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Facile Synthesis of Lanthanidocenes by the “Borohydride/Alkyl Route” and Their Application in Isoprene Polymerization

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Several borohydridolanthanidocenes were synthesized by means of a straightforward approach starting from equimolar amounts of $Ln(BH_4)_3(thf)_3$ (Ln = Nd, Sm) and *n*-butylethylmagnesium (BEM) in the presence of 2 equiv. of a cyclopentadiene derivative. Depending on the nature of the cyclopentadiene, monometallic $Cp^{*}_2Nd(BH_4)(thf)$ ($Cp^{*} = C_5Me_5$) (**1**), heterodimetallic $[Cp_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_4$ ($Cp = C_5H_5$) (**2**), $[(CMe_2C_5H_4)_2Ln(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ (Ln = Nd, **3a**; Ln = Sm, **3b**), and monometallic anilidocyclopentadienyl compounds $(C_5Me_4CH_2SiMe_2NPh)Ln(BH_4)(thf)_2$ (Ln = Nd, **4a**; Ln = Sm, **4b**) were isolated. The complexes were characterized by ^1H NMR spectroscopy, elemental analysis, and X-ray structural analysis. $Mg(BH_4)_2(thf)_3$ (**5**) was isolated as a byproduct and structurally characterized, revealing an unprecedented structural arrangement. In combination with BEM, complexes **2a**, **3a**, and **4a** were found to be efficient in isoprene polymerization to afford highly stereoregular *trans*-polyisoprene. Similar results were obtained by an ″all in situ″ approach starting from $Nd(BH_4)_3(thf)_3$/BEM mixtures in the presence of 2 equiv. of cyclopentadiene derivative.

Introduction

Organometallic chemistry of the rare earths has been the subject of increasing interest over the past two decades, with high impact in the field of molecular catalysis[1] and particularly polymerization.[2] Most organometallic syntheses are carried out by ionic metathesis and with the very common trihalide derivatives LnX_3 (X = Cl, Br, I) as starting materials, but we and others have shown that the tris(borohydride)s $Ln(BH_4)_3(thf)_n$ ($n = 2,3$)[3] could be a valuable alternative in this frame.[4] More soluble, the latter precursors allowed the isolation, by ionic metathesis, of a growing assortment of organometallic structures, including mono- or bis(cyclopentadienyl)-supported borohydrides.[3,4] It was also observed that, depending on the substituents on the Cp group, half-sandwich borohydrido complexes, which were found to be more stable than their halo homologues versus comproportionation reactions, could be easily isolated.[4b,4c]

We just developed an advantageous one-pot synthetic pathway for the preparation of organolanthanides, which starts from the tris(borohydride)s, as an alternative to the classical ionic metathesis. This approach, which we called the “borohydride/alkyl route” (or B/A route), consists of the reaction of a $Ln(BH_4)_3(thf)_3$ compound, a cyclopentadienyl reagent in its protonated form (i.e. cyclopentadiene), and a stoichiometric amount of a dialkylmagnesium reagent.[5] Using this strategy, we were able isolate in high yield a new family of heterodimetallic trinuclear half-sandwiches of general formula $[Cp^RLn(BH_4)_3]_2[Mg(thf)_6]$ ($Cp^R = C_5H_4$, $CpPh_3$, C_5Me_5; Ln = Nd, La). We then wanted to validate this synthetic strategy and to extend it to the preparation of lanthanidocenes. For this purpose, we chose four different cyclopentadienyl-type ligands: the usual Cp*H ($Cp^* = C_5Me_5$), the nonsubstituted CpH ($Cp = C_5H_5$), an *ansa* ligand bearing a tetra(methyl)ethylene bridge $(CMe_2C_5H_5)_2$, and an anilidocyclopentadienyl ligand $HC_5Me_4CH_2SiMe_2NHPh$ recently prepared by Okuda et al.[6] These cyclopentadiene reagents were chosen in order to generalize our approach as an efficient synthetic method.

We describe in this contribution the synthesis and characterization of several new borohydridolanthanidocenes (For reasons of convenience, the term “lanthanidocenes” refers to all mono(borohydrido) disubstituted complexes described in this manuscript, including **4a** and **4b**.) obtained by this B/A route. All complexes were structurally characterized. Some results in isoprene polymerization involving isolated and in situ synthesized complexes are also presented.

Results and Discussion

Synthesis of Complexes 1–4

The mono(borohydrido) disubstituted complexes, $(C_5Me_5)_2Nd(BH_4)(thf)$ (**1**), $[(C_5H_5)_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_4$ (**2**), $[(CMe_2C_5H_4)_2Ln(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ (Ln = Nd, **3a**; Ln = Sm, **3b**), and $(C_5Me_4CH_2SiMe_2NPh)Ln$-

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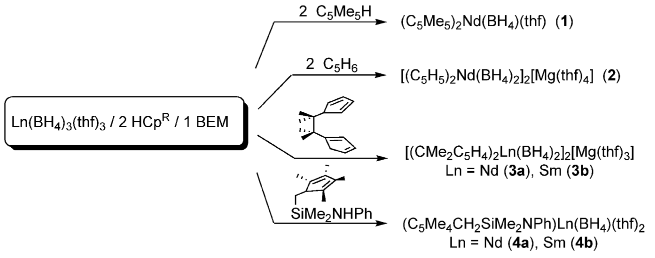
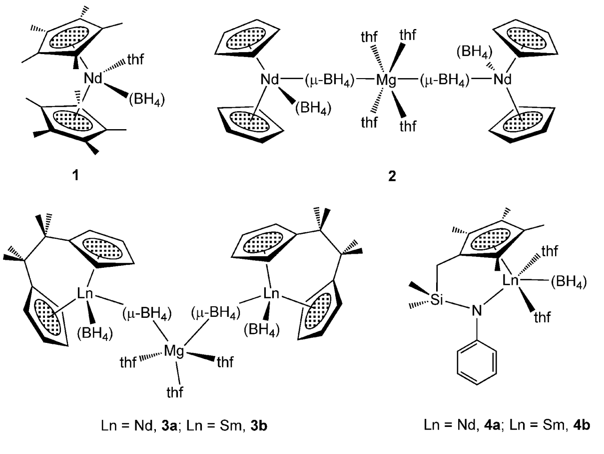
$(BH_4)(thf)_2$ (Ln = Nd, **4a**; Ln = Sm, **4b**), were prepared starting from the protonated form HCp^R (given for a general substituted cyclopentadiene) by the straightforward reaction described in Scheme 1, that is, addition of one equivalent of BEM (*n*-butylethylmagnesium) to a solution of $Ln(BH_4)_3(thf)_3$ in the presence of 2 equiv. of HCp^R.



Scheme 1. Synthesis of complexes **1**–**4** by the B/A route.

As shown by preliminary ^1H NMR spectroscopy-monitored syntheses, the reaction was in every case immediate and quantitative. Running the reaction in bulk is very simple, since no refluxing is necessary: the mixture is stirred at room temperature for a couple of hours to make sure that the reaction is complete (the reaction is immediate on the NMR scale) and until the color change is obvious.

