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Borohydride Complexes of Rare Earths, and their Applications in Various Organic Transformations.

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Abstract

Borohydride complexes of the rare earths have attracted most increasing interest since the last decade. This review aims at covering recent results over this period concerning the preparation, characterization, structure, and applications in organic chemistry of this family of compounds, including inorganic and organometallic complexes. A special emphasis is made on their use for polymerization catalysis.

Keywords: rare earths; borohydrides; tetrahydroborate; organolanthanides; polymerization catalysis

List of abbreviations

thf = tetrahydrofuran (C_4H_8O)
dme = 1,2-dimethoxyethane ($MeO(CH_2)_2OMe$)
diox = dioxane ($C_4H_8O_2$)
py = pyridine (C_5H_5N)
NBD = norbornadiene
Tpm* = tris(3,5-dimethylpyrazolyl)methane
TMS = trimethylsilyl ($SiMe_3$)
Mes = mesityl ($C_6H_2Me_3$-2,4,6)
Cy = cyclohexyl (C_6H_{11})
p-Tol = *para*-tolyl (*p*-Me-C_6H_4)
Cp = cyclopentadienyl (C_5H_5)
Cp’ = *tert*-butylcyclopentadienyl ($C_5H_4Bu^t$)
Cp^Q = methoxyethylcyclopentadienyl ($C_5H_4CH_2CH_2OCH_3$)
Cp* = pentamethylcyclopentadienyl (C_5Me_5)
Cp*’ = tetramethyl-*n*-propylcyclopentadienyl ($C_5Me_4Pr^n$)
Cp^{4i} = tetra-*iso*-propylcyclopentadienyl ($C_5HPr^i_4$)
Cp^{Ph3} = 1,2,4-tri-phenylcyclopentadienyl ($C_5H_2Ph_3$-1,2,4)
Cp^{ttt} = tri-*tert*-butylcyclopentadienyl ($C_5H_2Bu^t_3$-1,2,4)
P* = tetramethylphospholyl (C_4Me_4P)
Flu = fluorenyl (C_9H_7)
COT = cyclooctatetraenyl (C_8H_8)
(*p*-Tol)NN = *para*-tolyldiketiminate ([(*p*-CH_3-C_6H_4)$NC(CH_3)]_2CH$)
Nacnac = $[ArNC(CH_3)]_2CH$, Ar = $C_6H_3Pr^i_2$-2,6
Tp = tris(pyrazolyl)borate
Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate
(Pr^i)TP = 1,3-di(2-(isopropylamino)troponiminate)-propane
DAB = ($C_6H_3Pr^i_2$-2,6)NC(Me)=C(Me)N($C_6H_3Pr_2{}^i$-2,6)
DIP = 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl

N_2NN^R = (2-C_5H_4N)$CH_2N(CH_2CH_2NR)_2$

O_2N^L = $RCH_2N(CH_2$-2-O-3,5-$C_6H_2Bu^t_2)_2$ where R = CH_2OMe, CH_2NMe_2, (2-C_5H_4N), or Et for L = OMe, NMe_2, py, or Pr^n, respectively

DMADB = *N*,*N*-dimethylaminodiboranate ($H_3BNMe_2BH_3$)

9-BBN = 9-borabicyclo[3.3.1]nonane ($[C_8H_{14}BH]_2$)

dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate

tetrahydroSalen = [(2-OH-$C_6H_2Bu^t_2$-3,5)$CH_2N(CH_3)CH_2]_2$

BEM = *n*-butylethylmagnesium (Bu^nEtMg)

TB = trityl perfluorotetraphenylborate ($[CPh_3][B(C_6F_5)_4]$)

HNB = dimethylanilinium perfluorotetraphenylborate ($[HNMe_2Ph][B(C_6F_5)_4]$)

B = perfluotriphenylborane ($B(C_6F_5)_3$)

NMR: Nuclear Magnetic Resonance

MS: Mass Spectroscopy

IR: Infra Red

FTIR: Fourier Transform Infra Red

PDI: Polydispersity Index = M_w/M_n

SEC: Steric Exclusion Chromatography

ROP: Ring Opening Polymerization

1. Introduction

The chemistry of borohydride (also called tetrahydroborate) complexes of the rare earths has attracted increasing interest since the last two decades. Several well-documented reviews had adressed this promising field in the past, but surprisingly not since the last one written by Makhaev in 2000, which was restricted to the structural properties of borohydride complexes, and mostly in the solid state [1]. The last general review describing most aspects of the organometallic chemistry of the rare earths borohydrides was written by Ephritikhine in 1997 [2]. This article was more widely devoted to the hydrides of the f-elements, with a section specific to the borohydrides, and gathers the state of the art until 1996. At the same time, a survey of borohydride complexes of the transition metals including also the lanthanides was proposed by Lin [3], but it rather described the structure and the modes of bonding in the metal-(BH_4) unit, with no chemical reactivity at all.

This manuscript is thus intended to provide an overview on recent progress in the chemistry of rare earths compounds that contain a borohydrido group, including not only their synthesis and characterization, but also their reactivity, with a special emphasis on the use of such complexes for polymerization reactions, which represents nowadays an area in spectacular expansion.

The discussion is divided into three major sections: i) coordination compounds, ii) organometallic complexes, and iii) their applications in molecular chemistry. The first two sections consist of synthesis, characterization, and structure of the typical complexes. The third one gathers the results reported relative to the use of the borohydrides of the rare earths for further organometallic syntheses and organic transformations, including stoichiometric and catalytic reactions. In this last part, we will focus on their behaviour as catalysts for polymerization reactions, since this represents a most important field of applications of these complexes. Divalent and trivalent compounds will be reviewed, and classified according to the type of ligand. Akylborohydrides, which have not been until now the subject of a specific highlight, will also be integrated in this survey.

The definition of "rare earth" in this article applies as it should to scandium, yttrium, and the elements from lanthanum through to lutetium, but for simplicity in the general schemes the representation "Ln" will refer to as rare earths. The term "lanthanide" in the text applies specifically to the elements from lanthanum to lutetium, excluding yttrium and scandium.

Generally, borohydride complexes are complexes comprising at least one BH_4 anionic ligand. One of the major interests of this ligand is its versatility, not only regarding its coordination behaviour, as already discussed in the above-mentioned reviews, but also from the chemical point of view: on one hand, the BH_4 ligand may be considered as a *pseudo* halide, and thus borohydrido compounds display a chemistry which must be compared to that of halide (chloride) compounds; on the other hand, the borohydride ligand can be seen as a hydride supported by a borane molecule, which implies a specific and wide area of possible reactions connected to this hydridic moiety. Actually, this has been particularly exploited in polymerization in the last five years.

Structurally speaking, the borohydride group, which is bound to a lanthanide metal through hydrogen Ln(μ-H)B bridges, appears very versatile in terms of modes of coordination. It can be tri-hapto η^3, di-hapto η^2, and exceptionally mono-hapto η^1. The borohydride group may be connected to one single metal, but it may also link two, and even three metal atoms. If one BH_4 is coordinated to one single metal, it is called terminal, most generally in a tridentate fashion. As an example, a BH_4 bridge connecting two metals together, each in a dihapto mode, will be written as μ_2-$\eta^{2:2}$. Due to this variety of coordination facilities, the borohydride group will possibly lead to the formation of neutral monomeric compounds, or also to associated complexes (from dimers to clusters), through μ-(BH_4) bridges between metal centers. IR spectroscopy can be useful to clearly establish the exact nature of the mode of bridging but in many cases it is not easy to arbitrate. The X-ray structure determination, which is nowadays generalized, is considered as the best method for that purpose, ideally with the location of H atoms, and alternatively with Ln-B distances [4].

Whereas it has been claimed that the borohydride and the chloride ligand are quite isosteric [5], the former is often considered as being more electron donating than the latter [6,7], and borohydride complexes show a clear tendency to be more covalent than their chloride homologues [8]. Noteworthy, the borohydride group is also considered as isolobal with a chloride, or with a cyclopentadienyl (triply bridging BH_4^- groups are closely analogous to the η^5-$C_5H_5^-$ functionality in their bonding capabilities) [9]. As a consequence of all these features, whereas "ate" complexes are frequently encountered in the chloride series, especially with the lighter lanthanides (the larger ones) belonging to the ceric family [10], borohydride complexes may be obtained in most cases under a neutral form since the borohydride group can adapt its own hapticity to complete the coordination sphere of a metal, by comparaison with a halide which occupies only one coordination site. Overall, borohydride complexes being more covalent, they are generally more soluble than their halide homologues in non polar solvents. Interestingly, the borohydride group enables ^1H as well as ^{11}B NMR analyses, and by a simple integration of the BH_4 protons, it is possible to differentiate mono- or di-substituted complexes, which was not achievable with the homologous halide complexes in a given series.

Since pioneering studies of Ephritikhine, the lanthanide trisborohydrides $Ln(BH_4)_3(thf)_n$ proved to be valuable precursors for the elaboration of inorganic and organometallic derivatives, *via* the substitution of the BH_4 groups by anionic reagents, similarly as done with $LnCl_3$ precursors (hence the term *pseudo* halide), or also, in a lesser extent and just recently, by reaction with proton acidic substrates. These lanthanide trisborohydrides precursors are simply obtained straightforwardly from the trichlorides in the presence of an excess of $NaBH_4$ as reported initially by Mirsaidov [11], and later by Ephritikhine [6].

Several synthetic methods have been described to prepare organometallic or inorganic borohydrido derivatives of the rare earths, which are listed below:

i. the traditional one consists in the substitution of a ligand (in general a halide one) by a borohydrido anionic reagent MBH_4 (M = alkaline metal), in the last step of a synthesis, starting firstly most frequently from the trihalides (method A),

$$LnX_3 + n\,MZ \xrightarrow[-MX]{} Z_nLnX_{3-n} \xrightarrow[-M'X]{M'(BH_4)} Z_nLn(BH_4)_{3-n}$$

X = halide; n = 1, 2; Z = anionic ligand;
M, M' = alkaline metal

ii. a more recent general method is based on the use of the lanthanide trisborohydrides instead of the conventional trihalides $LnCl_3$ as starting materials, *via* ionic metathetical reactions (method B),

$$Ln(BH_4)_3(thf)_x + n\,MZ \xrightarrow[-M(BH_4)]{} Z_nLn(BH_4)_{3-n}$$

n = 1, 2; Z = anionic ligand; M = alkaline metal

iii. the "borohydride/alkyl route" (“B/A route”), which just involves a ligand under its protonated form, similarly as with amido, alkyl or hydride derivatives (method C),

$$Ln(BH_4)_3(thf)_x + n\,ZH \xrightarrow[-n\,RH]{n/2\ MgR_2} Z_nLn(BH_4)_{3-n}$$

n = 1, 2; ZH = protonated form of an anionic ligand

iv. comproportionation reactions (method D),

$$Ln(BH_4)_3(thf)_x + Z_2Ln(BH_4) \rightleftharpoons 2\,ZLn(BH_4)_2(thf)_{x'}$$

Z = anionic ligand

v. the reaction of a hydride with a borane molecule (method E),

$$Z_nLn(H)_{3-n} \xrightarrow{BR_3} Z_nLn(HBR_3)_{3-n}$$

n = 1, 2; Z = anionic ligand; R = H, alkyl

vi. the reduction from a trivalent precursor, in the case of divalent complexes (method F).

$$Z_nLn(BH_4)_{3-n} \xrightarrow{\text{reduction}} Z_nLn(BH_4)_{2-n}$$

n = 0, 1; Z = anionic ligand

In terms of reactivity, the borohydride group can be easily substituted for subsequent reactions, and hence borohydride compounds can be considered as starting materials, or intermediate reagents, similarly as the chloride or triflate ones. Many examples have been demonstrating this since the late 1990s and will be described in this article. But as a hydride, the borohydride group may also react with protic compounds, or behave as a reducing agent; this has been largely exploited in organic reactions, especially in polymerization. Moreover, it has been recently reported that cationic active species obtained by protonation of acidic reagents afford very active polymerization catalysts. The third part of this review intends to examine most aspects of the chemical reactivity of borohydride compounds, including also alkylborohydrides, which contain ligands of general formula ($BH_{4-n}R_n$).

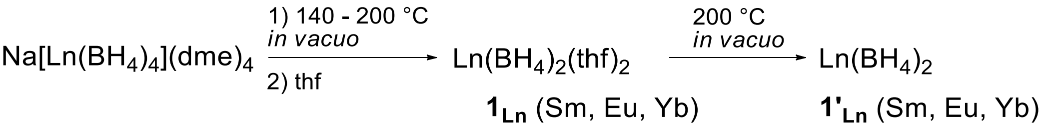
We will limit our scope to the results published after 1996, ie subsequently to the review of Ephritikhine [2]; however, exceptionally, additional results which had not been mentioned before will be included.

Tables 1-4 summarize the borohydride and alkylborohydride compounds, including their methods of preparation (methods A-E, as defined above), and their characterization data.

2. Coordination compounds

2.1. Divalent complexes

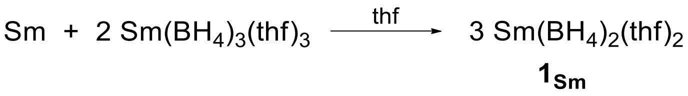
A series of compounds $Ln(BH_4)_2(thf)_2$ (**1$_{Ln}$**: Ln = Sm, Eu, Yb) and their non solvated analogs $Ln(BH_4)_2$ (**1'$_{Ln}$**) were prepared in 1999 by thermal reduction of the $NaLn(BH_4)_4(dme)_4$ precursors, according to scheme 1 [12]. The compounds were only characterized by IR and elemental analysis.



$$Na[Ln(BH_4)_4](dme)_4 \xrightarrow[\text{2) thf}]{\text{1) 140 - 200 °C, } \textit{in vacuo}} \underset{\mathbf{1_{Ln}}\text{ (Sm, Eu, Yb)}}{Ln(BH_4)_2(thf)_2} \xrightarrow{\text{200 °C, } \textit{in vacuo}} \underset{\mathbf{1'_{Ln}}\text{ (Sm, Eu, Yb)}}{Ln(BH_4)_2}$$

Scheme 1.

A new synthesis of **1$_{Sm}$** was recently achieved in high yield, by comproportionation between samarium metal and two equivalents of $Sm(BH_4)_3(thf)_3$ (scheme 2) [13]. The ^1H NMR borohydride resonances of this complex, observed at very high field (δppm = -135 ppm in deuteriated thf), is typical of a divalent samarium compound.



$$Sm + 2\ Sm(BH_4)_3(thf)_3 \xrightarrow{\text{thf}} 3\ \underset{\mathbf{1_{Sm}}}{Sm(BH_4)_2(thf)_2}$$

Scheme 2.

X-ray single crystal analysis revealed polymeric molecular arrangement with μ_2-$\eta^{2:2}(BH_4)$ bridges (Fig. 1).

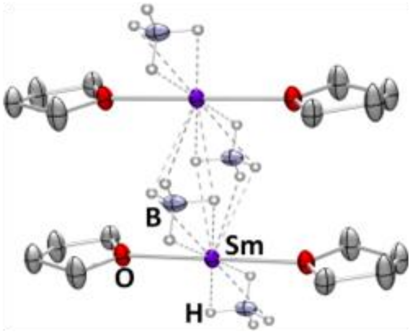


Fig. 1. The crystal structure of complex $\mathbf{1}_{\mathbf{Sm}}$. Reprinted with permission from Ref. [13]. Copyright 2010 The Royal Society of Chemistry.

