydride derivatives, which also have a high catalytic potential are prepared from [Ln(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>n</sub>] making lanthanide trisborohydrides as valuable starting materials. Even though various diamagnetic borohydride complexes with other lanthanide elements are studied extensively, the studies of samarium and erbium borohydride complexes are limited due to the paramagnetic nature of the complexes.<sup>[24]</sup> To have controlled reactivity of the lanthanide borohydrido complexes a supporting ligand plays an important role. In this context the tunable ancillary ligands such as pyrrolyl-based ligands have been proved wide range of versatility in organolanthanide chemistry.<sup>[25]</sup> Recent reports from Hou et al. demonstrated that the lanthanide aminobenzyl complexes having pyrrolide moiety count for a high catalytic activity and stereocontrol ability for the polymerization of styrene, and in contrast, metal aminobenzyl complexes showed no catalytic activity for the styrene polymerization.<sup>[26]</sup> Mashima and co-workers also reported that the rare-earth metal amides with pyrrolyl moieties showed high catalytic activities on the ROP of *ɛ*-caprolactone, but homoleptic tris(pyrrolyl) yttrium complexes had no activity, indicating initiation step did not proceed.<sup>[27]</sup> Wang et al. also demonstrated various rare-earth metal complexes with the tris iminopyrrolyl ligands and their catalytic activities on the ROP of ɛ-caprolactone.<sup>[28]</sup> Roesky et al. also showed clearly that pyrrolyl ligands can serve as unique monoanionic nitrogen ligands in coordination chemistry of transition metal and rare earth metals.<sup>[29]</sup> Thus to have lanthanide borohydrido complexes having pyrrolyl imine ligands into the coordination sphere can serve as unique example of hybrid pyrrole iminoborohydrido lanthanide complex.

Herewith we describe the preparation and structural characterization of samarium and erbium borohydride complexes supported by N-aryliminopyrrole ligand.

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### **Results and Discussion**

Reaction of  $[2-(2,6-iPr_2C_6H_3N=CH)-C_4H_3NK]$  (1) with samarium tris-borohydride  $[Sm(BH_4)_3(THF)_3]^{[30]}$  in THF at ambient temperature followed by filtration and evaporation of the solvent resulted in a samarium ate complex  $[\eta^2-\{2-(2,6-iPr_2C_6H_3N=CH)-C_4H_3N\}_3Sm(\eta^1-BH_4)\{K(THF)_6\}]$  (2) as colorless crystals in good yield after re-crystallization from THF/ pentane (Scheme 1). The title compound was characterized by standard analytical/spectroscopic techniques and the solid-state structure was established by single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of samarium and erbium complexes.

Even though compound 2 is slightly paramagnetic, <sup>1</sup>H and  $^{13}C{^{1}H}$  NMR can be measured for characterization of 2 along with elemental analysis. In the <sup>1</sup>H NMR spectrum, a doublet at  $\delta = 1.14$  ppm corresponds to 36 methyl protons. A septet signal at  $\delta = 3.18$  is observed due to resonance of two isopropyl methine protons. The iminopyrolyl moiety shows signals at expected regions for the protons attached to it. The most characteristic signal is the BH<sub>4</sub><sup>-</sup> anion which shows a broad peak at  $\delta = -2.41$  ppm which is significantly low frequency shifted compared to that of some borohydride complexes like  $[(C_5HiPr_4)Sm(BH_4)_2(THF)]$  ( $\delta = -10.5 \text{ ppm}$ ),<sup>[31]</sup>  $[Cp^{*'}Sm{(p-tol)NN}(BH_4)]$  ( $\delta = -9.3 \text{ ppm}$ ) ( $Cp^{*'}$ =  $C_5Me_4(nPr)$ , (p-tol)NN = (p-tol)-NC(Me)CHC(Me)N(ptol).<sup>[32]</sup> The solid-state structure was established by single crystal X-ray diffraction analysis. The structural parameters are given in Table 1. All hydrogen atoms are located in the difference Fourier map and subsequently refined.