With HCp* (Cp* = C_5Me_5), the ^1H NMR spectrum of the resulting compound showed the presence of a compound containing two Cp*, one BH_4, and approximately four thf ligands. This spectrum was identical to that of the neodymocene $Cp^*_2Nd(BH_4)(thf)$ (**1**, Scheme 2), which had been previously and alternatively prepared by ionic metathesis and structurally characterized.[4d] From the bulk synthesis, crystals of this neutral monometallic complex were isolated in low yield (24%), along with intractable blue oil, which did not afford more crystals.



Scheme 2. Molecular structures of complexes **1**–**4**.

The same strategy was undertaken with the nonsubstituted C_5H_5H. Prior to the synthesis of a bis(cyclopentadienyl) compound, we first checked by ^1H NMR spectroscopy (C_6D_6) that $Nd(BH_4)_3(thf)_3$ did not react with freshly cracked cyclopentadiene alone, even at 70 °C for prolonged reaction times. On the bulk scale, we found that it was necessary to perform the reaction in the presence of thf in order to improve the yield of isolated product. After experimental work-up, blue microcrystalline solid **2** was isolated in high yield (91%). According to an X-ray analysis of suitable crystals obtained after recrystallization (thf/pentane), the molecular formula was found as $[(C_5H_5)_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_4$ (Scheme 1). Elemental analysis was found to match a tris(thf) adduct, which denotes the tendency to lose one thf molecule (see further). In the case of the *ansa*-cyclopentadienyl ligand $(CMe_2C_5H_4)_2$, the reaction afforded, after extraction of the crude product with thf, crystalline complex $[(CMe_2C_5H_4)_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ (**3a**, Scheme 1) (from X-ray data and elemental analysis) in good yield (70%). Samarium analogue **3b** (Scheme 1) could also be isolated and characterized by X-ray crystallography and ^1H NMR spectroscopy. However, it was not possible to get a satisfactory elemental analysis result for this compound, possibly because of a partial loss of a $Mg(BH_4)_2$ unit. To confirm the molecular structure of **3b**, the latter was treated with 2 equiv. of allylLi(dioxane) in the NMR tube (C_6D_6). As expected, a bis(allyl) derivative (Scheme 3), a homologue of the dimethoxyethane adduct previously described by some of us,[7] was obtained immediately and quantitatively.

$$\mathbf{3b} + 2\ \mathrm{Li(allyl)(dioxane)} \longrightarrow [Me_4C_2(C_5H_4)_2]Sm(allyl)_2(dioxane)(thf)_x$$

Scheme 3. Formation of a bis(allyl) derivative from **3b**.

Finally, by using the B/A route, complexes **4a** and **4b** (Scheme 1) were isolated from the reaction in thf of the starting tris(borohydride) with the aniline-tethered cyclopentadiene ligand $(C_5Me_4)CH_2SiMe_2NHPh$ recently described by the group of J. Okuda.[6] X-ray structure determination established that both complexes are mononuclear and monomeric.

X-ray Structures of Complexes 2–4

Complex **2** is a very rare example of nonsubstituted cyclopentadienyl lanthanidocene in the early series.[1a] It is a dimetallic trinuclear Nd_2Mg compound that crystallizes in the monoclinic $P2_1/c$ space group (see Figure 1). The unit cell comprises two nonsymmetrical Nd_2Mg subunits, in which each neodymium is linked to the magnesium atom through a mono-BH_4 bridge, with a quasi-linear arrangement of the three metal atoms [Nd3–Mg1–Nd1 = 176.29(7)°]. The Nd–Mg distances are between 5.518(4) and 6.008(4) Å, which accounts for a rather covalent trimetallic compound, in contrast to observations in the corresponding half-sandwich series, where discrete ionic moieties were clearly identified $[(C_5H_5)Nd(BH_4)_3^-$, $Mg(thf)_6^{2+}$, $(BH_4)_3$-

$Nd(C_5H_5)^-$, Nd–Mg distance 7.22 Å].[5a] However, the two Nd–B–Mg bridges are found to be clearly dissymmetric [Mg1–B1 2.656(11) Å, Mg1–B7 3.253(10) Å], and if the Nd–B distances fall in the commonly observed range for (μ-BH_4) dimers,[4a,8] one can observe one particularly short Nd–B bridge length [Nd3–B7 2.738(10) Å]. Therefore, the molecular arrangement is better described as: $[(C_5H_5)_2Nd(BH_4)_2][Mg(BH_4)(thf)_4][(C_5H_5)_2Nd(BH_4)]$.

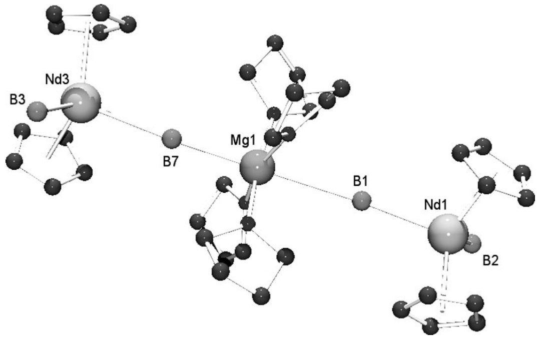


Figure 1. One of the two entities of the asymmetric unit showing the molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg1–Nd1 5.518(4), Mg1–Nd3 5.918(4), Nd1–B1 2.905(10), Nd1–B2 2.657(12), Nd3–B3 2.652(12), Nd3–B7 2.738(10), Mg1–B1 2.656(11), Mg1–B7 3.253(10), Nd3–Mg1–Nd1 176.29(7).

Mg–B distances are in the range 2.65–3.33 Å [Mg1–B1 2.656(11), Mg1–B7 3.253(10), Mg2–B5 2.613(13), Mg2–B6 3.332(13) Å]. The consequence of one long Mg–B distance in each subunit is the presence of four molecules of thf coordinated to the magnesium atom in **2** (Mg–O mean value 2.06 Å), which denotes a partial ionic character of the magnesium moiety (in contrast to complex **3a**, see further), while six thf molecules were necessary to complete the coordination sphere in the true cationic Mg moiety of ionic half-lanthanidocenes.[5] Despite the fact that the hydrogen atoms could not be located due to the poor quality of the crystal, Nd–B distances clearly indicate that the bridged BH_4 here are η^2 rather than η^3 coordinated, whereas each neodymium center in **2** bears one additional terminal BH_4, most likely trihapto according to the Nd–B distance observed (Nd–B is typically between 2.62 and 2.66 Å for an η^3 coordinated BH_4).[4,9]