2.2. Trivalent complexes

2.2.1. Mixed halogen/borohydride complexes

Zinck *et al* just isolated the $La(BH_4)_2Cl(thf)_n$ ($\mathbf{2}_{\mathbf{La}}$) mixed complex, which crystallized unexpectedly (for n = 4) during a synthesis of $La(BH_4)_3(thf)_3$ from metathesis between $LaCl_3$ and $NaBH_4$ in thf [14]. NMR and elemental analysis performed several months later revealed a partially desorbed complex with n = 2.6. Single crystal X-ray analysis of the tetra-thf adduct compound revealed a monomer having two terminal μ_2-$\eta^{3:1}$ borohydride groups *trans* to each other (Fig. 2).

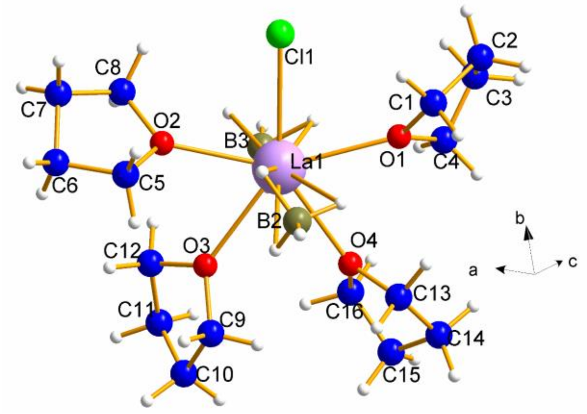


Fig. 2. The crystal structure of complex $\mathbf{2}_{\mathbf{La}}$ (for n = 4 thf). Reprinted with permission from Ref. [14]. Copyright 2010 Wiley Interscience.

In an alternative synthetic strategy towards the trisborohydride $Nd(BH_4)_3(thf)_n$, as reported originally by Mirsaidov from the trichloride $NdCl_3$ and $NaBH_4$ in excess [11], Klein *et al.* used a stoichiometric quantity of $LiBH_4$ (3 equiv.) that they reacted with the $NdCl_3(MeOH)$ adduct (scheme 3) [15]. They isolated after reaction the first member of a family of binuclear, mixed halogen/borohydride "ate" complexes of the rare earth elements: $[Li(thf)_4]_2[Nd_2Cl_2(BH_4)_6(thf)_2]$ ($\mathbf{3}_{\mathbf{Nd}}$).

$$2\ NdCl_3(MeOH) + 6\ LiBH_4 \xrightarrow[-\ 4\ LiCl]{thf} \underset{\mathbf{3}_{\mathbf{Nd}}}{[Li(thf)_4]_2[Nd(thf)(BH_4)_3(\mu\text{-}Cl)_2(BH_4)_3Nd(thf)]_2}$$

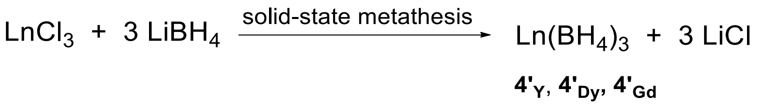
Scheme 3.

The X-ray structure of **3_{Nd}** revealed a dimer of the $[ClNd(BH_4)_3(thf)]^-$ subunit, in which each neodymium atom is coordinated by three borohydride anions, one thf molecule, and two μ_2-bridging chloro ligands. Though the hydrogens pertaining to the borohydride ligand were not located, the short Nd-B distances account for a tridentate borohydride coordination. The charge of the $[Nd_2(\mu\text{-}Cl)_2(BH_4)_6(thf)_2]^{2-}$ anion is compensated by two $[Li(thf)_4]^+$ cations.

2.2.2. Trisborohydride complexes and their adducts

Recently, the trisborohydrides of ytterbium and erbium, $Ln(BH_4)_3(thf)_3$ (**4_{Ln}**, Ln = Er, Yb), which had not been the subject of specific studies yet, were reexamined by Yuan *et al.* [16]. These complexes were synthesized by means of the original Mirsaidov's method [11], and fully characterized, including X-ray diffraction analysis. Both complexes were isostructural, displaying two η^3- and one η^1-(BH_4) ligands, as already observed in the case of yttrium [17] and scandium [18].

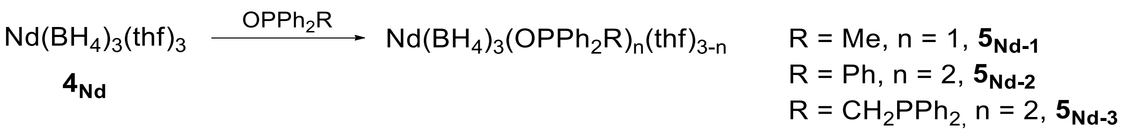
Quite surprisingly, it is only in 2008 that the solvent-free trivalent rare earth metal borohydrides $Ln(BH_4)_3$ (**$4'_{Ln}$**: Ln = Y, Gd, Dy) were prepared [19]. Their synthesis was performed in the absence of solvent from $LnCl_3$ and $LiBH_4$ through solid-state metathesis reactions (scheme 4). The compounds were characterized by powder X-ray, neutron diffraction measurement, and Raman spectroscopy. The crystal structure of all three complexes was clarified to adopt a primitive cubic structure in which BH_4^- anions locate on the edges of a distorted cube composed of Ln^{3+}, with μ_2-$\eta^{2:2}$ bridges between two metal atoms.



$$LnCl_3 + 3\ LiBH_4 \xrightarrow{\text{solid-state metathesis}} \underset{4'_Y,\ 4'_{Dy},\ 4'_{Gd}}{Ln(BH_4)_3} + 3\ LiCl$$

Scheme 4.

The phosphine oxide adducts of neodymium trisborohydride: $Nd(BH_4)_3(OPPh_2R)_n(thf)_{3-n}$ (R = Me, n = 1, **5_{Nd-1}** ; R = Ph, n = 2, **5_{Nd-2}**; R = CH_2PPh_2, n = 2, **5_{Nd-3}**) were prepared nearly two decades ago by the straightforward reaction of **4_{Nd}** with the corresponding phosphine oxide (scheme 5), and characterized by ^1H and ^{31}P NMR [20].

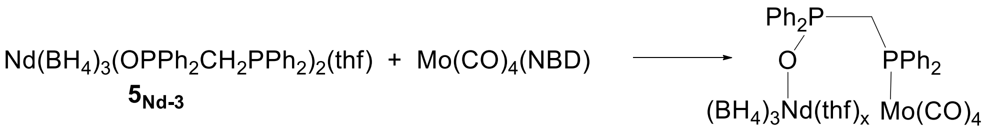


$$\underset{4_{Nd}}{Nd(BH_4)_3(thf)_3} \xrightarrow{OPPh_2R} Nd(BH_4)_3(OPPh_2R)_n(thf)_{3-n}$$

R = Me, n = 1, **5_{Nd-1}**
R = Ph, n = 2, **5_{Nd-2}**
R = CH_2PPh_2, n = 2, **5_{Nd-3}**

Scheme 5.

Addition of one equivalent of $Mo(CO)_4(NBD)$ (NBD = norbornadiene) to **5_{Nd-3}** lead to the formation of a bimetallic Nd-Mo compound, along with free norbornadiene (Scheme 6), on the basis of ^{31}P NMR analysis.



Scheme 6.

The pyrazolylmethane adduct [(Tpm*)Nd(BH_4)$_3$(thf)] (**6$_{Nd}$**) resulted from the displacement of two thf molecules in Nd(BH_4)$_3$(thf)$_3$ (**4$_{Nd}$**) with Tpm* (Tpm* = tris(3,5-dimethylpyrazolyl)methane). IR data were consistent with tridentate borohydride coordination [21]. Complex **6$_{Nd}$** was insoluble in hydrocarbon solvent, but displayed higher solubility in thf than its chloro analog [(Tpm*)$NdCl_3$(thf)].

2.2.3. Tetraborohydride anionic complexes

The salts (Bu_4N)[Ln(BH_4)$_4$(dme)$_n$] (**7a$_{Ln}$**: Ln = La-Nd, Sm-Gd, n = 1 ; Tb-Lu, n = 0) were obtained by an exchange reaction of NaLn(BH_4)$_4$(dme)$_m$ compounds with tetrabutylammonium tetrahydroborate in CH_2Cl_2 (Scheme 7). The compounds were characterized by elemental analysis, IR and thermogravimetry [22].

$$\mathrm{Na[Ln(BH_4)_4](dme)_m + Bu_4NBH_4 \xrightarrow{CH_2Cl_2} \underset{\mathbf{7a_{Ln}}}{(Bu_4N)[Ln(BH_4)_4(dme)_n]} + NaBH_4}$$

Scheme 7.

The ionic metathesis between the same starting material and (Ph_4P)(BH_4) afforded the unsolvated salts (Ph_4P)[Ln(BH_4)$_4$] (**7b$_{Ln}$**: Ln = Y, Tm, Lu) [23]. All compounds were studied by IR spectroscopy, and **7b$_{Lu}$** was characterized by elemental analysis. The crystal structure of **7b$_{Tm}$** was determined by X-ray crystallography, revealing an ionic pair composed of $(Ph_4P)^+$ cations and $[Tm(BH_4)_4]^-$ anions in close interaction. The anion displayed η^3-coordinated BH_4 ligands (Fig. 3).

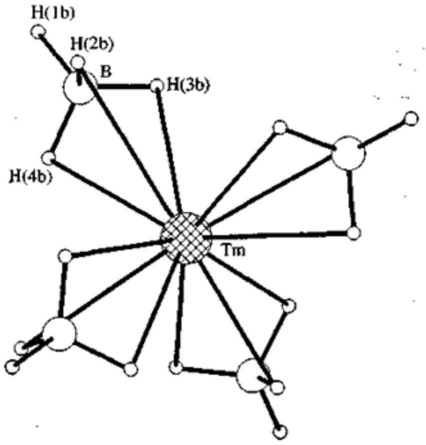
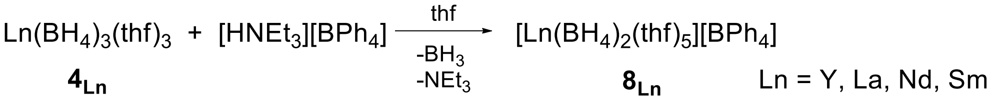


Fig. 3. The crystal structure of the Tm(BH_4)$_4$ anion in **7b$_{Tm}$**. Reprinted with permission from Ref. [23]. Copyright 2004 MAIK Nauka/Interperiodica.

2.2.4. Borohydrido cationic compounds

Treatment of the trisborohydrides **4$_{Ln}$** with NEt_3HBPh_4 in thf afforded the ionic complexes $[Ln(BH_4)_2(thf)_5]^+[BPh_4]^-$ (**8$_{Ln}$**: Ln = Y, La, Nd, Sm) as reported by Okuda *et al.* in 2008 (scheme 8) [24]. This reaction proceeded as same as firstly published for borohydride derivatives of the rare earths [25], with formation of dihydrogen, along with release of borane and triethylamine. The complexes **8$_Y$**, **8$_{Nd}$**, and **8$_{Sm}$** were characterized by X-ray diffraction; they all consist of charge-separated ion pairs in the solid state. The cationic counterpart was similar to the previously described in $[Y(BH_4)_2(thf)_5]^+[Y(BH_4)_4]^-$ in which four thf molecules were enough to complete the coordination sphere of the smaller yttrium [26].

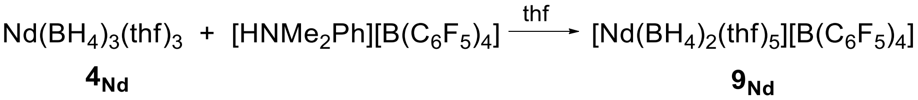


$$\underset{\mathbf{4_{Ln}}}{Ln(BH_4)_3(thf)_3} + [HNEt_3][BPh_4] \xrightarrow[-BH_3 \atop -NEt_3]{thf} \underset{\mathbf{8_{Ln}}}{[Ln(BH_4)_2(thf)_5][BPh_4]} \quad Ln = Y, La, Nd, Sm$$

Scheme 8.

The cerium derivative $\mathbf{8_{Ce}}$ was prepared by the same method by Ephritikhine *et al.* one year later [27]. They showed in addition that such cationic compounds are transformed into $[Ln(BH_4)_2(18\text{-crown-6})][BPh_4]$ ($\mathbf{8'_{Ln}}$, Ln = Nd, Ce) in the presence of 18-crown-6. The same authors also isolated crystals of the tetrahydrothiophene adduct of the cerium counterpart: $[Ce(BH_4)_2(thf)_5][BPh_4](C_4H_8S)$ ($\mathbf{8''_{Ce}}$). DFT calculations were carried out, giving insights into the poor covalent contribution of the cerium-borohydride bond, with practically no participation of the 4f orbitals, in contrast with the results obtained with the uranium analogous derivative.

The same year as Okuda, Visseaux *et al.* showed that the protonation reaction of $\mathbf{4_{Nd}}$ with $[HNMe_2Ph][B(C_6F_5)_4]$ in thf afforded straightforwardly the ionic pair $[Nd(BH_4)_2(thf)_5][B(C_6F_5)_4]$ ($\mathbf{9_{Nd}}$) (scheme 9) [28]. X-ray structure analysis revealed the same molecular arrangement for the cationic $[Nd(BH_4)_2(thf)_5]$ (Fig. 4) as reported by Okuda, and Ephritikhine. All borohydride ligands exhibited a η^3-H_3BH bonding mode, as same as for $\mathbf{8_{Ce}}$.



$$\underset{\mathbf{4_{Nd}}}{Nd(BH_4)_3(thf)_3} + [HNMe_2Ph][B(C_6F_5)_4] \xrightarrow{thf} \underset{\mathbf{9_{Nd}}}{[Nd(BH_4)_2(thf)_5][B(C_6F_5)_4]}$$

Scheme 9.

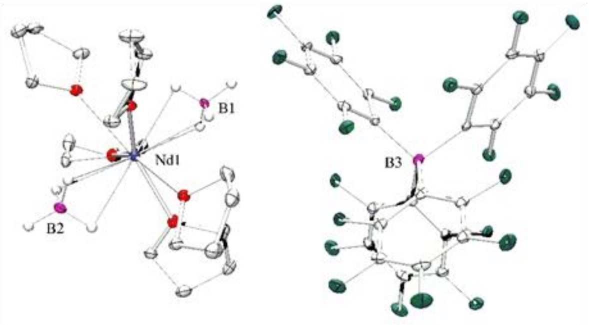


Fig. 4. The crystal structure of complex $\mathbf{9_{Nd}}$. Reprinted with permission from Ref. **[28]**. Copyright 2008 The Royal Society of Chemistry.

Crystals of a penta-thf adduct of general formula $[(Cp^{*\prime})Sm_2(BH_4)_5(thf)_5]$ ($Cp^{*\prime}$ = $C_5Me_4Pr^n$) ($\mathbf{10_{Sm}}$) were isolated from a solution of half-samarocene $Cp^{*\prime}Sm(BH_4)_2(thf)$, probably resulting from comproportionation reactions. X-ray structure determination revealed an ionic compound $[Sm(BH_4)_2(thf)_5]^+[(Cp^{*\prime})Sm(BH_4)_3]^-$ with two discrete mononuclear samarium polyhedrons (Fig. 5) [29]. The cationic moiety was identical to that observed later [25].