The samarium complex **2** crystallizes in the orthorhombic space group  $Pna2_1$  with four molecules of **2** and one molecule of THF in the unit cell (Figure 1). The molecular structure of **2** consists of an ion pair composed of a  $[K(THF)_6]^+$  cation and an  $[\eta^2-\{2-(2,6-iPr_2C_6H_3N=CH)-C_4H_3N\}_3Sm(\eta^1-BH_4)]^-$  anion. In the anionic part of the molecule, the central metal samarium is coordinated by three bidentate N-aryliminopyrrolyl ligand moieties through the chelation of two nitrogen atoms of the each ligand. Thus three five member rings (Sm1–N1–C4–C5–N2; Sm1–N3–C21–C22–N4; Sm1–N5–C38–C39–N6) are formed due to the coordination of the three iminopyrrolyl ligands onto the samarium atom. Most interesting is the coordination mode of the BH<sub>4</sub><sup>-</sup> group onto the central samarium atom. It is observed that BH<sub>4</sub><sup>-</sup> group is coordinated to the samarium atom through  $\eta^1$  fashion with a Sm1–B1 bond length

**Table 1.** Crystallographic details of  $[\eta^2-\{2-(2,6-iPr_2C_6H_3N=CH)-C_4H_3N\}_3Sm(\eta^1-BH_4)\{K(THF)_6\}$  (2) and  $[\eta^2-\{2-(2,6-iPr_2C_6H_3-N=CH)-C_4H_3N\}Er(\eta^3-BH_4)_2(THF)_2]$  (3)<sup>a)</sup>.

	2	3
Formula	C <sub>79</sub> H <sub>124</sub> BKN <sub>6</sub> O <sub>7</sub> Sm	C <sub>25</sub> H <sub>45</sub> B <sub>2</sub> Er N <sub>2</sub> O <sub>2</sub>
Formula weight	1470.11	594.51
Crystal system	orthorhombic	trigonal
Space group	$Pna2_1$	RĪ
a /Å	18.4419(5)	23.9043(11)
<i>b</i> /Å	34.7908(9)	23.9043(11)
<i>c</i> /Å	12.3954(4)	27.4845(12)
a /°	90	90
β /°	90	90
γ /°	90	120
V /Å <sup>3</sup>	2252.4(2)	13601.0(11)
Ζ	4	18
Density /mg·m <sup>3</sup>	1.257	1.307
<i>Т /</i> К	150(2)	150(2)
Radiation	CuKα	CuKa
	$(\lambda = 1.54184 \text{\AA})$	$(\lambda = 1.54184 \text{Å})$
$\mu$ /mm <sup>-1</sup>	6.427	5.296
F(000)	3128	5454
Absorption correction	empirical	empirical
Reflections collected	21908	10520
Unique reflections	12239 $[R_{int} =$	5656 $[R_{int} = 0.0343]$
1	0.0523]	
Completeness to	98.2%	96.9%
GOF	1.052	1.10
Refinement method	Full-matrix least-	Full-matrix least-
	squares on $F^2$	squares on $F^2$
$R_1; wR_2$	0.0721; 0.2058	0.0479; 0.1549