Complexes **3a** and **3b** $\{[(CMe_2C_5H_4)_2Ln(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ Ln = Nd, Sm$\}$ are isostructural, and both crystallize in the $P\bar{1}$ space group. Both can be described as dimetallic trinuclear structures (Figure 2), as complex **2**, but the trinuclear arrangement in **3a** (or **3b**) is bent, with a Nd–Mg–Nd angle of 88.29(5)° [88.68(6)° in **3b**], in sharp contrast to that observed in **2**. This is likely related to the pentacoordinate trigonal bipyramidal geometry of the magnesium center, which bears only three thf molecules (one additional thf was found in **2**). The magnesium is linked to both lanthanide centers through a typical η^2 BH_4 bridge (hydrogen atoms belonging to BH_4 groups could be located for **3a**), and this $Mg(BH_4)_2$ moiety appears to be almost symmetrical [Mg–B distances: 2.467(12) and 2.511(12) Å in **3a**]. Since, on the other hand, the two Nd–B distances (bridging BH_4) are approximately equal to each other as well (mean value 2.80 Å), one can think that each BH_4 group is shared equivalently between Mg and Nd atoms, with shorter intermetallic distances [4.888(4) and 5.066(4) Å] relative to those in complex **2**. Therefore, the molecular arrangement in **3a** (and **3b**) can be seen as including a more covalent $Mg(BH_4)_2$ unit than that in **2**, that is, $(CMe_2C_5H_4)_2Nd(BH_4)(\mu\text{-}BH_4)Mg(thf)_3(\mu\text{-}BH_4)(BH_4)Nd(C_5H_4CMe_2)_2$. In both cases, the lanthanide (Nd or Sm) bears a second BH_4 group in a terminal η^3 mode, allowing a short mean Ln–B (terminal) distance of approximately 2.62 Å (2.59 Å for **3b**). Mg–O distances are found to be smaller in **3a** (mean value 2.04 Å) than in complex **2**. The CP–Nd–CP (CP is the centroid of a cyclopentadienyl ring) angles (115.4 and 116.0° in **3a**, 116.1 and 117.1° in **3b**) are comparable to those observed in other complexes in this *ansa* series[10] and are, as expected, lower than those in complex **2** (mean value 121.4°), which clearly demonstrates the constrained effect of the (CMe_2–CMe_2) link. Finally, it should be noted that the two cyclopentadienyl cycles have an almost eclipsed conformation when viewed perpendicular to the $[Nd(BH_4)_2]$ plane, as already observed with such a ligand,[10] with a mean torsion angle C(Cp)–CMe_2–CMe_2–C(Cp) of 38.20° (37.59° for **3b**).

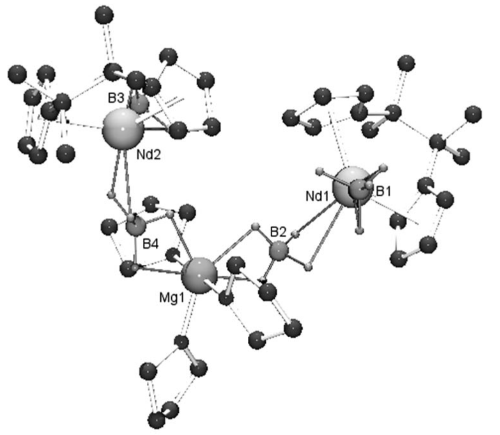


Figure 2. Asymmetric unit showing the molecular structure of **3a**. Non-BH_4 hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg1–Nd1 5.066(4), Mg1–Nd2 4.888(4), Nd1–B2 2.834(14), Nd1–B1 2.629(10), Nd2–B3 2.613(8), Nd2–B4 2.773(13), Mg1–B4 2.511(12), Mg1–B2 2.467(12), Nd1–Mg1–Nd2 88.29(5).

Complexes **4a** and **4b** $[(C_5Me_4CH_2SiMe_2NPh)Ln(BH_4)(thf)_2$, Ln = Nd, **4a**; Ln = Sm, **4b**] crystallize in the *Pnma* space group and are isostructural. The molecular structure shows a distorted square pyramidal arrangement, similar to that observed with yttrium,[6] with a base around the lanthanide atom comprising two thf, one BH_4, and one anilido ligand (Figure 3).

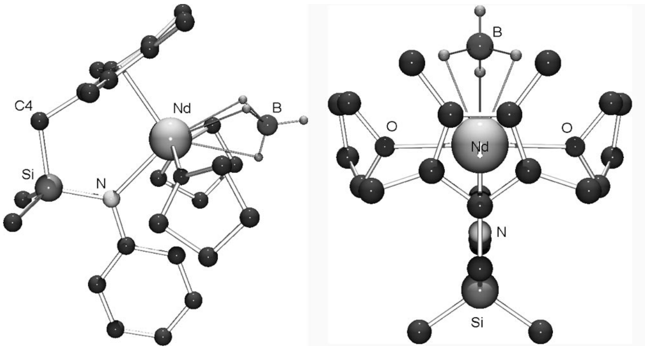


Figure 3. Molecular structure of **4a** (symmetrical subunit, top view, left; side view, right). Non-BH_4 hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Nd1–B1 2.706(8), Nd1–O1 2.534(4), Nd–N 2.362(5), Nd–CP 2.42, N–Nd–B 142.5(2), Nd–N–C_{ipso} 118.9(4), C4–Si–N 107.4(3).

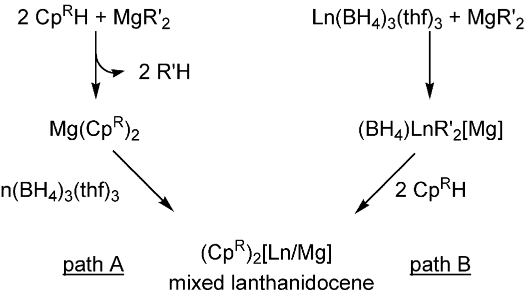
The B/A Route

The one-pot strategy used to prepare the lanthanidocenes (and related compounds) described in this paper displays several advantages: (1) it involves the easily available tris(borohydride)s as starting materials; (2) the tedious preparation of the anionic Cp^RM reagent (M = alkaline metal) used for ionic metathesis can be avoided; (3) it requires short-time reactions at room temperature and affords quantitative yields; (4) work-ups are simplified, as there is no inorganic precipitate to eliminate.

Straightforward alternative synthetic routes to circumvent the drawbacks of ionic metathesis, that is, formation of salts and disproportionation reactions as a result of the use of thf, have been developed in the literature. The "silylamide route",[11] described by Anwander, involves amido starting materials, and this methodology requires heating toluene at reflux for a long time. More recently, the same author published another approach starting from tretraalkylaluminolanthanide compounds, which also allows the preparation of complexes at room temperature within short reaction times.[12] However, it was recalled in this paper that the volatile byproduct $AlMe_3$ reacts violently when exposed to air. Other methods use hydrocarbyl LnR_3 derivatives,[13] which are known to be thermally sensitive and hence not easy to store and manipulate, in contrast to the very stable tris(borohydride)s.

Mechanism of Formation by the B/A Route

In order to ensure the formation of the desired product, the dialkylmagnesium reagent must be added to a solution of lanthanide tris(borohydride) in the presence of the cyclopentadiene reagent. Two mechanistic pathways can be envisaged to rationalize the formation of the (dimetallic) complexes, as represented in Scheme 4.