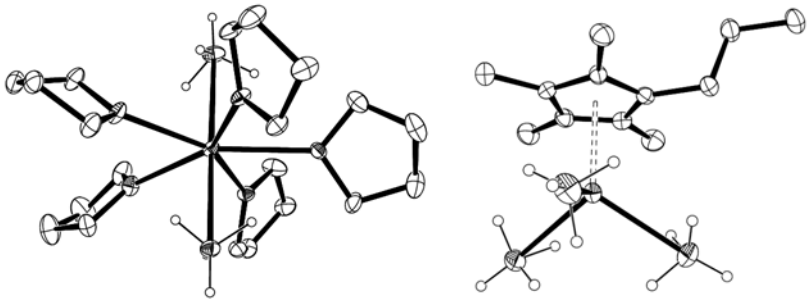


Fig. 5. The crystal structure of ionic complex **10_{Sm}** (left, cation ; right, anion). Reprinted with permission from Ref. [29]. Copyright 2007 Elsevier.

Table 1

Borohydride Coordination Compounds and their Characterization

Compound	Synthesis [a]	NMR	Infra Red	Elem. Anal.	X-ray (H-(BH_4) located)	Reference
Ln(BH$_4$)$_2$(thf)$_2$ (Ln = Sm, Eu, Yb) ($\mathbf{1_{Ln}}$)	- [b]	-	✓	✓	-	[12]
Ln(BH$_4$)$_2$ (Ln = Sm, Eu, Yb) ($\mathbf{1'_{Ln}}$)	- [b]	-	✓	✓	-	[12]
Sm(BH$_4$)$_2$(thf)$_2$ ($\mathbf{1_{Sm}}$)	D	^{1}H	-	✓	✓ (yes)	[13]
La(BH$_4$)$_2$Cl(thf)$_n$ ($\mathbf{2_{La}}$)	A	^{1}H	-	✓ (n = 2.6)	✓ (n = 4, yes)	[14]
[Li(thf)$_4$]$_2$[Nd$_2$(μ-Cl)$_2$(BH$_4$)$_6$(thf)$_2$] ($\mathbf{3_{Nd}}$)	A	^{1}H, ^{11}B	-	-	✓ (no)	[15]
Ln(BH$_4$)$_3$(thf)$_3$ (Ln = Er, Yb) ($\mathbf{4_{Ln}}$)	A	-	✓	✓	✓ (yes)	[16]
Ln(BH$_4$)$_3$ (Ln = Y, Dy, Gd) ($\mathbf{4'_{Ln}}$)	A	-	Raman	-	✓	[19]
Nd(BH$_4$)$_3$(OPPh$_2$R)$_n$(thf)$_{3-n}$ (n = 1, R = Me, $\mathbf{5_{Nd\text{-}1}}$; n = 2, R = Ph, $\mathbf{5_{Nd\text{-}2}}$; n = 2, R = CH$_2$PPh$_2$, $\mathbf{5_{Nd\text{-}3}}$)	- [c]	^{1}H, ^{31}P	-	-	-	[20]
[Nd(Tpm*)(BH$_4$)$_3$(thf)] ($\mathbf{6_{Nd}}$)	- [d]	^{11}B	✓	✓	-	[21]
(Bu$_4$N)[Ln(BH$_4$)$_4$(dme)$_n$] (Ln = La-Nd, Sm-Gd, n = 1; Tb-Lu, n = 0) ($\mathbf{7a_{Ln}}$)	B [e]	-	✓	✓	-	[22]
(Ph$_4$P)[Ln(BH$_4$)$_4$] (Ln = Y, Tm, Lu) ($\mathbf{7b_{Ln}}$)	B [e]	-	✓	✓ (Lu)	✓ (Tm, yes)	[23]
[Ln(BH$_4$)$_2$(thf)$_5$][BPh$_4$] [Ln = Y, La, Ce, Nd, Sm)] ($\mathbf{8_{Ln}}$)	B	^{1}H, ^{11}B	✓ (Nd, Ce)	✓	✓ (yes: Ce ; no: Y, Nd, Sm)	[24] [27] (Ce)
[Ln(BH$_4$)$_2$(18-crown-6)][BPh$_4$] [Ln = Nd, Ce)] ($\mathbf{8'_{Ln}}$)	B	^{1}H, ^{11}B (Nd)	✓	✓	✓ (yes)	[27]
[Ce(BH$_4$)$_2$(thf)$_5$][BPh$_4$](C$_4$H$_8$S) ($\mathbf{8''_{Ce}}$)	B	-	-	-	✓ (yes)	[27]
[Nd(BH$_4$)$_2$(thf)$_5$][B(C$_6$F$_5$)$_4$] ($\mathbf{9_{Nd}}$)	B	^{1}H, ^{11}B	✓	✓	✓ (yes)	[28]
[Sm(BH$_4$)$_2$(thf)$_n$][(Cp*')Sm(BH$_4$)$_3$] ($\mathbf{10_{Sm}}$)	B, D	^{1}H	✓	✓ (n = 3)	✓ (n = 5, yes)	[29]

[a] See the synthetic methods as defined in the introduction;

[b] thermal decomposition from (Na)[Ln(BH$_4$)$_4$(dme)$_n$];

[c] addition of phosphine oxides to Nd(BH$_4$)$_3$(thf)$_3$;

[d] addition of Tpm* to Nd(BH$_4$)$_3$(thf)$_3$;

[e] ionic metathesis from (Na)[Ln(BH$_4$)$_4$(dme)$_n$].

3. Organometallic compounds

3.1. Mono-substituted complexes

3.1.1. Divalent derivatives

3.1.1.1. Cyclopentadienyl complexes

To our knowledge, only one divalent compound was described and fully characterized in the borohydride series: (Cp*)Sm(BH_4)(thf)$_2$ (**11_{Sm}**) (Cp* = C_5Me_5). This half-sandwich compound was prepared by the reaction of the bis(borohydrido) samarium **1_{Sm}** with K(Cp*) (scheme 10). The very high field ^{1}H NMR borohydride resonance (δ = -163 ppm) was typical of a divalent samarium compound [13].

$$\mathrm{K(Cp^*)} + \underset{\mathbf{1_{Sm}}}{\mathrm{Sm(BH_4)_2(thf)_2}} \xrightarrow{\mathrm{thf}} \underset{\mathbf{11_{Sm}}}{\mathrm{(Cp^*)Sm(BH_4)(thf)_2}}$$

Scheme 10.

X-ray single crystal analysis revealed a dimeric molecular arrangement, similarly to that of the previously described Sm(II) dimer [(Cp*)Sm(μ-I)(thf)$_2$]$_2$ [30], with the two samarium atoms bridged by two tridentate borohydrides, thus featuring a coordination number of seven (Fig. 6).

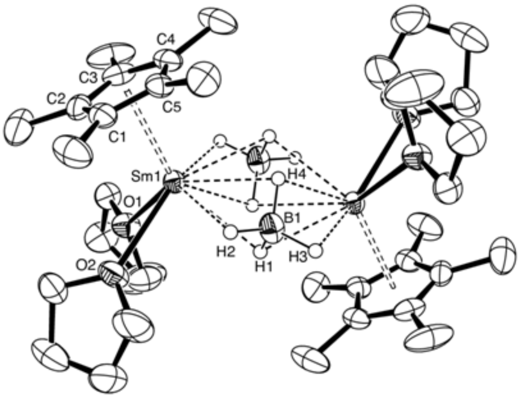


Fig. 6. The crystal structure of dimeric complex **11_{Sm}**. Reprinted with permission from Ref. [13]. Copyright 2010 The Royal Society of Chemistry.

3.1.1.2. Pyrazolylborate complexes

Takats *et al.* reported the synthesis and characterization of (Tp$^{tert\text{-}Bu,Me}$)Yb(BH_4)(thf)$_n$ (**12_{Yb}**, n = 1; **$12'_{Yb}$**, n = 0) complexes [31]. The thf adduct **12_{Yb}** was obtained by the traditional route of substitution of an iodide by a borohydride (scheme 11, up), whereas the solvent-free derivative **$12'_{Yb}$** was prepared in an original way by trapping a molecule of borane with the corresponding hydride (scheme 11, down). Attempts to synthesize similarly the samarium analog failed.

$$(Tp^{tBu,Me})YbI(thf) + MBH_4 \xrightarrow[-\ MI]{solvent} \underset{\mathbf{12_{Yb}}}{(Tp^{tBu,Me})Yb(BH_4)(thf)} \quad M = Na, K ; solvent = thf, CH_3CN$$

$$[(Tp^{tBu,Me})YbH]_2 + 2\ BH_3.NMe_3 \xrightarrow{RT,\ C_6H_6} 2\ \underset{\mathbf{12'_{Yb}}}{(Tp^{tBu,Me})Yb(BH_4)} + 2\ NMe_3$$

Scheme 11.

The X-ray crystal structure of **12Yb** shows a monomeric, formally seven-coordinate ytterbium center, bearing one η^3-bonded $Tp^{tert\text{-}Bu,Me}$ ligand, a trihapto tetrahydroborate ligand and a coordinated thf molecule. IR spectroscopy data were consistent with the solid-state structure. The ^1H NMR spectra of both **12Yb** and **12’Yb** showed one set of resonances each for the borohydride and the pyrazolylborate ligands, indicating dynamic solution behavior.

3.1.2. Trivalent derivatives

3.1.2.1. Cyclopentadienyl complexes

The ionic mono(cyclopentadienyl) derivative $[(Cp)Nd(BH_4)_3]_2[Mg(thf)_6]$ (**13Nd**) (Cp = C_5H_5) was prepared in high yield by means of the “B/A route” [1] as represented in scheme 12 [32]. This compound represents one of the rare examples of a half-lanthanidocene in the simple C_5H_5 series that was structurally characterized, and the first borohydride one.

$$\underset{\mathbf{4_{Nd}}}{Nd(BH_4)_3(thf)_3} + 1/2\ BEM + HC_5H_5 \xrightarrow{toluene,\ thf} 1/2\ \underset{\mathbf{13_{Nd}}}{[(Cp)Nd(BH_4)_3]_2[Mg(thf)_6]}$$

Scheme 12.

Complex **13Nd** is a trinuclear ionic compound comprising two anionic half-neodymocene trisborohydride $[(Cp)Nd(BH_4)_3]^-$ moieties and one cationic hexa-thf magnesium $[Mg(thf)_6]^{2+}$ adduct (Fig. 7) that alternate in the unit cell without particular cation–anion interaction.

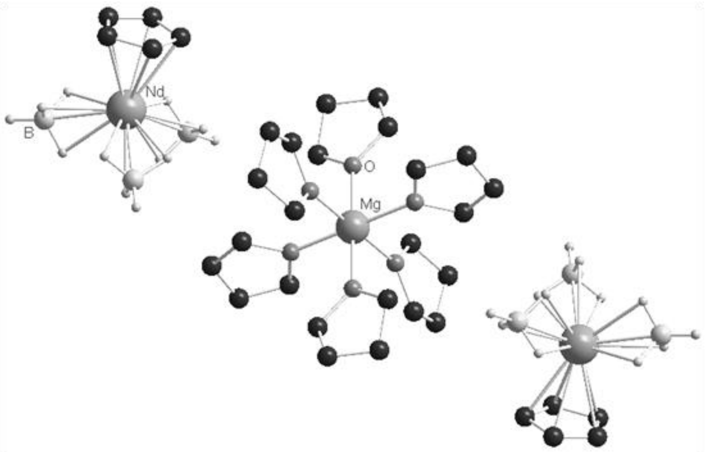


Fig. 7. The crystal structure of complex **13Nd**. Reprinted with permission from Ref. [32]. Copyright 2008 Elsevier.

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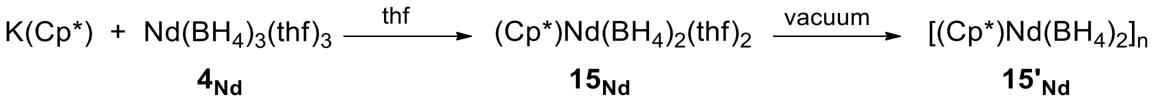
[1] As defined as synthetic method C in the introduction.

The geometric parameters are typical of monomeric borohydrido complexes bearing a tridentate Ln–η^3(BH_4) terminal group. It is noteworthy that the thf molecules are all coordinated to the magnesium atom, indicating a higher oxophilicity of this metal.
Following the same strategy, the authors succeded in the synthesis and X-ray determination of $[(Cp^{Ph3})Nd(BH_4)_3]_2[Mg(thf)_6]$ ($\mathbf{14_{Nd}}$) (Cp^{Ph3} = 1,2,4-PhC_5H_2), which molecular structure was very similar to that of $\mathbf{13_{Nd}}$. It is noteworthy that on the other hand, the synthesis of a pure sample of neutral $(Cp^{Ph3})Sm(BH_4)_2(thf)_2$ ($\mathbf{14'_{Sm}}$) by ionic metathesis from $Sm(BH_4)_3(thf)_3$ failed: this compound was always contaminated with small amounts (15 %) of the di-substituted $(Cp^{Ph3})_2Sm(BH_4)_2(thf)$ [33].

In 1998, following the ionic metathesis strategy from a rare earth trisborohydride, Ephritikhine *et al.* showed that the reaction of $\mathbf{4_{Nd}}$ with 1 equiv. of K(Cp*) afforded cleanly the neutral $(Cp^*)Nd(BH_4)_2(thf)_2$ ($\mathbf{15_{Nd}}$) (scheme 13) [6]. IR data suggested the presence of both bidentate and tridentate BH_4 units, supporting a likely monomeric structure in the solid state. This supposed molecular structure differed from that of the halides $(Cp^*)LnX_2$ (X = Cl, Br, I), which form either monomeric adducts with thf [34] or “ate” species such as $(Cp^*)Nd(\mu\text{-}Cl)_3Na(Et_2O)$ [35], with retention of the alkali metal halide. It was mentioned that $\mathbf{15_{Nd}}$ can be desolvated upon gentle heating under reduced pressure to form $[(Cp^*)Nd(BH_4)_2]_n$ ($\mathbf{15'_{Nd}}$), whose unique IR absorption at 2291 cm^{-1}, typical of bridging borohydride groups, is indicative of a polymeric structure in the solid state.



$$\underset{\mathbf{4_{Nd}}}{K(Cp^*) + Nd(BH_4)_3(thf)_3} \xrightarrow{thf} \underset{\mathbf{15_{Nd}}}{(Cp^*)Nd(BH_4)_2(thf)_2} \xrightarrow{vacuum} \underset{\mathbf{15'_{Nd}}}{[(Cp^*)Nd(BH_4)_2]_n}$$

Scheme 13.

The half-sandwich analogs $(Cp^*)Sc(BH_4)_2(thf)$ ($\mathbf{15_{Sc}}$) and $(Cp^*)La(BH_4)_2(thf)_2$ ($\mathbf{15_{La}}$), were synthesized only very recently [36][**37**]. The synthesis was in both cases conducted *via* ionic metathesis starting from the corresponding trisborohydride. Whilst $\mathbf{15_{La}}$ behaves similarly as $\mathbf{15_{Nd}}$, with a progressive loss of thf upon vacuum, the formation of $\mathbf{15_{Sc}}$ was accompanied by two by-products, a metallocene, $(Cp^*)_2Sc(BH_4)$, and a half-metallocene, $[(Cp^*)Sc(BH_4)\{\mu\text{-}O(CH_2)_3CH_3\}]_2$ (see further sections). The molecular structure of $\mathbf{15_{Sc}}$ was further confirmed by X-ray analysis, which revealed a monomeric mono-thf adduct, with both borohydride groups acting as tridentate ligands, in accordance with short Sc–B bond lengths (Fig. 8).