a) Programs used: SHELXS-97,<sup>[37]</sup> SHELXL-97.<sup>[38]</sup>

of 2.600(10) Å. To the best of our knowledge this the first example where borohydride anion shows  $\eta^1$  coordination mode towards central samarium(III) atoms.<sup>[24]</sup> Such kind of coordination modes are rarely observed in transition metal chemistry as well and one example is [Ru(H)(BH<sub>4</sub>)(CO)<sub>2</sub>- $(P(C_6H_{11})_3)_2]$ .<sup>[33]</sup> A steric congestion around the central metal atom presumably prevents the higher coordination mode for the borohydride moieties. The central metal samarium is heptacoordinated and adopts distorted capped octahedral arrangement, where  $BH_4^-$  group acts as a cap to the octahedron. The average Sm-N<sub>pyr</sub> [Sm1-N1 2.533(7), Sm1-N3 2.433(7), Sm1-N5 2.460(7) Å] and Sm-N<sub>imine</sub> distances [Sm1-N2 2.6227, Sm1-N4 2.610(7), Sm1-N6 2.655(7) Å] are in the range of the reported values [2.373(5) -2.561(5) Å] observed in analogous samarium complexes  $[(L-L)Sm_2(THF)_4]$  (L-L = C-C-bonded 1,2-benzenediamine N,N'-bis(pyrrolyl)methylene dimer).<sup>[34]</sup> In the cationic part of the molecule, the potassium atom is hexacoordinate by six THF molecules to adopt an octahedron arrangement.

When compound **1** was treated with erbium tris-borohydride  $[Er(BH_4)_3(THF)_3]^{[9]}$  in THF at ambient temperature, an erbium borohydride complex of composition  $[\eta^2-\{2-(2,6-iPr_2C_6H_3N=CH)C_4H_3N\}Er(\eta^3-BH_4)_2(THF)_2]$  (**3**) was obtained in good yield as pink crystals (Scheme 1).

As the title compound **3** is highly paramagnetic, <sup>1</sup>H or  ${}^{13}C{}^{1}H{}NMR$  spectra were not obtained and therefore **3** was fully characterized by FT-IR spectroscopy, elemental analysis, and the solid-state structure was established by single crystal



Figure 1. Molecular structure of compound 2 showing atom labeling scheme, ellipsoids are drawn to encompass 30% probability, hydrogen atoms are omitted except H1, H2na, H2nb, H2Nc. Shown is only the anionic part of the molecule. Selected bond lengths /Å or angles /°: Sm1–N1 2.453(7), Sm1–N2 2.622(7), Sm1–N3 2.433(7), Sm1–N4 2.610(7), Sm1–N5 2.460(7), Sm1–N6 2.655(7), Sm1–H1 1.23(5), Sm1–B1 2.600(10), N1–Sm1–N2 66.9(2), N3–Sm1–N4 66.7(2), N5–Sm1–N6 66.7(2), N1–Sm1–N3 77.3(2), N1–Sm1–N4 142.2(2), N1–Sm1–N5 76.4(3), N1–Sm–N6 83.8(2).

X-ray diffraction analysis. In the FT-IR spectrum a strong absorption at 2460–2200 cm<sup>-1</sup> was observed and assigned as the characteristic peak for v(B–H) and indicates  $\eta^3\mbox{-}coordination$ mode of the  $BH_4^-$  anions.<sup>[24]</sup> The erbium complex 3 crystallizes in the trigonal space group  $R\bar{3}$  having eighteen molecules in the unit cell (Figure 2). All hydrogen atoms are located in the difference Fourier map and subsequently refined. Unlike samarium complex 2, complex 3 is a neutral molecule and only one bidentate iminopyrrolyl ligand is coordinated to the central erbium atom to form the coordination polyhedron. Thus one five-membered ring Er1-N1-C4-C5-N2 is formed due to coordination of pyrrolyl nitrogen and imine nitrogen atoms. The distances of Er1-N1 [2.336(5) Å] and Er1-N2 [2.482(4) Å] are in the range of reported values of 2.32(8) and 2.559(4) Å for [{(Me<sub>3</sub>Si)<sub>2</sub>NC(NCy)<sub>2</sub>}Er(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub>].<sup>[35]</sup> Additionally two borohydride ligands are attached to the erbium atom in a  $\eta^3$ fashion showing a bond length of Er1-B1 2.535(7) Å. This kind of coordination mode is typical for Ln-BH4 compounds.<sup>[6,24,36]</sup> In the coordination polyhedron two THF molecules are also binding to the erbium metal [Er1-O1 2.345(4) Å, Er1-O2 2.353(4) Å] to give an overall pseudo-octahedral arrangement around the central erbium atom considering BH<sub>4</sub>as pseudo monodentate ligands.