Scheme 4. Possible pathways leading to the mixed Ln/Mg lanthanidocenes.

To probe which of the two possible pathways occurs, we ran a reaction according to path A in an NMR tube starting with bis(cyclopentadienyl)magnesium. One equivalent of $Nd(BH_4)_3(thf)_3$ was added to Cp_2Mg in C_6D_6. The reaction was found to be very slow (see Experimental Section) and needed 48 h at 50 °C to finally lead to a mixture of Cp_3Nd (40%) and $Cp_2Nd(BH_4)$ (60%). On the other hand, we had already observed by NMR spectroscopic monitoring that the reaction of $Nd(BH_4)_3(thf)_3$ with BEM affords a rapid darkening of the solution, along with formation of α-olefins, probably resulting from β-H elimination.[14] Thus, since it is well known that LnR species instantaneously react with cyclopentadienes,[13a] it is likely that the lanthanidocenes presented in this work are formed according to path B.

Heterodimetallic vs. Monometallic Complexes

The results presented above show that the molecular structure of complexes **1**–**4** strongly depends on the nature of the precursor ligand, affording trinuclear dimetallic or monometallic compounds. Regarding the dimetallic complexes, a $Mg(BH_4)_2(thf)_n$ moiety is found to be included in the structure, under a rather ionic "$Mg(BH_4)(thf)_4{}^+$" (in **2**), or neutral $Mg(BH_4)_2(thf)_3$ (in **3a**,**b**) form. It is noteworthy that the half-sandwich compounds already prepared using the same B/A route all display an ionic $[Cp^RLn(BH_4)_2]^-[Mg(thf)_6]^{2+}[(BH_4)_2LnCp^R]^-$ form, as mentioned previously.

Mixed lanthanide/magnesium complexes are rather scarce in the organometallic chemistry of the lanthanides and result mostly from syntheses involving Mg alkylating reagents in stoichiometric amounts. Actually, a small number of them have been structurally characterized. Moreover, catalytic combinations in polymerization reactions involving a lanthanide-based precatalyst associated to a magnesium cocatalyst have been largely developed since the 1980s, and heterodimetallic species have often been proposed as acting as active species.[4d,14,15] As far as we know, just one example resulting from a catalytic combination, $[Nd(thf)(\mu^3\text{-O}t\text{Bu})_2(\mu^2\text{-O}t\text{Bu})_2(\text{O}t\text{Bu})Mg_2(CH_2SiMe_3)_2]$, could be isolated.[16] Regarding organometallic syntheses, mono(cyclopentadienyl)lanthanide complexes have been cited as incorporating a MgX_2 molecule (X = halide), but the structure of these complexes remain unclear because crystallographic studies were not carried out.[17] In the *ansa* series, the reaction of $[CMe_2(C_5H_4MgCl)_2(thf)_4]$ (in 50% excess) with $SmCl_3$ in thf was reported to afford $[(CMe_2C_5H_4)_2Sm(\mu-Cl)_2MgCl(thf)_3(thf)]_2$.[10b] In this complex, the dimer comprises two Mg–Sm subunits, linked together through $Sm(\mu-Cl)_2Sm$ bridges. The $MgCl_2$ moiety is not shared between the two samarium atoms, as in complex **3a** (or **3b**), but each magnesium atom is associated to its samarium counterpart through a bis(chlorido) bridge and bears three additional thf ligands. The Mg–Sm distance is 4.26(4) Å, revealing a strong interaction through the Cl bridges. By varying the experimental conditions (1:1 *ansa* ligand vs. Sm), the same authors isolated a monometallic (i.e. without any Mg included) samarocene.[10c] This emphasizes the occurrence (and thus the difficulty of predicting) of the dissociation of a $MgX_2(thf)_n$ moiety from a dimetallic association in the $(CMe_2C_5H_4)_2$ series, as we observed during the synthesis of **3a**,**b** (vide supra). A few years ago, in the same *ansa* series, the presence of a $MgCl_2$ unit was clearly established by XPS analysis in the molecular formula of allyl complexes bearing this bridging ligand.[18] Unfortunately, none of them yielded suitable crystals for X-ray studies. Other allyllanthanide complexes including $MgCl_2$,[19] or more recently $Mg(allyl)_2$,[20] were also described. The magnesium moiety does not act as a bridging ligand between two lanthanide atoms in the latter compound, in contrast to observations in the present work. Moreover, depending on the experimental conditions, mixed Ln/Mg dimetallic or monometallic complexes were isolated as well.

In the course of our previous studies devoted to borohydridolanthanide-based polymerization catalysts, it was postulated that $Nd(\mu-BH_4)Mg$ species, coming from the binary Ln/MgR_2 catalytic systems used,[4d,14,15c,15d,15e] could be related to the high *trans*-selectivity observed for isoprene polymerization. The unprecedented isolation of complexes **2**, **3a**, and **3b** supports well the hypothesis that a borohydride bridge can indeed efficiently link Nd and Mg moieties. One can note that with the poor electron-donating C_5H_5 or $(C_5H_4CMe_2)_2$, the magnesium moiety is retained within the molecular structure. However, during attempted crystallizations of **3a**, large colorless crystals of a byproduct were also isolated. This compound was further identified, by ^1H NMR spectroscopy and X-ray diffraction studies, as $Mg(BH_4)_2(thf)_3$ (**5**) (Figure 4). As the cell parameters were different from those of the published data,[21] a full X-ray structure determination was carried out. We found that the isolated compound corresponded to the same molecular formula, $Mg(BH_4)_2(thf)_3$, but in a different unprecedented crystalline form.

Compound **5** crystallizes in the $P\bar{1}$ group. BH_4 hydrogen atoms could be located despite the low quality of the crystal (**5** was found to be highly reactive towards moisture), and Mg–B distances fit well with a dihapto $Mg(\mu-H)_2(BH_2)$ terminal BH_4 ligand.[22] It is therefore possible that, if the $Mg(BH_4)_2$ moiety displays a covalent character, it may be leached from the heterodimetallic trinuclear structure. This supports well the overall neutral character of complex **3a** (and **3b**), $Mg(BH_4)_2(thf)_3$ acting as a simple donor ligand towards the lanthanide center. It is to be noted that, with the electron-rich Cp* and using the B/A route as synthetic strategy, monometallic $Cp^*_2Nd(BH_4)(thf)$ complex **1** was isolated. The BH_4 group seems to bring enough electronic density along with the two Cp* groups to ensure the formation of neutral compound **1**, in contrast to its chlorido homologue, which is generally obtained in an "ate" $Cp^*_2NdCl_2M(ether)_2$ form (M = alkaline metal) [$Cp^*_2NdCl(thf)$ has, however, been cited in the literature].[1a] The molecular structure of **1**, prepared by ionic metathesis, was solved by us recently.[4d] The CP–Nd–CP angle (133.18°) may prevent the formation of an ionic ate complex, when compared with less substituted neodymocenes, though the "$Cp^*_2NdCl_2$" unit is highly stable in this series. The isolation of neutral monometallic **1** by the B/A route thus most likely proceeds by loss of a $[Mg(BH_4)_2]$ unit, which compares well with the different behavior of the neodymium complex in the *ansa* series (see above, molecular structure of **3a**,**b**).