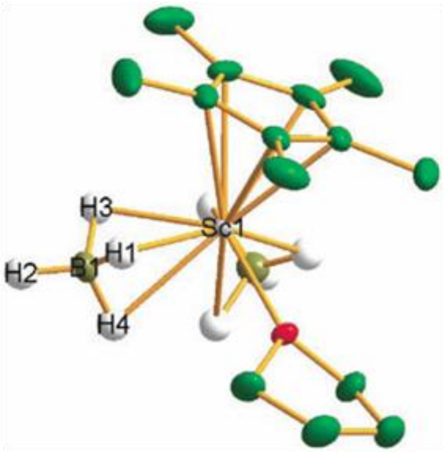


Fig. 8. The crystal structure of complex **15$_{Sc}$**. Reprinted with permission from Ref. [36]. Copyright 2009 The Royal society of Chemistry.

It is however worth to be noted that half-sandwiches of general formula [(Cp*)Ln(BH$_4$)$_2$] (**15'$_{Ln}$**, Ln = Sm, Dy, Yb) had been initially prepared in 1996 by Edelmann *et al.* who carried out the first reaction with rare earths borohydride compounds as starting materials to prepare organolanthanide complexes [2] [38]. This reaction, which was conducted between the Cl/BH$_4$ mixed LnCl(BH$_4$)$_2$ and KCp* in 1:1 ratio, suggests that a chloride is easier to displace than a borohydride by ionic metathesis.

Using the "B/A route", anionic mono(pentamethylcyclopentadienyl) trisborohydrides [(Cp*)Ln(BH$_4$)$_3$]$_2$[Mg(thf)$_6$] (**16$_{Ln}$**, Ln = Nd, La) were also isolated, similarly as described in scheme 12 but with Cp*H as starting cyclopentadiene reagent [32,39]. Both **16$_{Nd}$** and **16$_{La}$** displayed the same heterobimetallic trinuclear arrangement, with discrete ionic units in close association (Fig. 9), like observed with the less substituted cyclopentadienyl series. Despite H atoms belonging to BH$_4$ groups were not located for **16$_{La}$**, the very similar bond distances and angles in both complexes support tridentate η^3-(BH$_4$) coordination. Remarkably, these complexes were stable *vs.* disproportionation reactions after several hours heating in solution.

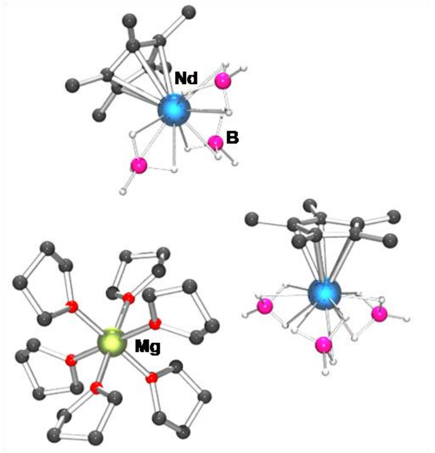
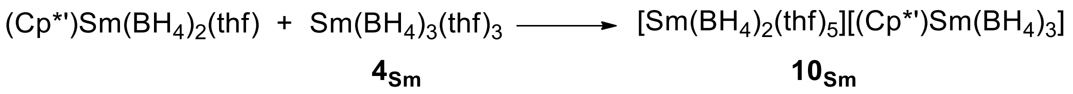


Fig. 9. The crystal structure of complex **16$_{Nd}$**. Reprinted with permission from Ref. **[39]**. Copyright 2007 Académie des Sciences.

The (Cp^R)Ln(BH$_4$)$_3^-$ anion (Cp^R for a given cyclopentadienyl ligand) is a very stable entity in the borohydrido half-sandwich series, since it has already been found in **10$_{Sm}$** (see section 2.2.4). The latter ionic compound was also available from comproportionation between (Cp*')Sm(BH$_4$)$_2$(thf)$_2$ and Sm(BH$_4$)$_3$(thf)$_3$ (Scheme 14) [29].



$$\underset{\mathbf{4_{Sm}}}{(Cp^{*\prime})Sm(BH_4)_2(thf)} + Sm(BH_4)_3(thf)_3 \longrightarrow \underset{\mathbf{10_{Sm}}}{[Sm(BH_4)_2(thf)_5][(Cp^{*\prime})Sm(BH_4)_3]}$$

Scheme 14.

A series of half-sandwich complexes (Cp*')Ln(BH$_4$)$_2$(thf)$_n$ (**17$_{Ln}$**; Ln = Sm, n = 1 ; Ln = Nd, n = 2; Cp*' = C$_5$Me$_4$Pr^n) were prepared by metathetical reaction starting from K(Cp*')

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[2] As described as synthetic method B in the introduction.

and **4$_{Ln}$** precursors [40]. By recrystallization in toluene, they were isolated as unsolvated [(Cp*’)Ln(BH_4)$_2$]$_6$ (**17’$_{Ln}$**) according to X-ray analysis. Compounds **17’$_{Nd}$** and **17’$_{Sm}$** were isostructural, and they exhibited a hexameric structure in the solid state, made of the association of [(Cp*’)$_3$Ln$_3$(BH_4)$_5$] cationic building blocks with a BH_4^- anion (Fig. 10). Hexamers of C_2 and C_i symetry were observed. The mode of ligation of BH_4: μ_2-$\eta^{1:1}$ and μ_2-$\eta^{3:1}$, depending on the type of hexamer, was deduced from Ln-B distances since the hydrogen atoms could not be located. The easy clustering of thf adducts firstly isolated is illustrative of the well-known bridging ability of the BH_4 group. A similar behaviour may be expected with the non-solvated [(Cp*)Nd(BH_4)$_2$] which resulted from (Cp*)Nd(BH_4)$_2$(thf)$_2$ upon vacuum treatment, and likely displays the same hexameric structure according to IR data [6].

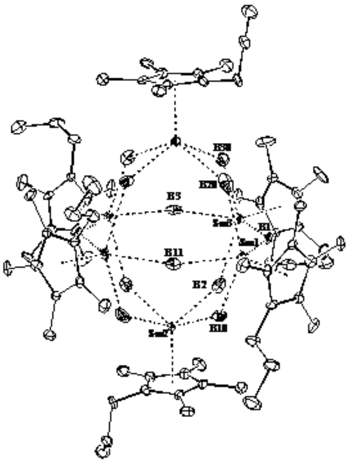


Fig. 10. The crystal structure of complex **17’$_{Sm}$** (***C_2***-cluster). Reprinted with permission from Ref. [40]. Copyright 2004 American Chemical Society.

Interestingly, mixed borohydrido/chloro bridged [(Cp*')$_6$Ln$_6$(BH_4)$_{(12-x)}$Cl$_x$(thf)$_{n'}$] (**17a’’$_{Ln}$**: Ln = Sm, Nd, x = 10, n' = 4; **17b’’$_{Sm}$**: x = 5, n = 2) complexes were also isolated as by-products during theses syntheses. X-ray structure determinations revealed hexameric molecules in which the chlorine atoms substitute most of the BH_4 groups [40].

Half-metallocenes bearing the bulky tetraisopropylcyclopentadienyl ligand (Cp^{4i})Ln(BH_4)$_2$(thf) (**18$_{Ln}$**: Ln = Sm, Nd; Cp^{4i} = $C_5HPr^i_4$) were synthesized by ionic metathesis from the **4$_{Ln}$** precursors [7]. Both complexes were isostructural, with small differences due to the metal atom. The presence of the sterically demanding Cp^{4i} and of the borohydride ligands allowed the formation of rare monomeric, four-coordinate complexes. The BH_4 groups were terminal tridentate (Fig. 11).

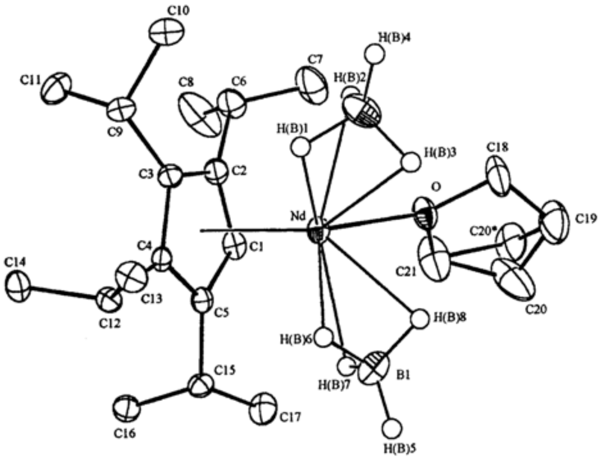


Fig. 11. The crystal structure of complex $\mathbf{18_{Nd}}$. Reprinted with permission from Ref. [7]. Copyright 2000 Wiley.

The bulkiness of the tetraisopropylcyclopentadienyl ligand was claimed to account for the very slow exchange process observed between $(Cp^{4i})_2Sm(BH_4)$ and $\mathbf{4_{Sm}}$ to form $\mathbf{18_{Sm}}$ by comproportionation (scheme 15).

$$\underset{}{(Cp^{4i})_2Sm(BH_4)} + \underset{\mathbf{4_{Sm}}}{Sm(BH_4)_3(thf)_3} \xrightarrow[\text{1 week}]{\text{thf}} \underset{\mathbf{18_{Sm}}}{(Cp^{4i})Sm(BH_4)_2(thf)}$$

Scheme 15.

The straightforward metathesis reaction of $\mathbf{4_{Ln}}$ (Ln = Sc, Sm) with equimolar amino-functionalized cyclopentadienyl ligand $(C_5Me_4\text{-}C_6H_4\text{-}o\text{-}NMe_2)Li$ in thf medium yielded the first linked half sandwich ligand stabilized thf-free rare-earth metal bis(borohydrido) complexes $(C_5Me_4\text{-}C_6H_4\text{-}o\text{-}NMe_2)Ln(BH_4)_2$ ($\mathbf{19_{Ln}}$). The scandium derivative displays terminal tridentate borohydrides, as evidented by X-Ray analysis (Fig. 12) [41].

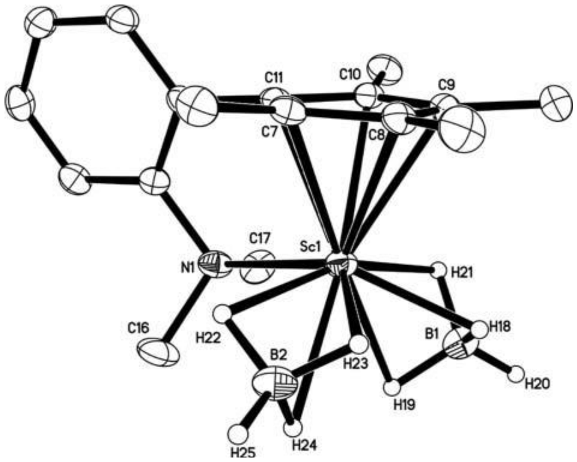
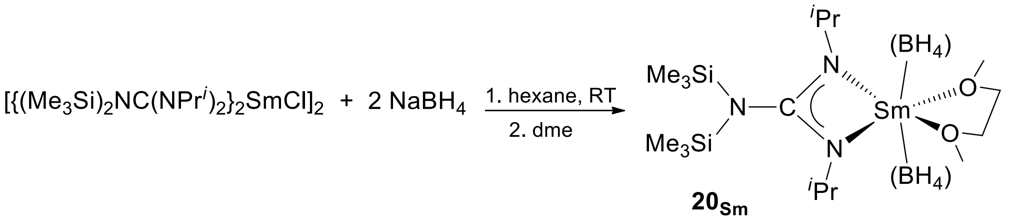


Fig. 12. The crystal structure of complex $\mathbf{19_{Sc}}$. Reprinted with permission from Ref. [41]. Copyright 2010 The Royal Society of Chemistry.

3.1.2.2. Nitrogen-based ligands supported complexes

The reaction of the chloro bis(guanidinate) derivative $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ with $NaBH_4$ in hexane followed by treatment with dimethoxyethane yielded unexpectedly, *via* redistribution of the ligands, the monoguanidinate bisborohydride $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2(dme)$ (**20_{Sm}**) (Scheme 16). X-ray diffraction studies showed that both borohydride ligands in this complex are terminal tridentate [42].



Scheme 16.

The comparable mono(guanidinate) lanthanide borohydride complexes $[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(thf)_2$ (**21_{Ln}**: Ln = Er, Yb; Cy = cyclohexyl) were synthesized in 2006 by the reactions of the corresponding **4_{Ln}** with sodium guanidinate $[(Me_3Si)_2NC(NCy)_2]Na$ in a 1:1 molar ratio in thf (scheme 17) [43].

$$\underset{\mathbf{4_{Ln}}}{Ln(BH_4)_3(thf)_3} + [(Me_3Si)_2NC(NCy)_2]Na \xrightarrow[-\ NaBH_4]{thf} \underset{\mathbf{21_{Ln}}:\ Ln\ =\ Yb,\ Er}{[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(thf)_2}$$

Scheme 17.

The complexes were characterized by elemental analysis, IR spectroscopy, and they display a similar molecular structure from X-ray diffraction analysis: the lanthanide ion is bonded by a η^2-guanidinate ligand, two η^3-(BH_4) and two thf molecules as a distorted octahedron (Fig. 13).

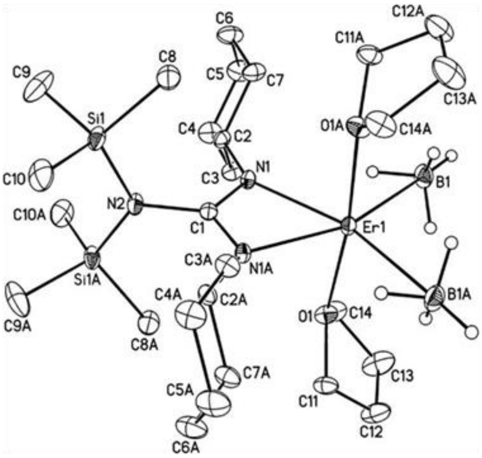
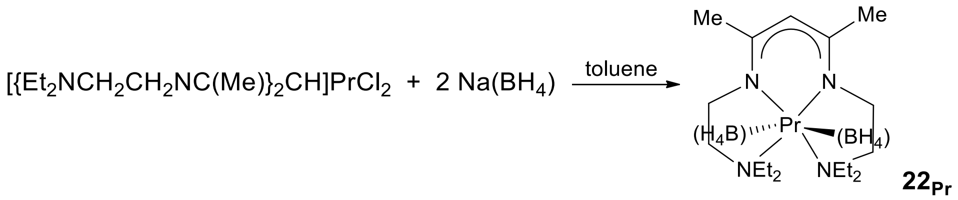


Fig. 13. The crystal structure of complex **21_{Er}**. Reprinted with permission from Ref. [43]. Copyright 2006 Elsevier.

A little later and in the same series, Trifonov et *al.* reported on a mono-substituted dme-adduct of gadolinium $[(Me_3Si)_2NC(NCy)_2]Gd(BH_4)_2(dme)$ (**$21'_{Gd}$**) which had been unexpectedly prepared, by metathetic reaction between **4_{Gd}** and two equivalents of the corresponding sodium guanidinate [44]. Redistribution reactions due to the presence of dme were tentatively advanced to explain this result. The X-ray structure of **21’$_{Gd}$** was comparable to that of **21$_{Er}$**, with tridentate borohydride ligation.