### Conclusions

We have prepared samarium and erbium borohydride complexes supported by N-aryliminopyrrole ligand. In the samarium borohydride complex we observe an unusual  $\eta^1$ -coordination mode of BH<sub>4</sub><sup>-</sup> ligand, whereas for the erbium complex we observe usual  $\eta^3$ -cordination mode of the same BH<sub>4</sub><sup>-</sup> group presumably due to the difference in ion radii of the central metal atoms.



**Figure 2.** Molecular structure of compound **3** showing atom labeling scheme, ellipsoids are drawn to encompass 30% probability, hydrogen atoms are omitted except H2, H1a, H1d, H1e. Selected bond lengths /Å or angles /°: Er1–N1 2.336(5), Er1–N2 2.482(4), Er1–B1 2.535(7), Er1–B2 2.535(7), Er1–O1 2.345(4), Er1–O2 2.353(4), Er1–H1a 2.53(8), Er1–H1d 2.38(8), Er1–H1e 2.39(8), Er1–H1c 2.30(7), Er1–H1f 2.37(7), Er1–H1b 2.34(6), N1–Er1–N2 69.65(15), N1–Er1–B1 158.0(2), N1–Er1–B2 96.4(2), N2–Er1–B1 88.4(2), N2–Er1–B2 166.0(2), N1–Er1–O1 83.15(14), N1–Er1–O2 83.41(15), N2–Er1–O1 87.96(13), N2–Er1–O2 87.10(14), O1–Er1–O2 166.56(14).

#### **Experimental Section**

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenktype glassware either on a dual manifold Schlenk line, interfaced to a high vacuum ( $10^{-4}$  Torr) line, or in an argon-filled M. Braun glove box. THF was pre-dried with sodium wire and distilled in a nitrogen atmosphere from sodium and benzophenone ketyl prior to use. Hydro-carbon solvents (toluene and *n*-pentane) were distilled in a nitrogen atmosphere from LiAlH<sub>4</sub> and stored in the glove box. <sup>1</sup>H NMR (400 MHz) and <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz) spectra were recorded with a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed with a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. [(ImP<sup>Dipp</sup>)K] (1),<sup>[34]</sup> [Sm(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>],<sup>[30]</sup> and [Er(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>]<sup>[9]</sup> were prepared according to the literature procedure.

**Preparation of [η<sup>2</sup>-{2-(2,6-***i***Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)-C<sub>4</sub>H<sub>3</sub>N}<sub>3</sub>Sm(η<sup>1</sup>-BH<sub>4</sub>)-{K(THF)<sub>6</sub>] (2): (ImP<sup>Dipp</sup>)K (1) (300 mg, 1.03 mmol) and (141 mg, 0.34 mmol) of [Sm(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>] were dissolved in THF and the reaction mixture was stirred at ambient temperature for 18 h. White precipitate separated by filtration, and the solvent was evaporated in vacuo giving a pale yellow powder. Yield 225 mg, 47 %. Single crystals were obtained by recrystallization from THF/pentane at -35 \,^{\circ}C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) : \delta = 1.14 (d, J\_{H,H} = 6.68 Hz, 36 H, CH***Me***<sub>2</sub>), 3.18 (sept, J\_{H,H} = 6.5 Hz, 6 H,** *CHMe***<sub>2</sub>), 6.08 (s, 3 H, 4-pyr), 6.15 (s, 3 H, 3-pyr), 6.41 (s, 3 H, 5-pyr), 6.93 (m, 9 H,** *m***,***p***-C<sub>6</sub>H<sub>3</sub>), 7.77 (s, 3 H, N=C-***H***), 0.29 (s, 3 H, H–B***H***<sub>3</sub>), -2.41 (s, 1 H, Sm-***H***-BH<sub>3</sub>), 3.55 (br., 24 H, thf), 1.39(br., 24 H, thf) ppm. <sup>13</sup>C NMR (101.6 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): \delta = 24.36 (12C, CH***Me***<sub>2</sub>), 26.94 (6C, CHMe<sub>2</sub>), 108.94 (3C, 5-pyr), 115.23 (3C, 4-pyr), 122.35 (3C, 3-pyr), 137.44 (6C,** *o***-C<sub>6</sub>H<sub>3</sub>), 129.12 (3C,** *ipso***-pyr), 137.44 (6C,** *o***-C<sub>6</sub>H<sub>3</sub>),** 