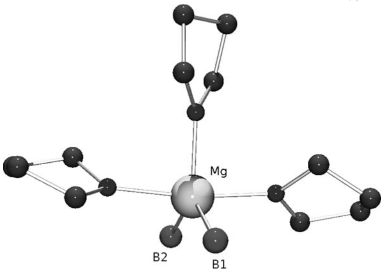


Figure 4. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg–B1 2.438(7), Mg–B2 2.496(7), Mg–O (average) 2.07, B1–Mg–B2 128.7(3).

Complexes **4a** and **4b** exist as mononuclear bis(thf) adducts. The coordination number (CN) of the lanthanide atom is 9 in complexes **1**, **2**, and **3a** (**3b**). Complex **4a** (**4b**) displays the same CN value if one considers the linked anilidocyclopentadienyl ligand as a L_3X_2 one.[23] The Nd–N distance in **4a** is quite long [2.362(5) Å] and slightly higher than usual ones (ca. 2.20–2.30 Å with late lanthanoids) for linked amidocyclopentadienyl complexes.[6,23,24] Likewise, Nd–O and Nd–CP distances are rather long as well (average 2.53 and 2.42 Å, respectively) when compared to those found for the yttrium analogue.[6] These structural features do not speak in favor of a poor electron density at the metal center, in contrast to what is generally observed in the Cp-amido "CGC" family. It is noteworthy that isolated complexes **4a** and **4b** are "$Mg(BH_4)_2$-free": the anilido moiety obviously hampers the coordination of the latter. As a consequence, the $Nd(BH_4)$ moiety is trihapto, and it is to be mentioned that, as observed during the preparation of **3a**, $Mg(BH_4)_2(thf)_3$ was obtained as a byproduct, under the same unprecedented crystalline form as before. Finally, since there is obviously enough space to coordinate a bis(borohydrido)magnesium moiety in complexes **4**, the preference of a thf molecule over a $Mg(BH_4)_2(thf)_3$ in the latter, as well as in **1**, may be attributed to electronic factors rather than to steric ones. To the best of our knowledge, complexes **4a** and **4b** are the first borohydrido derivatives supported by this linked anilidocyclopentadienyl ligand, and thus $C_5Me_4CH_2SiMe_2NPh$ appears also well-suited for larger lanthanides.

Finally, one can observe that in all the heterodimetallic complexes, the thf molecules are in every case coordinated to magnesium rather than to the lanthanide atom, which denotes a higher oxophilicity of the former element.

^{1}H NMR Spectroscopic Analysis

Despite the paramagnetism of the lanthanides, all ^{1}H NMR signals could be assigned (Table 1). The ^{1}H NMR spectrum of complex **4a** is given as an example in Figure 5. It was interpreted on the basis of DEPT (distortionless enhancement by polarisation transfer) 135 and ^{1}H-^{13}C HSQC (^{1}H single quantum coherence) experiments.

Table 1. ^{1}H NMR spectroscopic data for complexes **1**–**4** (in C_6D_6 at 300 K; δ in ppm vs. TMS).

Comp.	**1**[a]	**2**[b]	**3a**	**3b**	**4a**	**4b**
Cp(*H*)	–	5.4	32.0 (4H) –20.0 (4H)	14.9; 8.1 (4 H, 4 H)	–	–
Cp(*Me*)	9.8 (30H)	–	–	–	14.8 (6H) –9.0 (6H) 14.6 (2H)	–2.0 (6H) 1.1 (6H) 3.6 (2H)
C*Me*$_2$ / Si*Me*$_2$	–	–	–1.5 (12H)	1.7 (12H)	14.4 (6H)	1.8 (6H)
o-Ph	–	–	–	–	2.9 (2H)	6.5 (2H)
m-Ph	–	–	–	–	7.8 (2H)	7.3 (2H)
p-Ph	–	–	–	–	5.4 (1 H)	7.1 (1 H)
B*H*$_4$	35.1 (4H)	[c]	14 (8H)	–5.4 (8H)	35.0 (4H)[d]	–1.3 (4H)
thf	–11.7 (4H) –34.9 (4H)	–	2.2 (12H) 0.9 (12H)	2.7 (12H) 0.8 (12H)	–4.2 (8H) –6.6 (8H)	2.1 (8H) 0.4 (8H)

[a] Identical with data in ref.[4d] [b] In [D_8]thf. [c] May be lost in the baseline. [d] At 323 K.

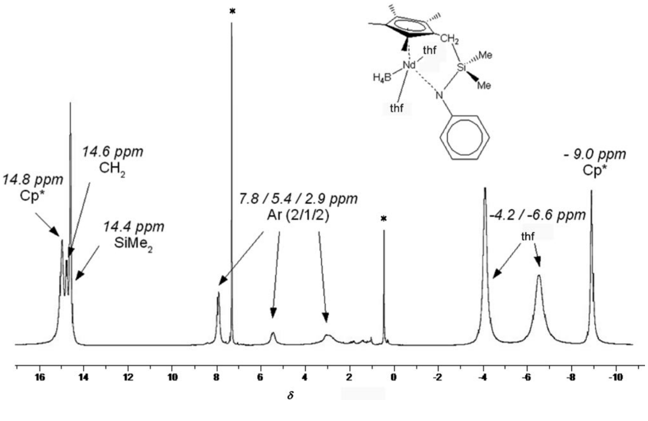


Figure 5. ^{1}H NMR spectrum of complex **4a** in C_6D_6 at 300 K (the BH_4 signal appears in the range 30–40 ppm at higher temperatures; * residual C_6D_5H, silicon grease).

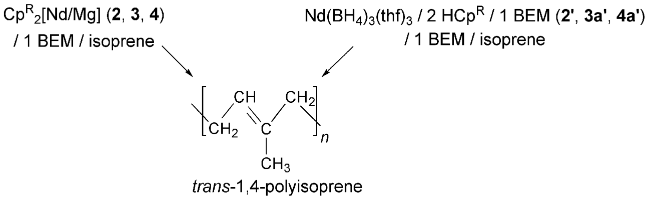
The spectrum of **2** showed the presence of two additional compounds in [D_8]thf, which denotes a disproportionation (so-called "ligand scrambling") process in this polar solvent (Scheme 5), as commonly reported for this chemistry.[23,25] Cp_3Nd[26] (17%), the monocyclopentadienyl derivative[5a] (17%), and the metallocene (66%) were identified. It is noteworthy that, if structurally characterized Cp_2LnX compounds are very scarce with the larger lanthanides,[1a] this is probably connected to the occurrence of such disproportionation reactions in solution.

$$2\ Cp_2Nd(BH_4)(thf)_x \rightleftharpoons CpNd(BH_4)_2(thf)_y + Cp_3Nd$$

Scheme 5. Disproportionation of **2** in thf solution (Mg moiety omitted).