The trivalent praseodymium complex with a β-diketiminato ligand possessing two pendant arms, LPr$(BH_4)_2$ (**22$_{Pr}$**) [L = $\{Et_2NCH_2CH_2NC(Me)\}_2CH$] was not prepared from **4$_{Pr}$** but by displacement of chlorides in $LPrCl_2$ with an excess of $NaBH_4$ in boiling toluene [45] (scheme 18). A temperature-dependent ^{11}B NMR study indicated that both BH_4 groups are equivalent in solution.



Scheme 18.

X-ray structural and elemental analysis showed that this complex is neutral, monomeric and solvent-free (Fig. 14). It adopts a pseudo-octahedral geometry with the two terminal trihapto BH_4 arranged in the *trans* positions.

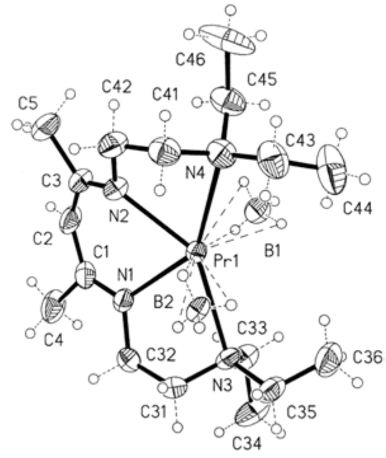
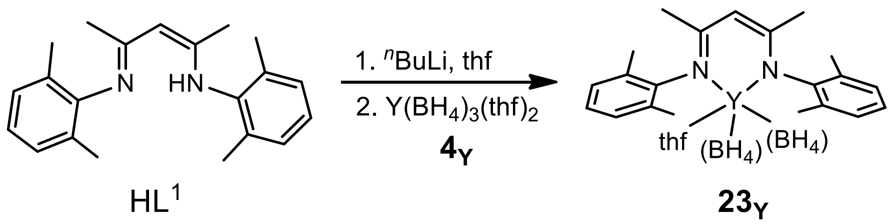


Fig. 14. The crystal structure of complex **22$_{Pr}$**. Reprinted with permission from Ref. [45]. Copyright 2002 Elsevier.

Just recently, Cui *et al.* published the one-pot synthesis of $L^1Y(BH_4)_2(thf)$ (**23$_Y$**) (HL^1 = $[(2,6\text{-}C_6H_3Me_2)NH{=}C(Me)CH{=}C(Me)N(2,6\text{-}C_6H_3Me_2)]$) by *in situ* lithiation of the β-diketimine by Bu^{n}Li, followed by subsequent metathesis reaction with **4$_Y$** (scheme 19) [46].



Scheme 19.

X-ray diffraction analysis revealed **23_Y** as a monomer of a thf solvate, adopting a trigonal-bipyamidal geometry, in which the borohydrido groups act as tridentate ligands in accordance with short Y-B distances (Fig. 15).

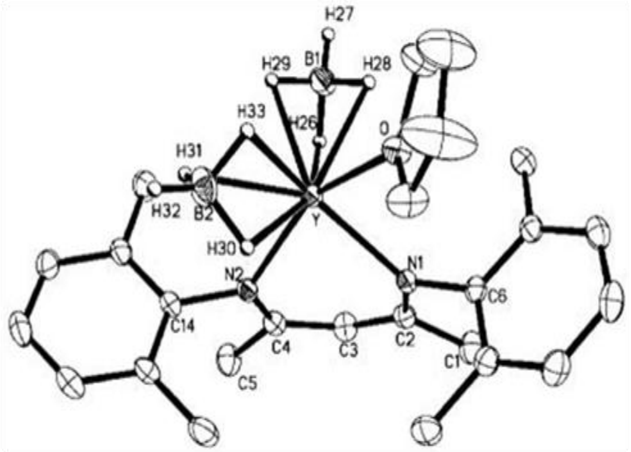
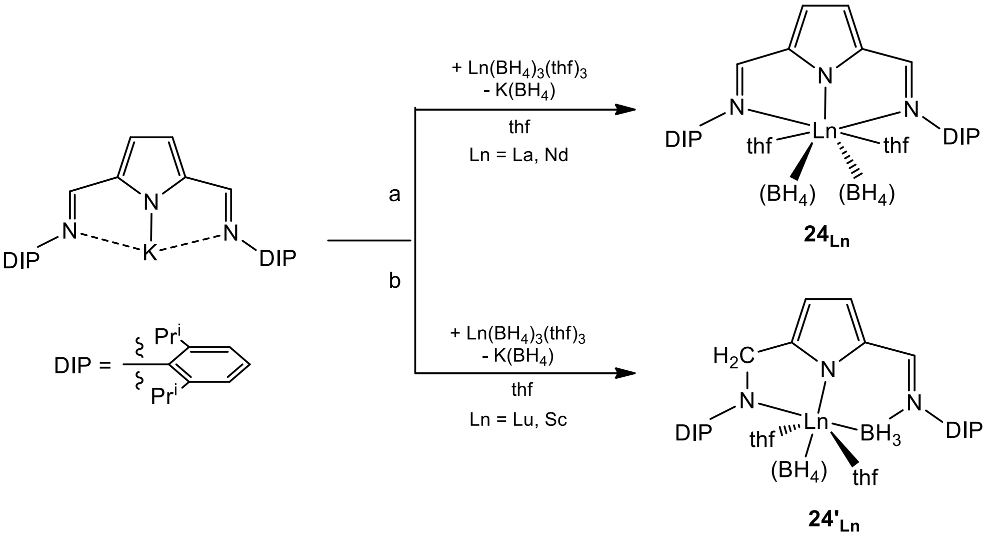


Fig. 15. The crystal structure of complex **23_Y**. Reprinted with permission from Ref. [46]. Copyright 2010 American Chemical Society.

Transmetalation of $(DIP_2\text{-pyr})K$ (DIP = 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) with **4_{Ln}** in thf afforded the monosubstituted product $(DIP_2\text{-pyr})Ln(BH_4)_2(thf)_2$ (**24_{Ln}**: Ln = La, Nd) (Scheme 20, path a) [47,48]. The X-ray structure revealed a neutral monomeric compound comprising two trihapto BH_4 groups. Under the same reaction conditions, **4_{Lu}** and **4_{Sc}** reacted differently with reduction of one of the two Schiff-base functions of the ligand, to afford $\{(DIP)(DIP\text{-}BH_3)\text{-pyr}\}Ln(BH_4)(thf)_2$ (**$24'_{Ln}$**: Ln = Sc, Lu) (Scheme 20, path b).



Scheme 20.

X-ray structural analysis carried out at 6 K established that the byproduct BH_3 of this reduction was trapped by the remaining imino nitrogen atom. The resulting $N–BH_3$ unit binds in a η^2-fashion *via* two three-center-two-electron bonds onto the lutetium (or scandium) atom (Fig. 16). Steric reasons were advanced to rationalize this unusual reactivity with lutetium and scandium.

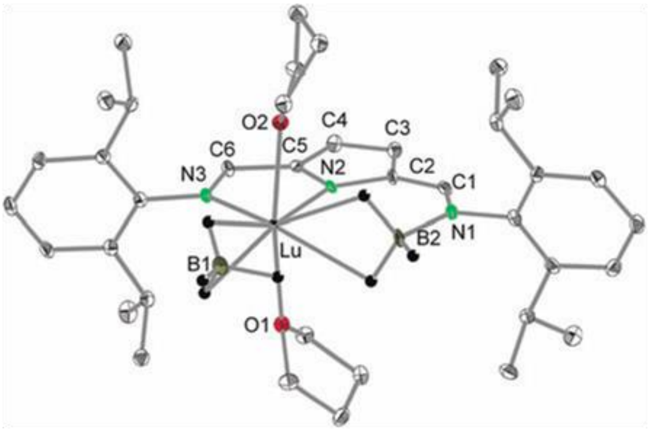
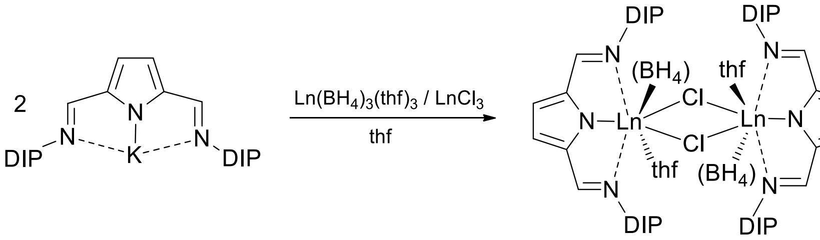


Fig. 16. The crystal structure of complex **24’$_{\mathbf{Lu}}$**. Reprinted with permission from Ref. [47]. Copyright 2009 The Royal Society of Chemistry.

Mixed borohydride-chloride complexes [(DIP$_2$-pyr)Ln(BH$_4$)Cl(thf)]$_2$ (**25$_{\mathbf{Ln}}$**: Ln = La, Nd) having the same DIP ligand in the coordination sphere were synthesized by the reaction of the potassium derivative [(DIP$_2$-pyr)K] with a 1:1 mixture of Ln(BH$_4$)$_3$(thf)$_3$ (**4$_{\mathbf{Ln}}$**) and LnCl$_3$ (scheme 21) [49].

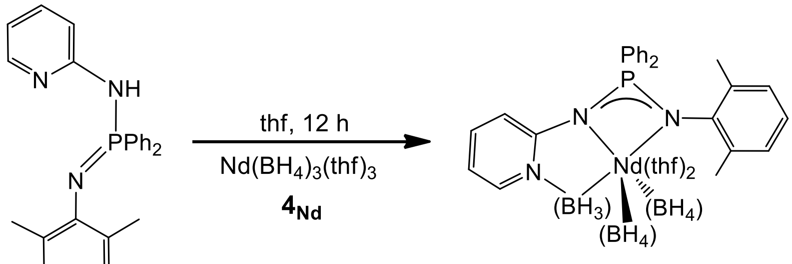


25$_{\mathbf{La}}$, 25$_{\mathbf{Nd}}$

Scheme 21.

Both compounds were dimeric in the solid state, and a bridging of the metal *via* the chlorine atoms rather *via* the BH$_4$ groups was preferred, as already observed for other mixed borohydride-chloride complexes [15,40]. The BH$_4$ groups show a η^3-coordination, as found by X-ray analysis, and confirmed from IR data. Theoretical calculations confirmed that the dimerisation was favoured over the coordination of another thf molecule.

The unprecedented straightforward reaction between Nd(BH$_4$)$_3$(thf)$_3$ (**4$_{\mathbf{Nd}}$**) and an equimolar amount of iminophosphine-aminopyridinyl ligand 2-Pyridyl-NHPPh$_2$=NC$_6$H$_3$-2,6-Me$_2$ in thf generated the bis(borohydrido) neodymium complex **26$_{\mathbf{Nd}}$** (Scheme 22) [50].



26$_{\mathbf{Nd}}$

Scheme 22.

The molecular structure of **26**$_{\textbf{Nd}}$ was confirmed by X-ray crystallographic analysis, in which both the borohydride groups and the newly formed N–BH$_3$ species coordinate to neodymium in the unusual η^2-H–B mode.

3.1.2.3. Alkoxides and related complexes

One-pot reactions of LnCl$_3$, NaBH$_4$ and ArONa (Ar = C$_6$H$_2$-Bu$^t{}_3$-2,4,6) in 1:3:1 molar ratio in thf afforded the neutral and isostructural aryloxide lanthanide borohydrides (ArO)Ln(BH$_4$)$_2$(thf)$_2$ (**27**$_{\textbf{Ln}}$: Ln = Yb, Er) [51]. Both of the borohydride ligands in each monomeric complex were η^3-coordinated (Fig. 17).

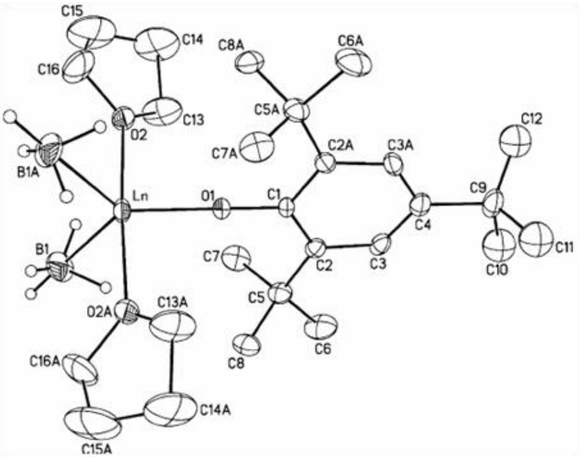
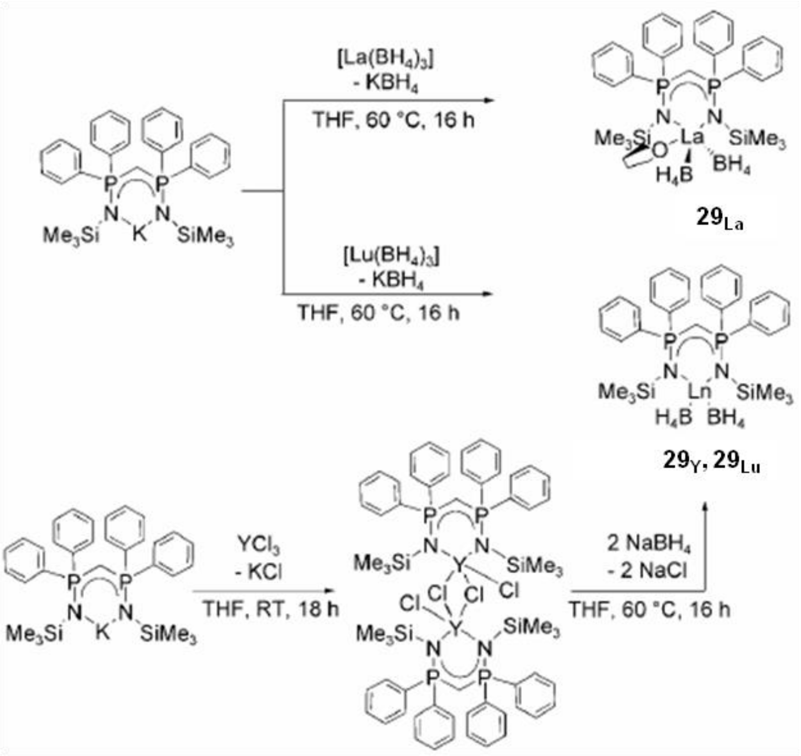


Fig.17. The crystal structure of complex **27**$_{\textbf{Ln}}$. Reprinted with permission from Ref. [51]. Copyright 2006 Elsevier.

Grafting of **4**$_{\textbf{Ln}}$ derivatives (Ln = La, Nd) onto dehydroxylated silica afforded materials containing bis(borohydride) surface species of formula [(≡SiO)Ln(BH$_4$)$_2$(thf)$_{2.2}$] (**28**$_{\textbf{Ln}}$), according to elemental analysis, and solid-state NMR spectroscopy. IR studies showed typical absorbances for η^3-bound terminal BH$_4$ groups [52].