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148.15 (3C, *ipso*-C<sub>6</sub>H<sub>3</sub>), 151.21(3C, N=*C*-H), 24.26(12C, thf), 66.45(12C, thf) ppm. **IR** (selected peaks):  $\tilde{v} = 860$  (m), 1034 (s), 1134 (m), 1311 (w), 1625 (vs), 2279 (w), 2867 (m), 2960 (s). C<sub>79</sub>H<sub>124</sub>BKN<sub>6</sub>O<sub>7</sub>Sm (1470.85): calcd. C 64.54, H 8.50, N 5.72%; found C 63.97, H 8.14, N 5.32%.

**Preparation of [η<sup>2</sup>-{2-(2,6-***i***Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)C<sub>4</sub>H<sub>3</sub>N}Er(η<sup>3</sup>-BH<sub>4</sub>)<sub>2</sub>-(THF)<sub>2</sub>] (3): (ImP<sup>Dipp</sup>)K (1) (100 mg, 0.34 mmol) and [Er(BH<sub>4</sub>)<sub>3</sub>-(THF)<sub>3</sub>] (146.37 mg, 0.34 mmol) were dissolved in THF and the reaction mixture was stirred at ambient temperature for another 18 h. Filtration and evaporation of thf in vacuo gives a pink color crystal. Single crystals were obtained by recrystallization from THF/pentane at -35 °C. Yield 142 mg, 70%. <b>IR** (selected peaks):  $\tilde{v} = 801$  (s), 1086 (m), 1166 (s), 1458 (m), 1573 (vs), 2227 (m), 2297 (w), 2446 (m), 2866 (s), 2961 (vs). C<sub>25</sub>H<sub>45</sub>B<sub>2</sub>ErN<sub>2</sub>O<sub>2</sub> (594.5): calcd. C 50.51, H 7.63, N 4.71 %; found C 49.89, H 7.45, N 4.22 %.

X-ray Crystallographic Analyses: Single crystals of compounds 2 and 3 were grown from THF/pentane at -35 °C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made with a Oxford Supernova X-Calibur Eos CCD detector with graphite-monochromatic  $Cu-K_{\alpha}$  (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in the Table 1. The structures were solved by direct methods (SIR92)<sup>[37]</sup> and refined on  $F^2$  by full-matrix leastsquares methods; using SHELXL-97.<sup>[38]</sup> Non-hydrogen atoms were anisotropically refined. All hydrogen atoms are located in the ·difference Fourier map and subsequently refined. The function minimized was  $[\Sigma w (F_0^2 - F_c^2)^2]$  (w = 1/[ $\sigma^2 (F_0^2) + (aP)^2 + bP$ ]), where P =  $(Max(F_o^2,0)+2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The function  $R_1$  and  $wR_2$  were  $(\Sigma ||F_0| - |F_c||)/\Sigma |F_0|$  and  $[\Sigma w (F_0^2 - F_c^2)^2 / \Sigma (wF_0^4)]^{1/2}$ , respectively. The ORTEP-3 program was used to draw the molecule.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-898517 (2) and CCDC-898518 (3) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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