Isoprene Polymerization Catalysis

Catalytic systems combining a lanthanide precatalyst and a magnesium cocatalyst are well known to be highly efficient towards olefins,[2e,4d,15a,15d,27] conjugated dienes,[2a,5,14,15c,28] styrene,[29] and copolymerizations.[15e,30] Using such dual catalysts, it has been proposed that the reaction proceeds through Ln/Mg dimetallic active species. We and others demonstrated in this frame that borohydridolanthanide precatalysts compare well with the more conventional chloride ones regarding activities and selectivities.[4d,30d] When we used the B/A route to prepare hemilanthanidocenes, this approach also allowed the rapid screening of the impact of a given ligand towards the reactivity in polymerization by an "all in situ" approach, consisting of both preparing and alkylating the precatalyst in situ as represented in Scheme 6 (right).[5b,29c,31]



Scheme 6. Isoprene polymerization with isolated (left) and in situ generated (right) complexes as precatalysts.

We tested the metallocenes presented in this work in isoprene polymerization, in the presence of BEM as cocatalyst, and the results were compared to the "all in situ" approach (Scheme 6). In this frame, the *ansa*-$(HC_5H_4CMe_2)_2$ ligand was of particular interest, because we had prepared some years ago several complexes of samarium and neodymium in this series, which revealed high efficiency for homo- and copolymerizations.[7,18,32] Selected results are given in Table 2.

Not surprisingly, these catalysts are not as active as the half-sandwich derivative $Cp^*Nd(BH_4)_2(thf)_2$,[14] likely due to steric limitations. The low yield observed with precatalysts **2** and **2′** (runs 1, 2) may be related to their poor solubility in toluene and to a possible ligand scrambling in solu-

Table 2. Isoprene polymerization with isolated (**2**, **3a**, **4a**) and "in situ" synthesized (**2′**, **3a′**, **4a′**) precatalysts.

Run[a]	Precatalyst	Yield [%]	*trans*-1,4 [%][b]	3,4 [%]	M_n(exp.)× 10^{-3} [gmol^{-1}][c]	PDI[d]
1	**2**	18	90.0	9.0	21.3	1.80
2	**2′**	27	81.2	8.0	15.0	1.40
3	**3a**	72	92.5	6.5	9.9	2.12
4	**3a′**	83	93.1	5.9	12.1	1.76
5	**4a**	83	85.2	14.5	8.4	1.73
6	**4a′**	82	84.9	14.3	17.5	1.57

[a] Experimental conditions: V(isoprene) = V(toluene) = 1 mL, [isoprene]/[Nd] = 1000, [BEM]/[Nd] = 1, T = 50 °C, t = 72 h. [b] Determined by ^{1}H and ^{13}C NMR spectroscopy, residual proportion = *cis*-1,4 defects. [c] Determined by size exclusion chromatography (SEC), with a correction factor of 0.5.[33] [d] Polydispersity index M_w/M_n.

tion, as noted above. All the catalysts are highly *trans*-selective, the most selective ones being observed in the *ansa*-$(C_5H_4CMe_2)_2$ series, as expected.[7,18] The 3,4-content observed with anilidocyclopentadienyl-supported complexes could be explained by a single η^2 coordination of the monomer to the metal center rather than by an η^4 one,[34] due to the presence of the anilido group, which was already suspected to hamper the inclusion of a $Mg(BH_4)_2$ moiety in **4a**. Interestingly, there is a good correlation between the results obtained with the isolated and the in situ generated precatalysts, which clearly validates the in situ B/A route as an efficient strategy to rapidly screen the efficiency of a series of ligands towards a catalytic polymerization process. Moreover, polymolecularities are significantly lower with precatalysts **2′**, **3a′**, **4a′**, which may be related to a faster initiation stage with the latter ones, as compared to **2**, **3**, **4**. This may be connected to the dissociation of isolated complexes in solution to generate the active species.

Conclusions

The synthetic strategy described in this work allows the one-pot preparation, in good yields, of lanthanidocene-like complexes, by simply starting from the protonated form of the ligand. Depending on the stoichiometry of the Cp^RH ligand, it is now demonstrated that lanthanidocenes can be easily prepared by the B/A route, as already shown for hemi-lanthanidocenes. It is noteworthy that the nature of the HCp^R ligand has a strong impact on the molecular structure of the isolated complex. With the simple C_5H_5, or a monosubstituted cyclopentadienyl ligand, mixed Ln/Mg dimetallic compounds are obtained, whereas monometallic neutral complexes are provided by a reaction with a peralkyl-substituted ligand. The Ln/Mg mixed dimetallic complexes are the first examples of compounds comprising a BH_4 group linking a lanthanide and a magnesium center, which supports well the hypothesis of formation of Ln(μ-BH_4)Mg active species involved in previously reported catalytic processes. An unprecedented crystalline form of $Mg(BH_4)_2(thf)_3$ could also be isolated during the course of our organometallic syntheses, as an example of polymorphism that exists in magnesium chemistry. The results presented in isoprene polymerization clearly validate the B/A route as an efficient method to assess a given ligand, directly used in its protonated form, in polymerization experiments.

Experimental Section

Materials and Methods: The solvents were dried with sodium/benzophenone ketyl, deoxygenated by distillation, and stored on molecular sieves (3 A) in a glovebox. They were condensed directly in the reaction flask by trap-to-trap distillation. Isoprene (Aldrich) was dried with calcium hydride, distilled twice, and stored over molecular sieves (3 A) in a glovebox. C_5H_6 was freshly cracked before use. BEM (*n*-butylethylmagnesium, 20% solution in hexanes, Texas Alkyl), $(C_5H_5)_2Mg$ (Aldrich), and Cp*H (Aldrich) were used as received. $Nd(BH_4)_3(thf)_3$,[35] allylLi(dioxane),[36] $C_5Me_4CH_2SiMe_2NHPh$,[6] and $(CMe_2C_5H_5)_2$[37] were synthesized as previously reported. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 instrument at 300 K, with specific DEPT and HSQC Bruker sequences when necessary. The chemical shifts were calibrated by using the residual resonances of the solvent. Elemental analyses were carried out by the Centre d'Analyses de l'Université de Dijon. Size exclusion chromatography (SEC) was performed in thf as eluent at 40 °C with a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel column (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards. A correction factor of 0.5 was applied for the determination of the true number-average molecular weight of polyisoprenes.[33]