3.1.2.4. Bis(phosphinimino)methanide complexes

Roesky *et al.* reported recently on the use of the bulky bis(phosphinimino)methanide ligand directed to the preparation of monosubstituted borohydrides. The neutral monomeric bis-borohydrides [{CH(PPh$_2$NSiMe$_3$)$_2$}La(BH$_4$)$_2$(thf)] (**29**$_{\textbf{La}}$) and [{CH(PPh$_2$NSiMe$_3$)$_2$}Ln(BH$_4$)$_2$] (**29**$_{\textbf{Ln}}$: Ln = Y, Lu) were obtained, but the synthetic routes differed depending on the metal: **29**$_{\textbf{La}}$ and **29**$_{\textbf{Lu}}$ resulted from the metathesis between **4**$_{\textbf{Ln}}$ and the bis(phosphinimino)methanide potassium, whereas **29**$_{\textbf{Y}}$ was obtained in a two-step one-pot procedure from *in situ* prepared [{CH(PPh$_2$NSiMe$_3$)$_2$}YCl$_2$]$_2$, and NaBH$_4$ (scheme 23) [53].



Scheme 23.

The solid state structures were established by single crystal X-ray diffraction (Fig. 18). The **29_{La}** compound is a thf adduct, whereas **29_{Lu}** and **29_{Y}** are not solvated, as a result of the smaller ion radius of the central metal atom. Noteworthy, a weak interaction between the central carbon atom (C1) and the metal atom was observed in all three complexes. All borohydride groups adopt a tridentate coordination mode.

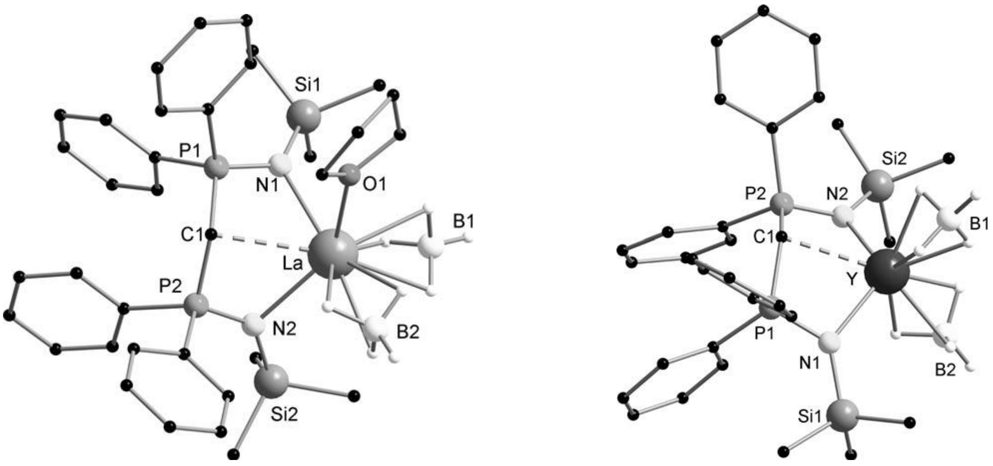


Fig. 18. The crystal structure of complexes **29_{La}** (left) and **29_{Y}** (right). Reprinted with permission from Ref. [53]. Copyright 2010 Wiley Interscience.

Table 2

Mono-substituted Borohydride Organometallic Compounds and their Characterization

Compound	Synthesis [a]	NMR	Infra Red	Elem. Anal.	X-ray (H-(B*H*$_4$) located)	Reference
$(Cp^*)Sm(BH_4)(thf)_2$ (**11$_{Sm}$**)	B	^1H	-	✓	✓ (yes)	[13]
$(Tp^{\textit{tert}\text{-Bu,Me}})Yb(BH_4)(thf)_n$ (n = 1, **12$_{Yb}$**; n = 0, **12'$_{Yb}$**)	E, A	^1H, ^{11}B, ^{13}C	✓	✓ (n = 0)	✓ (n = 1, yes)	[31]
$[(Cp)Nd(BH_4)_3]_2[Mg(thf)_6]$ (**13$_{Nd}$**)	C	^1H	-	✓	✓ (yes)	[32]
$[(Cp^{Ph3})Nd(BH_4)_3]_2[Mg(thf)_6]$ (**14$_{Nd}$**)	C	^1H	-	✓	✓ (yes)	[32]
$(Cp^{Ph3})Sm(BH_4)_2(thf)_2$ (**14'$_{Sm}$**)	B	^1H	-	-	-	[33]
$(Cp^*)Sc(BH_4)_2(thf)$ (**15$_{Sc}$**)	B	^1H	-	✓	✓ (yes)	[36]
$(Cp^*)Nd(BH_4)_2(thf)_n$ (**15$_{Nd}$**)	B	^1H (n = 2)	✓ (n = 2, 0)	✓ (n = 0)	-	[6]
$(Cp^*)La(BH_4)_2(thf)_n$ (**15$_{La}$**)	B	^1H (n = 2)	-	✓ (n = 0)	-	[37]
$[(Cp^*)Ln(BH_4)_2]$ (Ln = Sm, Dy, Yb) (**15'$_{Ln}$**)	B [b]	^1H, ^{11}B	✓	✓	-	[38]
$[(Cp^*)Ln(BH_4)_3]_2[Mg(thf)_6]$ (Ln = La, Nd) (**16$_{Ln}$**)	C	^1H	-	✓	✓ (yes: Nd ; no: La)	[39] (Nd), [32] (La)
$(Cp^{*\prime})Ln(BH_4)_2(thf)_n$ (Ln = Nd, n = 2 ; Ln = Sm, n = 1) (**17$_{Ln}$**)	B	^1H	✓	✓	-	[40]
$[(Cp^{*\prime})Nd(BH_4)_2]_6$ (Ln = Nd, Sm) (**17'$_{Ln}$**)	B	-	-	-	✓ (no)	[40]
$[(Cp^{*\prime})_6Ln_6(BH_4)_{(12-x)}Cl_x(thf)_{n'}]$ (**17a''$_{Ln}$**: x = 10, n' = 4, Ln = Sm, Nd; **17b''$_{Sm}$**: x = 5, n' = 2, Ln = Sm)	B	-	-	-	✓ (no)	[40]
$(Cp^{4i})Ln(BH_4)_2(thf)$ (Ln = Sm, Nd) (**18$_{Nd}$**)	B, D (Sm)	^1H	✓	✓	✓ (yes)	[7]
$(C_5Me_4\text{-}C_6H_4\text{-}\textit{o}\text{-}NMe_2)Ln(BH_4)_2$ (Ln = Sc, Sm) (**19$_{Ln}$**)	B	^1H, ^{11}B, ^{13}C (Sc)	-	✓	✓ (Sc, yes)	[41]
$\{(Me_3Si)_2NC(NPr^i)_2\}Sm(BH_4)_2(dme)$ (**20$_{Sm}$**)	A	-	✓	✓	✓ (yes)	[42]
$[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(thf)_2$ (Ln = Yb, Er) (**21$_{Ln}$**)	B	-	✓	✓	✓ (yes)	[43]
$[(Me_3Si)_2NC(NCy)_2]Gd(BH_4)_2(dme)$ (**21'$_{Gd}$**)	B	-	✓	✓	✓ (yes)	[44]
$\{[Et_2NCH_2CH_2NC(Me)]_2CH\}Pr(BH_4)_2$ (**22$_{Pr}$**)	A	^{11}B	-	✓	✓ (yes)	[45]
$(C_6H_3Me_2\text{-}2{,}6)NHC(Me)CHC(Me)N(C_6H_3Me_2\text{-}2{,}6)Y(BH_4)_2(thf)$ (**23$_Y$**)	B	^1H, ^{13}C	-	✓	✓ (yes)	[46]
$(DIP_2\text{-pyr})Ln(BH_4)_2(thf)_2$ (Ln = La, Nd) (**24$_{Ln}$**)	B	^1H, ^{11}B, ^{13}C	✓	✓	✓ (yes)	[47] (La), [48] (Nd)
$\{(DIP)(DIP\text{-}BH_3)\text{-pyr}\}Ln(BH_4)(thf)_2$ (Ln = Sc, Lu) (**24'$_{Ln}$**)	B	^1H, ^{11}B, ^{13}C	✓	✓	✓ (yes)	[47] (Lu), [48] (Sc)
$[(DIP_2\text{-pyr})Ln(BH_4)Cl]_2$ (Ln = La, Nd) (**25$_{Ln}$**)	B	-	✓	✓	✓ (yes)	[49]
$[N(C_6H_3\text{-}2{,}6\text{-}Me_2)PPh_22\text{-pyr-}N(BH_3)]Nd(BH_4)_2(thf)2$ (**26$_{Nd}$**)	- [c]	-	✓	✓	✓ (yes)	[50]
$(ArO)Ln(BH_4)_2(thf)_2$ (Ln = Yb, Er) (**27$_{Ln}$**)	A	-	✓	✓	✓ (yes)	[51]
$[(\equiv SiO)Ln(BH_4)_2(thf)_{2.2}]$ (Ln = La, Nd) (**28$_{Ln}$**)	- [c]	^1H, ^{11}B, ^{13}C	✓	✓	-	[52]
$[CH(PPh_2NSiMe_3)_2]Ln(BH_4)_2(thf)_n$ (Ln = Y,Lu, n = 0; Ln = La, n = 1) (**29$_{Ln}$**)	A (Y), B	^1H, ^{13}C, ^{11}B, ^{31}P	✓	✓	✓ (yes)	[53]

[a] See the synthetic methods as defined in the introduction;

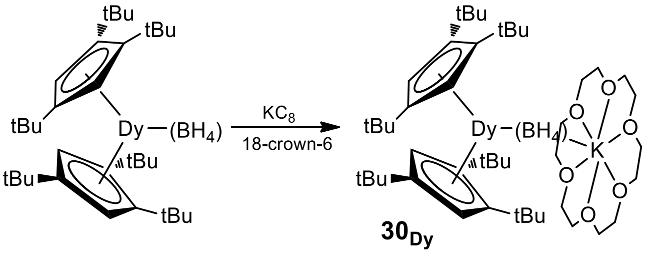
[b] from $Ln(BH_4)_2Cl$ as starting material;

[c] from the reaction of **4$_{Ln}$** with the corresponding protio pro-ligand.

3.2. Di-substituted complexes

3.2.1. Divalent derivatives

Reduction of the bis(tri-*tert*-butylcyclopentadienyl)(borohydride)dysprosium(III) $(Cp^{ttt})_2Dy(BH_4)$ (Cp^{ttt} = C_5H_2-Bu^t_3-1,2,4) by potassium/graphite in the presence of a crown ether afforded the unique example of divalent organolanthanide “ate” borohydride $[(Cp^{ttt})_2Dy(BH_4)][K(18\text{-crown-}6)]$ complex (**30$_{Dy}$**) (scheme 24) [54].



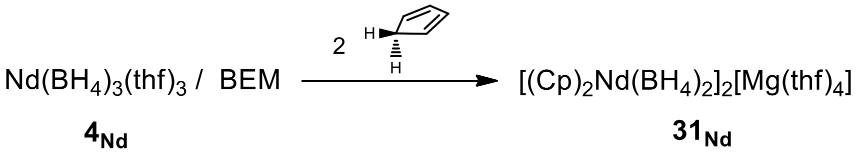
Scheme 24.

NMR data and further reactions with oxidants (see further, section 4.1.3) established unambiguously the divalent nature of **30$_{Dy}$**. The BH_4 group was μ_2-$\eta^{2:2}$ bonded to form a Dy(μ-H)$_2$B(μ-H)$_2$K bridge from X-ray structure determination.

3.2.2. Trivalent derivatives

3.2.2.1. Bis(cyclopentadienyl) and related complexes

The bis(cyclopentadienyl)borohydride $[(Cp)_2Nd(BH_4)]_2[Mg(BH_4)_2(thf)_4]$ (**31$_{Nd}$**) was synthesized by the “B/A route”, *i.e.* from equimolar amounts of **4$_{Nd}$** and *n*-butylethylmagnesium (BEM) in the presence of 2 equiv. of cyclopentadiene (scheme 25) [55].



Scheme 25.

X-ray structural analysis revealed a dimetallic trinuclear Nd_2Mg compound 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 (Fig. 19).

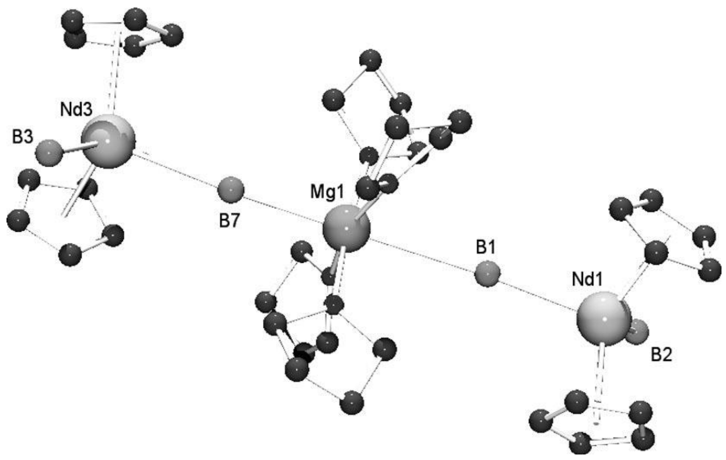


Fig. 19. One of the two entities of the asymmetric unit showing the crystal structure of complex **31**$_{\mathbf{Nd}}$. Reprinted with permission from Ref. [55]. Copyright 2010 Wiley Interscience.

The Nd–Mg distances account for a rather covalent trimetallic compound, in contrast to observations in the corresponding half-sandwich **13**$_{\mathbf{Nd}}$, where discrete ionic [Nd] and [Mg] moieties were clearly identified. The two Nd–B–Mg bridges were however clearly dissymmetric, and therefore, the molecular arrangement is better described as: $[(Cp)_2Nd(BH_4)_2][Mg(BH_4)(thf)_4][(Cp)_2Nd(BH_4)]$. Nd–B distances indicated bridged BH_4 η^2-rather than η^3- coordinated, whereas each neodymium center bears one additional terminal BH_4, most likely trihapto. ^1H NMR spectrum in thf showed that the complex was prone to disproportionation (so-called "ligand scrambling") process in this polar solvent (scheme 26).

$$2\ (Cp)_2Nd(BH_4)(thf)_x \rightleftharpoons (Cp)Nd(BH_4)_2(thf)_y + (Cp)_3Nd$$

Scheme 26.

In an article published in 1998, Schumann *et al.* described a series of metallocenes (**32**$_{\mathbf{Ln}}$, Ln = Y, Sm, Lu) prepared in two steps from the reaction of the thf adducts $LnCl_3(thf)_x$ firstly with two equivalents of *tert*-butyl-cyclopentadienyl (Cp' = $C_5H_4Bu^t$) reagent and then secondly with one equivalent of $NaBH_4$, without isolation of the chlorometallocene intermediate (scheme 27) [56]. The yields were fair, and the complexes were characterized by NMR, MS, and elemental analysis.

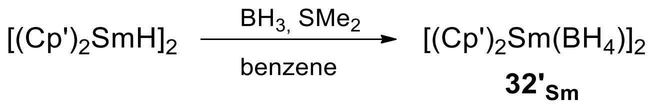
$$LnCl_3(thf)_x \xrightarrow[\text{2. NaBH}_4\text{, thf, reflux}]{\text{1. 2 Cp'Na, thf, reflux}} (Cp')_2Ln(BH_4)(thf)$$

32$_{\mathbf{Y}}$, **32**$_{\mathbf{Sm}}$, **32**$_{\mathbf{Lu}}$

Scheme 27.

It must be noted that the non solvated analog of **32**$_{\mathbf{Sm}}$, $[(Cp')_2Sm(BH_4)]_2$ (**32'**$_{\mathbf{Sm}}$), had been previously synthesized by Bulyshev and co-workers by displacement of the chloride of $(Cp')_2SmCl$ with $LiBH_4$ in Et_2O followed by pentane extraction [57]. Interestingly, it was shown that **32'**$_{\mathbf{Sm}}$ could also be prepared *via* insertion reaction of a borane molecule into the

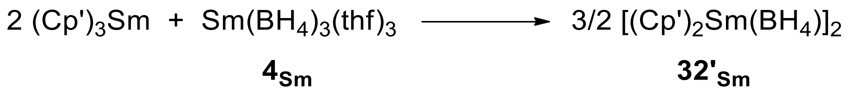
Sm-H bond of the hydride $[(Cp')_2SmH]_2$ (scheme 28) [58], following the well-known reactivity of lanthanide hydrides [4] [59].



$$[(Cp')_2SmH]_2 \xrightarrow[\text{benzene}]{BH_3,\ SMe_2} [(Cp')_2Sm(BH_4)]_2 \quad \mathbf{32'_{Sm}}$$

Scheme 28.

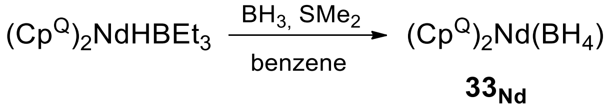
In the same article, it was reported that this compound was also available from a comproportionation reaction (scheme 29).



$$2\ (Cp')_3Sm\ (\mathbf{4_{Sm}}) + Sm(BH_4)_3(thf)_3 \longrightarrow 3/2\ [(Cp')_2Sm(BH_4)]_2\ (\mathbf{32'_{Sm}})$$

Scheme 29.

The ether-tethered borohydrido neodymocene $(Cp^Q)_2Nd(BH_4)$ (**33_{Nd}**) (Cp^Q = $C_5H_4CH_2CH_2OCH_3$) was prepared by the similar reaction of borane with a triethylborohydride (scheme 30) [60].This complex had already been synthesized but by ionic metathesis between $(Cp^Q)_2NdCl$ and $NaBH_4$ [61].



$$(Cp^Q)_2NdHBEt_3 \xrightarrow[\text{benzene}]{BH_3,\ SMe_2} (Cp^Q)_2Nd(BH_4) \quad \mathbf{33_{Nd}}$$

Scheme 30.

The non solvated $(Cp^{ttt})_2Ln(BH_4)$ **34_{Ln}** complexes (Ln = Tm [62], Dy [54]; Cp^{ttt} = C_5H_2-Bu^t_3-1,2,4) were synthesized by metathetical reaction of KCp^{ttt} with **4_{Ln}** in refluxing toluene. Interestingly, both compounds are very rare examples of non-solvated lanthanidocenes that yet bear a BH_4 group under a dihapto coordination mode, as established from X-ray structure analysis (Fig. 20).

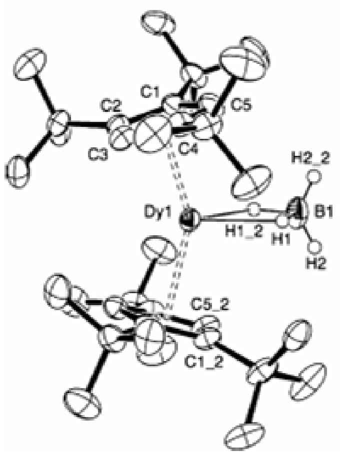


Fig. 20. The crystal structure of complex **34_{Dy}**. Reprinted with permission from Ref. [54]. Copyright 2007 American Chemical Society.

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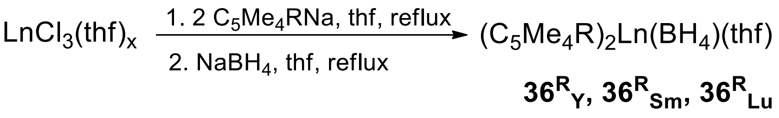
[4] As presented as synthetic method E in the introduction

When the substituents on the cyclopentadienyl ring are phenyl groups, a thf adduct was isolated: the (triphenyl)cyclopentadienyl derivative $(Cp^{Ph3})_2Sm(BH_4)(thf)$ $\mathbf{35_{Sm}}$ was prepared by ionic metathesis from $\mathbf{4_{Sm}}$ and the stoichiometric amount of KCp^{Ph3} in toluene, but no X-ray data are available for this complex [33].

A large family of (peralkylsubstituted)cyclopentadienyl borohydride metallocenes $(C_5Me_4R)_2Ln(BH_4)(thf)$ ($\mathbf{36^{R}_{Ln}}$: Ln = Y, Sm, Lu; R = H, Me, Et, Pr^{i}) was prepared in 1998 by Schumann *et al.*, without isolating the chloro homologues (scheme 31) [56]. Despite paramagnetism, all ^{1}H NMR spectra were interpreted.



$$LnCl_3(thf)_x \xrightarrow[\text{2. NaBH}_4\text{, thf, reflux}]{\text{1. 2 C}_5\text{Me}_4\text{RNa, thf, reflux}} (C_5Me_4R)_2Ln(BH_4)(thf)$$

$\mathbf{36^{R}_{Y}}$, $\mathbf{36^{R}_{Sm}}$, $\mathbf{36^{R}_{Lu}}$

Scheme 31.

The crystal structures of $\mathbf{36^{Me}_{Sm}}$ and $\mathbf{36^{Et}_{Y}}$ were determined, they confirmed the monomeric mono-thf adduct structure. Hydrogen atoms belonging to the BH_4 group were located for $\mathbf{36^{Et}_{Y}}$ only, showing a dihapto mode of coordination, whereas a tridentate BH_4 group was postulated for $\mathbf{36^{Me}_{Sm}}$ (Fig. 21).

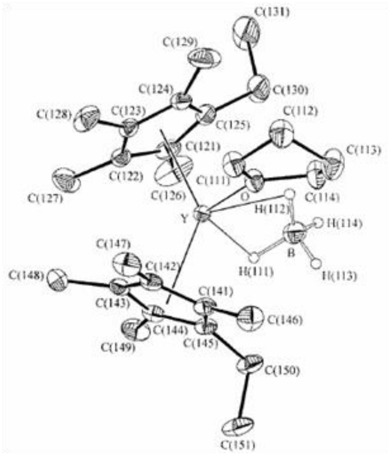


Fig. 21. The crystal structure of complex $\mathbf{36^{Et}_{Y}}$. Reprinted with permission from Ref. [56]. Copyright 1998 Wiley-VCH.

Tridentate ligation of the BH_4 group for larger lanthanides belonging to the *early* series postulated by Schumann was further confirmed in the Cp* series by Visseaux *et al.* who determined the molecular structure of $\mathbf{36^{Me}_{Nd}}$. This complex was prepared in two different manners, initially by ionic metathesis with $\mathbf{4_{Nd}}$ as starting material [63], and just recently by the “B/A route” [55]. Only one compound in this Cp* series was non solvated: the scandium analog $\mathbf{36^{Me}_{Sc}}$ [36], which was isolated serendipitously as a by-product in the synthesis of the half-sandwich $\mathbf{15_{Sc}}$, probably resulting from disproportionation reactions. X-ray single crystal analysis allowed to establish that the borohydride group was terminal tridentate.

The molecular structure of $(C_5Me_4Pr^{i})_2Sm(BH_4)(thf)$ $\mathbf{36^{\mathit{i}Pr}_{Sm}}$ was further resolved by Schumann *et al.*, and the trihapto mode of coordination of the terminal borohydride ligand was established unambiguously [64].

More recently, was published the X-ray structure of the neutral samarocene $(Cp^{*}{'})_2SmBH_4(thf)$ $\mathbf{36^{\mathit{n}Pr}_{Sm}}$, which was prepared by the reaction of $\mathbf{4_{Sm}}$ with two equivalents of K(Cp*’). X-ray structure analysis revealed a monomeric complex bearing a terminal borohydride ligand exhibiting a η^3-H_3BH bonding mode [29]. The neodymium parallel **36**$^{n\mathrm{Pr}}_{\mathrm{Nd}}$ was made *in situ* by ionic metathesis but it was not isolated [33].

With the roomy tetra-isopropylcyclopentadienyl ligand, the $(Cp^{4i})_2Ln(BH_4)$ complexes **37**$_{\mathrm{Ln}}$ (Ln = Nd, Sm), which were prepared by metathetic reaction between their **18**$_{\mathrm{Ln}}$ half-sandwich counterparts and 1 equiv. of $Na(Cp^{4i})$ (scheme 32), were also solvent free monomers, probably related both to the high bulkiness and to the electron donating ability of the cyclopentadienyl ligand (Fig. 22) [7].

$$\underset{\mathbf{18_{Ln}}}{(Cp^{4i})Ln(BH_4)_2(thf)} + Na(Cp^{4i}) \xrightarrow{C_6D_6} \underset{\mathbf{37_{Ln}}}{(Cp^{4i})_2Ln(BH_4)}$$

Scheme 32.

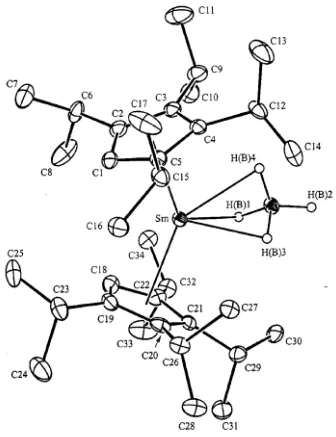


Fig. 22. The crystal structure of complex **37**$_{\mathrm{Sm}}$. Reprinted with permission from Ref. [7]. Copyright 2000 Wiley-VCH.

Both complexes were isostructural, and are unique examples of tricoordinated complexes of the *early* lanthanides. The difference of hapticity of the borohydride ligand with respect to the above-mentioned **34**$_{\mathrm{Ln}}$ (Ln = Dy, Tm) derivatives may be related to the nature of the lanthanide atom, since dysprosium and tullium belong to the *late* group. Additional structural information for the **37**$_{\mathrm{Ln}}$ complexes was deduced from an extensive ^{1}H NMR study [65]. Despite the paramagnetism of both neodymium and samarium, the molecular conformation of the hyperbulky Cp^{4i} ligand was fully resolved from 1D, 2D COSY and *T*1 relaxation experiments. The latter measurements allowed to conclude that a possible agostic Sm–$H(CH_3)$ interaction in **37**$_{\mathrm{Sm}}$ in the solid state was not retained in solution.

3.2.2.2. Bis(phospholyl) complexes

$[K(thf)][(P^*)_2Nd(BH_4)_2]$ (**38**$_{\mathrm{Nd}}$) ($P^* = C_4Me_4$) was obtained by metathetic reaction from **4**$_{\mathrm{Nd}}$ and K(P*) in thf (scheme 33) [6]. Formation of an “ate” complex was rationalized by the much weaker electron-donating ability of the P* ligand compared with the isosteric Cp* one.

$$2\,K(P^*) + \underset{\mathbf{4_{Nd}}}{Nd(BH_4)_3(thf)_3} \xrightarrow{thf} \underset{\mathbf{38_{Nd}}}{(P^*)_2Nd(BH_4)_2(thf)_2[K(thf)_2]}$$

Scheme 33.

Addition of crown-ether to this anionic compound allowed the preparation of [K(18-crown-6)(thf)$_2$][(P*)$_2$Nd(BH$_4$)$_2$] (**38’$_{\mathrm{Nd}}$**). The monomeric structure was determined by X-ray crystallography, showing discrete anion and cation [66]. Hydrogen atoms were not located but the Nd-B distances agree with the short distances observed for tridentate binding mode of a BH$_4$ ligand, as also confirmed by IR spectroscopy.

3.2.2.3. Bis(indenyl) complexes

Racemic bis(2-methoxyethylindenyl) borohydrides (MeOCH$_2$CH$_2$C$_9$H$_6$)$_2$Ln(BH$_4$) (**39$_{\mathrm{Ln}}$**: Ln = Y, La) were prepared by the reaction of the corresponding chloro-sandwich with NaBH$_4$ in thf [67]. The tetrahydroborate ligand was bidentate (**39$_{\mathrm{Y}}$**) or tridentate (**39$_{\mathrm{La}}$**), depending on the metal atom (Fig. 23). The Ln-O bond distances (O belonging to the sidearm) were longer than those of the cyclopentadienyl (Cp$^{\mathrm{Q}}$) analogs.

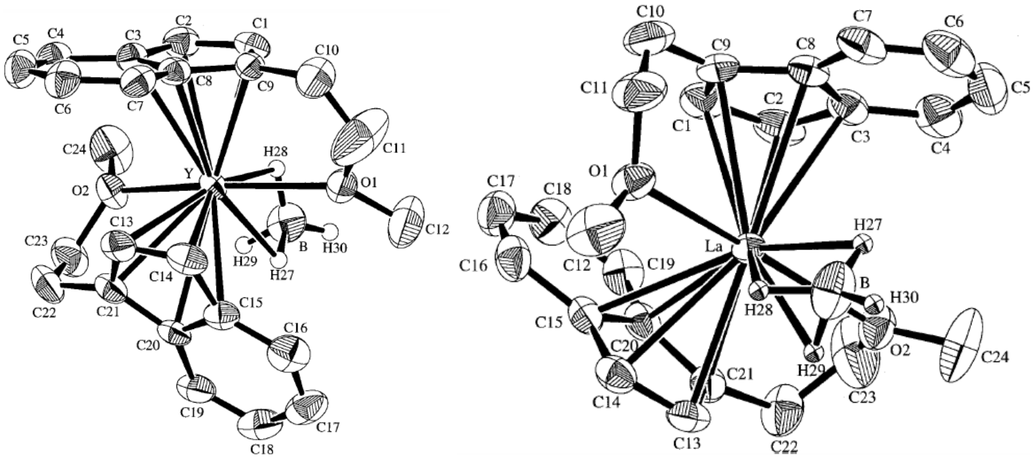


Fig. 23. The crystal structure of complexes **39$_{\mathrm{Y}}$** (left) and **39$_{\mathrm{La}}$** (right). Reprinted with permission from Ref. [67]. Copyright 2000 Elsevier.

3.2.2.4. *Ansa*-cyclopentadienyl complexes

The borohydride “ate” *ansa*-ytterbocene [*rac*-Me$_2$C(C$_5$H$_3$-3-SiMe$_3$)$_2$Yb(BH$_4$)$_2$Li(thf)$_2$] (**40$_{\mathrm{Yb}}$**) resulted from the two-step reaction in thf of YbCl$_3$ with successively Me$_2$C(3-SiMe$_3$-C$_5$H$_3$)$_2$Li$_2$, and a 50% excess of LiBH$_4$ [68]. From X-ray studies, one can observe a polymer of ytterbocene moieties, connected together into a {Li(μ-H)$_2$B(μ-H)$_2$Yb(μ-H)$_2$B(μ-H)$_2$} chain by two tetradentate borohydride groups (Fig. 24). The Cp–Yb–Cp angle is 111.0° which leads to the ‘opening’ of the wedge between cyclopentadienyl planes where two BH$_4$ groups can be located.