Crystallographic Data: Crystallographic and refinement data for complexes **2**–**5** are gathered in Table 3. A parallelepiped-shaped crystal with the dimensions reported in Table 3 was mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer (platform with full three-circle goniometer). The diffractometer was equipped with a 4 K CCD detector set 55.0 mm from the crystal. The crystal was cooled to 100(1) K with an OXFORD CRYOSTREAM 700 low-temperature device. Intensity measurements were performed by using graphite monochromated Mo-K_α radiation from a sealed ceramic diffraction tube (SIEMENS). Generator settings were 50 kV 40 mA^{-1}. APEX2[38] was used for preliminary determination of the unit cell constants and data collection control. Data integration and global cell refinement was performed with the program SAINT.[39] The final unit cell was obtained from the *xyz* centroids of the number of reflections reported in Table 3 for each complex. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, on the basis of the intensities of symmetry-related reflections measured at different angular settings (SADABS),[40] and reduced to F_o^2. The program suite JANA2006 was used for space group determination and full-matrix least square refinements based on F.[41] They were solved by direct methods with the program SIR97.[42] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Except hydrogen atoms pertaining to B, the positions of hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries, and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Note that the crystal quality for complexes **2** and **3b** was not satisfactory enough to allow the location of BH_4 hydrogen atoms. The structures were refined to the final agreement factors given in Table 3. CCDC-764030, -764034, -764035, -764031,

Table 3. Summary of crystal and refinement data for complexes **2**–**5** [recorded at T = 100 K; with $\lambda_{(\text{Mo-}K\alpha)}$ = 0.71073 Å].

Compound	**2**[a]	**3a**	**3b**[a]	**4a**	**4b**	**5**
Color	light blue	green blue	yellow	light blue	light orange	colorless
Chemical formula	$C_{36}H_{68}B_4MgNd_2O_4$	$C_{44}H_{80}B_4MgNd_2O_3$	$C_{44}H_{80}B_4MgNd_2O_3$	$C_{26}H_{45}BNNdO_2Si$	$C_{26}H_{45}BNNdO_2Si$	$C_{12}H_{32}B_2MgO_3$
Formula weight	920.96	1013.1	1009.3	586.8	592.90	270.3
Crystal system	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic	triclinic[b]
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*Pnma*	*Pnma*	$P\bar{1}$
a [Å]	15.5438(4)	13.414(6)	13.392(2)	17.2106(3)	17.2040(2)	8.495(2)
b [Å]	16.2479(4)	13.459(6)	13.493(2)	44.5052(8)	44.3324(6)	8.591(2)
c [Å]	32.5322(8)	16.499(7)	16.545(3)	10.9861(2)	10.9721(2)	12.339(3)
α [°]	90	87.781(7)	87.170(8)	90	90	102.95(3)
β [°]	90.033(2)	66.608(6)	66.370(9)	90	90	104.028(3)
γ [°]	90	61.350(6)	60.952(8)	90	90	92.43(4)
V [Å^3]	8216.1(4)	2356.3(18)	2354.9(7)	8414.9(3)	8368.4(2)	847.0(4)
Z	8	2	2	12	12	2
ρ [g cm^{-3}]	1.489	1.428	1.423	1.389	1.413	1.059
θ range [°]	1.25; 29.41	2.45; 28.61	1.37; 30.72	0.92; 30.63	1.84; 33.15	1.75; 31.33
Collected reflections	94804	12080	14294	13130	142417	11928
Unique	22535	9865	14294	13130	16144	5559
Obsd. [$I > 3\sigma(I)$]	12723	6991	9986	10787	10016	3071
R_{int}	0.0905	0.0602	0.0739	0.0422	0.0561	0.0562
Parameters	341	536	246	470	451	196
$R(F)$, $Rw(F)$ [$I > 3\sigma(I)$]	0.0733, 0.0739	0.0475, 0.0434	0.0757, 0.0692	0.0477, 0.0596	0.0822, 0.1145	0.1255, 0.1354
$R(F)$, $Rw(F)$ (all data)	0.1324, 0.0783	0.0734, 0.0465	0.1186, 0.0706	0.0626, 0.0613	0.0984, 0.1174	0.1795, 0.1420
ρmin, ρmax [e Å^{-3}]	–0.76; 5.36	–1.02; 1.60	–2.56; 3.57	–2.97; 2.38	–4.72; 3.78	–0.45; 1.23

[a] The crystal structure was refined from a twinned crystal. [b] Twin pseudomonoclinic.

-764032, and -764033 contain the supplementary crystallographic data for **2**, **3a**, **3b**, **4a**, **4b**, and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerizations: In a typical experiment conducted in a glovebox, the precatalyst (10 µmol) was weighed and diluted in toluene. The cocatalyst, BEM, was added with a microsyringe, and the monomer immediately after it at once. The flask was taken out from the glovebox and placed in a thermostatted bath at 50 °C for a given time. The flask was then opened to air, and the viscous mixture was diluted with undried toluene to quench the polymerization. The resulting solution was poured into a large volume of a 50:50 methanol/isopropyl alcohol mixture containing *tert*-butylcatechol as a stabilizing agent. An off-white polymer was filtered off and dried in vacuo until it reached constant weight.

Organometallic Syntheses

$(C_5Me_2)_2Nd(BH_4)(thf)$ (1): NMR scale: BEM (14.7 µL, 20.6 µmol) solution was added dropwise, at room temperature, to a solution of $Nd(BH_4)_3(thf)_3$ (8.5 mg, 20.6 µmol) and HC_5Me_5 (6.4 µL, 41.2 µmol) in C_6D_6 (0.4 mL). After evaporation of the solvents and dissolution in C_6D_6 only one product was observed. ^1H NMR (C_6D_6): δ = 44 (vbr, BH_4, 4 H), 10.07 (s, Cp*, 30 H), 6.01 (s, thf, 16 H), 3.31 (s, thf, 16 H) ppm. Bulk synthesis: A hexanes solution of BEM (0.8 mL, 1.00 mmol) was added dropwise to a solution of $Nd(BH_4)_3(thf)_3$ (406 mg, 1 mmol) and HC_5Me_5 (278 mg, 1.02 mmol) in toluene (40 mL). The mixture turned from light blue to blue-green. After stirring for 2 h at room temperature, the solution was concentrated to afford a blue oily material. After treatment with thf/pentane, a bluish crystalline powder was isolated. Yield: 121 mg (24%). The residual oily mother liquor did not crystallize properly. The ^1H NMR spectrum of the crystals was found to be identical to that of previously isolated $(C_5Me_2)_2Nd(BH_4)(thf)$.

$[(C_5H_5)_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_4$ (2): BEM solution (0.8 mL, 1 mmol) diluted in toluene (10 mL) was added dropwise, at room temperature, to a solution of $Nd(BH_4)_3(thf)_3$ (405 mg, 1 mmol) and an excess of HC_5H_5 (219 mg, 3.3 mmol) in toluene (50 mL). The mixture turned from deep blue to blue-green and then to light blue, while a blue solid deposited. After stirring for 1 h at room temperature, the solution was concentrated to dryness. Then, thf (50 mL) was added by vacuum transfer into the flask, giving a limpid blue solution. The solution was concentrated to dryness, and the residue was extracted with toluene (50 mL). After filtration to eliminate insoluble materials, the solution was concentrated (ca. 10 mL) and allowed to stand at room temperature to afford light blue crystals, which were collected for X-ray analysis. The mother liquor was concentrated to dryness, and a crystalline solid was isolated after washing with pentane (10 mL) and drying under vacuum. Yield: 412 mg (90%). ^1H NMR (C_4D_8O): δ = 5.45 (s, 10 H, Cp), the BH_4 signal may be lost in the baseline. Additional peaks: δ = 2.80 {corresponding to Cp_3Nd (ca. 17%)},[26] –2.50 {attributed to a monoCp derivative (ca. 17%)}[5a] ppm. Elemental analysis was correct for a tris(thf) adduct. $C_{36}H_{68}B_4MgNd_2O_4$ (920.96): calcd. C 45.28, H 7.12; found C 45.36, H 7.56.

$[(C_5H_4CMe_2)_2Nd(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ (3a): Same procedure as for **1**, starting from BEM (0.8 mL, 1 mmol), $Nd(BH_4)_3(thf)_3$ (400 mg, 1 mmol), and $(HC_5H_4CMe_2)_2$ (210 mg, 1 mmol) in toluene (50 mL). The mixture turned from green-blue to light orange within 1 h at room temperature. A crystalline green-blue solid was finally isolated after work-up. Yield: 0.355 g (70%). ^1H NMR (C_6D_6): δ = 32.0 (s, C_5H_4), 14.0 (br., BH_4), 2.2 (br., thf), 0.9 (br., thf), –1.5 (s, CMe_2), –20.0 (s, C_5H_4). $C_{44}H_{80}B_4MgNd_2O_3$ (1013.1): calcd. C 52.16, H 7.96; found C 52.34, H 8.30.

$[(C_5H_4CMe_2)_2Sm(BH_4)(\mu\text{-}BH_4)]_2Mg(thf)_3$ (3b): Same procedure as for **1**, starting from BEM (0.8 mL, 1 mmol), $Sm(BH_4)_3(thf)_3$ (415 mg, 1 mmol), and $(HC_5H_4CMe_2)_2$ (217 mg, 1 mmol) in toluene (50 mL). The mixture turned from pale yellow to deep orange within 1 h at room temperature, without formation of any solid. A crystalline yellow solid was finally isolated after work-up. Yield: 0.315 g (66%). ^1H NMR (C_6D_6): δ = 14.9 (s, C_5H_4), 8.1 (s, C_5H_4), 2.7 (s, thf), 1.7 (s, CMe_2), 0.8 (s, thf), –5.4 (br., BH_4) ppm. Recrystallization from thf/pentane gave large yellow crystals (105 mg), which were used for crystallographic analysis (H atoms pertaining to BH_4 could not be located). Reaction with allylLi-

(dioxane) (NMR scale experiment): allylLi(dioxane) (2 equiv., 3.4 mg, 19 µmol) was added to **3b** (4.9 mg, 4.9 µmol) in C_6D_6 (0.4 mL). The ^1H NMR spectrum recorded immediately showed the formation of a bis(allyl) derivative as the only product: ^1H NMR (C_6D_6): δ = 10.1 (s, 1 H, allyl), 8.9 (s, 2 H, allyl), 8.1 (s, 4 H, C_5H_4), 7.5 (s, 2 H, allyl), 5.9 (s, 4 H, C_5H_4), 3.3 (s, dioxane), 3.2 (s, thf), 1.9 (s, thf), 1.2 (s, 12 H, CMe_2) ppm.

$Mg(BH_4)_2(thf)_3$ (5): A small crop of highly air-sensitive large colorless crystals (ca. 50 mg) was also isolated from the above mother liquor after 12 h at –40 °C. ^1H NMR (C_4D_8O): δ = –0.25 (q, J = 91 Hz, BH_4). Elemental analysis was not possible due to the low quantity of the isolated product.

$[(C_5Me_4)CH_2SiMe_2NPh]Nd(BH_4)(thf)_2$ (4a): Same procedure as for **1**, starting from $Nd(BH_4)_3(thf)_3$ (809 mg, 2 mmol), $HC_5Me_4CH_2SiMe_2NHPh$ (570 mg, 2 mmol), and BEM (1.6 mL, 2 mmol) in thf (100 mL). The mixture turned from purple to light green within 1 h at room temperature. The thf was concentrated to ca. 10 mL, and pentane (10 mL) was added, affording large deep blue crystals after one night at –30 °C. Total yield of crystalline material: 288 mg (33%). ^1H NMR (C_6D_6):δ = 35 (vbr, BH_4), 14.8 (s, C_5Me_4, 6 H), 14.6 (s, CH_2, 2 H), 14.4 (s, $SiMe_2$, 6 H), 7.8 (s, *m*-Ph, 2 H), 5.4 (s, *p*-Ph, 1 H), 2.9 (s, *o*-Ph, 2 H), –4.2 (s, thf, 8 H), –6.6 (s, thf, 8 H), –9.0 (s, C_5Me_4, 6 H) ppm. $C_{26}H_{45}BNNdO_2Si$ (586.8): calcd. C 53.22, H 7.73, N 2.39; found C 52.37, H 7.75, N 2.26.

$[(C_5Me_4)CH_2SiMe_2NPh]Sm(BH_4)(thf)_2$ (4b): Same procedure as for **1**, starting from $Sm(BH_4)_3(thf)_3$ (432 mg, 1.05 mmol), $HC_5Me_4CH_2SiMe_2NHPh$ (300 mg, 1.05 mmol), and BEM (0.8 mL, 1 mmol) in thf (80 mL). The mixture turned from yellow to deep red-purple. The thf was concentrated to ca. 5 mL, and pentane (10 mL) was added, affording after one night at –30 °C a crop of orange crystals. Yield: 165 mg (28%). ^1H NMR (C_6D_6): δ = 7.29 (s, *m*-Ph, 2 H), 7.10 (s, *p*-Ph, 1 H), 6.49 (s, *o*-Ph, 2 H), 3.65 (s, CH_2, 2 H), 2.15 (s, thf, 8 H), 2.00 (s, C_5Me_4, 6 H), 1.82 (s, $SiMe_2$, 6 H), 1.08 (s, C_5Me_4, 6 H), 0.37 (s, thf, 8 H), –1.35 (vbr, BH_4) ppm.

Mechanistic Study of the Formation of Lanthanidocenes: An equimolar amount of $Nd(BH_4)_3(thf)_3$ was added to a C_6D_6 solution of Cp_2Mg (3.2 mg, 20 µmol) in an NMR tube equipped with a Teflon valve. The ^1H NMR spectrum recorded immediately showed the absence of any reaction. After 24 h at room temperature, a red-blue precipitate appeared, with just some residual neodymium tris(borohydride) in solution. After 48 h at 50 °C, the precipitate remained insoluble. The solvents were then evaporated off, and $[D_8]$thf was added. The ^1H NMR spectrum showed the presence of a mixture of Cp_3Nd (40%) and $Cp_2Nd(BH_4)$ (60%).

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