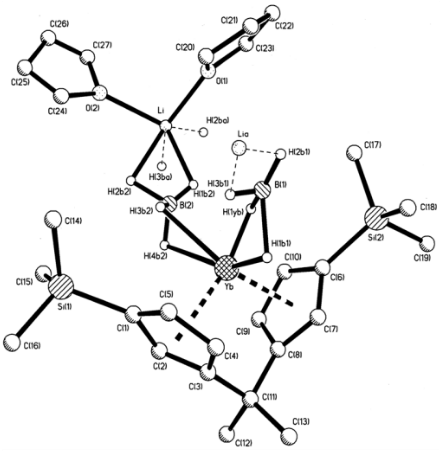


Fig. 24. The crystal structure of complex **40_{Yb}**. Reprinted with permission from Ref. [68]. Copyright 1998 Elsevier.

The dimethylsilylene-bridged homologue *meso*-$Me_2Si(C_5H_3$-3-$SiMe_3)_2Yb(BH_4)(thf)$ (**41_{Yb}**) was isolated from the metathetic reaction of the chloro-ytterbocene with $LiBH_4$ in diethyl ether [69]. According to X-ray structural analysis, this complex was monomeric under a solvated form, and bearing one η^3 terminal BH_4 group (Fig. 25). The Yb-B distance is shorter than those in **40_{Yb}**, where two borohydride groups are η^2-coordinated to the ytterbium atom. The Cp-Yb-Cp angle (121.5(2) °) is higher than found in the latter, reflecting the greater flexibility of the -$SiMe_2$- bridge compared to -CMe_2-. Several years later, in 2006, Boisson *et al.* prepared the neodymium derivative **41_{Nd}** in the same series, but by the reaction of the dilithium salt with trisborohydride **4_{Nd}**. The ^1H NMR analysis showed a mixture of *meso* and *racemic* forms with a ratio of 34/66 [70].

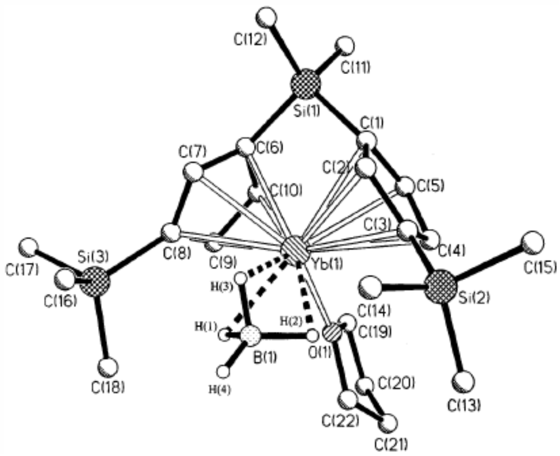
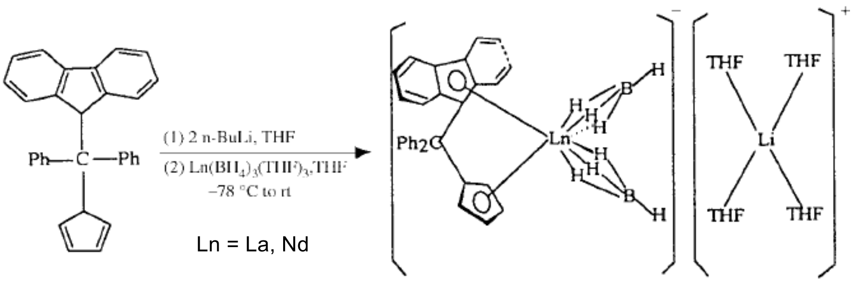


Fig. 25. The crystal structure of complex **41_{Yb}**. Reprinted with permission from Ref. [69]. Copyright 1999 Elsevier.

Treatment of the trisborohydrides **4_{Ln}** with an equivalent amount of the dilithium salt of the diphenylmethylene-bridged fluorenyl-cyclopentadienyl ligand $(C_{13}H_8)CPh_2(C_5H_4)Li_2$ in thf gave the anionic complexes $[Li(thf)_4][Ln(BH_4)_2\{(C_{13}H_8)CPh_2(C_5H_4)\}]$ (**42_{Ln}**: Ln = La, Nd) (Scheme 34) [71].



42_{Ln}

Scheme 34.

X-ray structure determination of both complexes indicated that they exist under an "ate" molecular form, with separated anionic and cationic moieties (Fig. 26). The metal was bonded in η^5 fashion to each cyclopentadienyl and fluorenyl ring along with two tridentate BH_4 groups.

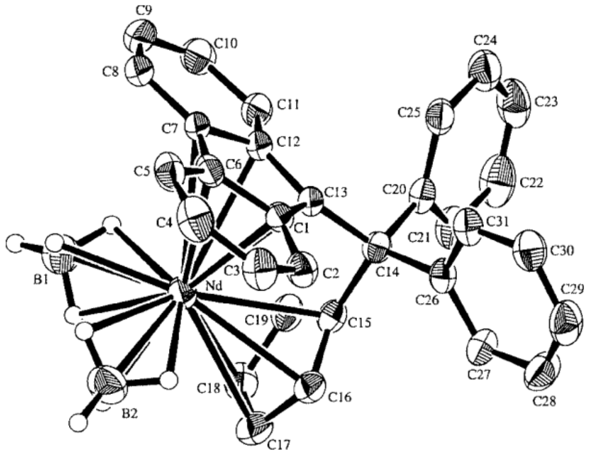


Fig. 26. The crystal structure of the $[Nd(BH_4)_2(C_{13}H_8)CPh_2(C_5H_4)]^-$ anion of complex $\mathbf{42_{Nd}}$. Reprinted with permission from Ref. [71]. Copyright 1999 The Royal Society of Chemistry.

By using the dipotassium salt of the same *ansa*- ligand, and in the presence of 18-crown-6 ether, the reaction with $\mathbf{4_{Nd}}$ in thf afforded the dinuclear anionic complex $\{[K(18\text{-crown-}6)][(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2]\}_2\cdot$dioxane $\mathbf{42'_{Nd}}$ (Scheme 35) [72].

$$\underset{\mathbf{4_{Nd}}}{Nd(BH_4)_3(thf)_3} + K_2[FluCPh_2Cp] \xrightarrow[\text{thf}]{\text{18-crown-6}} \underset{\mathbf{42'_{Nd}}}{\{K(18\text{-crown-}6)[(FluCPh_2Cp)Nd(BH_4)]\}_2(dioxane)}$$

Scheme 35.

The crystal structure of this complex consisted of the connection of the two discrete anions of the $[(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2]^-$ moiety by the cation of $\{[K(18\text{-crown-}6)]^{2+}\cdot$dioxane$\}$ through a weak η^2 interaction of the Flu units with the K^+ cations (Fig. 27). The two borohydrido groups were found to display a likely trihapto ligation geometry to the metal center (from Nd-B distances), as same as observed with $\mathbf{42_{Ln}}$.

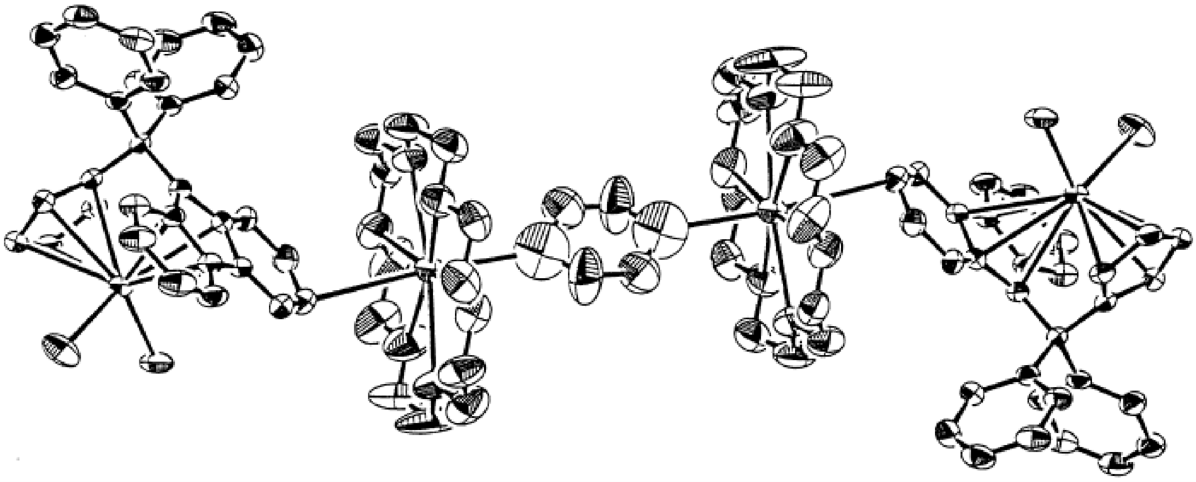


Fig. 27. The crystal structure of complex **42’**$_{\mathbf{Nd}}$. Reprinted with permission from Ref. [72]. Copyright 2001 Elsevier.

In 2006, Boisson *et al.* performed the synthesis of a silylene bridged *ansa*-FluCp neodymium compound by reaction of $Me_2Si(C_5H_4)(C_{13}H_8)Li_2(thf)_2$ with **4**$_{\mathbf{Nd}}$, yielding the “ate” compound $[Me_2Si(C_5H_4)(C_{13}H_8)Nd(BH_4)_2][Li(thf)].0.5LiBH_4$ (**43**$_{\mathbf{Nd}}$) according to ^1H NMR and elemental analysis [70].

The same group recently succeded in the preparation of two other *ansa*-fluorenyl complexes by reaction of the dilithium salts of silylenebridged bis(fluorenyl) ligands with the borohydride precursor **4**$_{\mathbf{Nd}}$: $\{(Me_2Si(C_{13}H_8)_2)Nd(\mu\text{-}BH_4)[(\mu\text{-}BH_4)Li(thf)]\}_2$ (**44**$_{\mathbf{Nd}}$) and $[Me_2Si(2,7\text{-}Bu^t{}_2C_{13}H_6)_2]Nd(BH_4)(\mu\text{-}BH_4)Li(ether)_3$ (**45**$_{\mathbf{Nd}}$). ^1H NMR integral of the BH_4 signal established the formation of (*ansa*-Flu)$Nd(BH_4)_2$ “ate” complexes, which was further confirmed by X-ray diffraction studies [73]. It is noteworthy that the introduction of *tert*-butyl substituents on fluorenyl ligands leads to the isolation of a monomeric structure, by comparison with the non-substituted complex which displays a dimeric one (Fig. 28). In **44**$_{\mathbf{Nd}}$, only one thf molecule is bonded to the lithium atom and its coordination sphere is completed with two bidentate borohydrides. The *ansa*-bis(fluorenyl) ligand is best described as bis-[η^5] bonded to the neodymium atom.

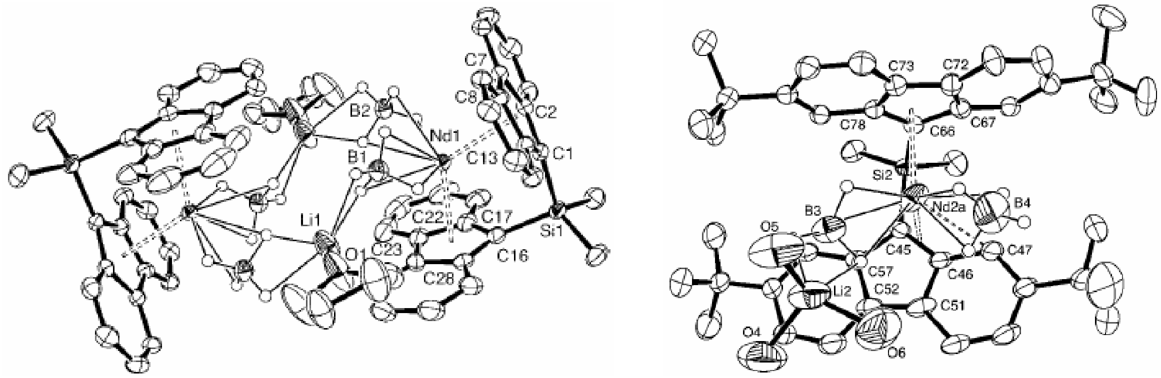


Fig. 28. The crystal structure of complex **44**$_{\mathbf{Nd}}$ and of one of the two representative molecules of complex **45**$_{\mathbf{Nd}}$ (right). Reprinted with permission from Ref. [73]. Copyright 2009 American Chemical Society.

The geometry was more open in **45**$_{Nd}$, which exists as two different molecules in the unit cell, than in **44**$_{Nd}$, due to steric repulsion between the *tert*-butyl groups. The neodymium atom is tilted away from the center of one 5-membered ring and the bonding situation of neodymium is best described as [η^3, η^2] in one molecule, and as bis-[η^4] in the other one. One BH_4 group is under a Li[μ–$\eta^{2:3}$(BH_4)]Nd bridging form and the second one is trihapto-coordinated to the metal atom.

The tetramethyl-ethylene *ansa*-lanthanidocenes [($CMe_2C_5H_4)_2Ln(BH_4)_2$)]$_2$Mg(thf)$_3$ (**46**$_{Ln}$: Ln = Nd, Sm) were synthesized by the "B/A route" from equimolar amounts of **4**$_{Ln}$ and *n*-butylethylmagnesium (BEM) in the presence of two equiv. of the related *ansa*-cyclopentadiene [55]. The complexes were characterized by ^{1}H NMR spectroscopy, elemental analysis, and X-ray structural analysis. Both **46**$_{Ln}$ complexes were isostructural, and they can be described as dimetallic trinuclear bent structures (Fig. 29). The magnesium center, which bears only three thf molecules, is linked to both lanthanides through a typical η^2-(BH_4) bridge, and this $Mg(BH_4)_2$ moiety appears almost symmetrical. Therefore, the molecular arrangement in these complexes can be seen as including a covalent $Mg(BH_4)_2$ unit, allowing to describe the complexes as $(CMe_2C_5H_4)_2Ln(BH_4)(\mu\text{-}BH_4)Mg(thf)_3(\mu\text{-}BH_4)(BH_4)Ln(C_5H_4CMe_2)_2$. In both cases, the second BH_4 group is coordinated in a terminal η^3 mode.

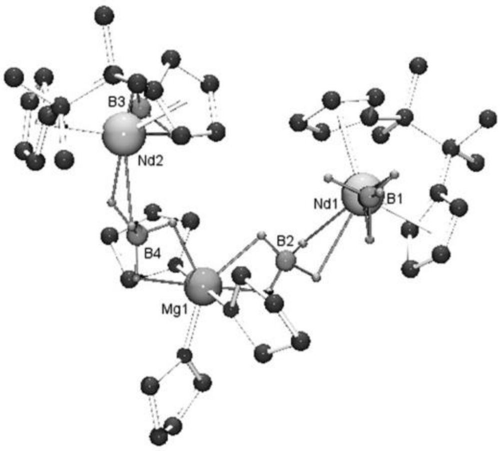
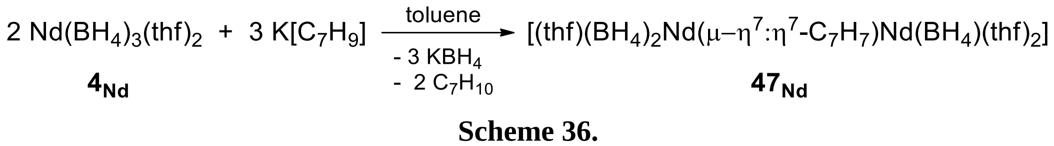


Fig. 29. The crystal structure of complex **46**$_{Nd}$. Reprinted with permission from Ref. [55]. Copyright 2010 Wiley Interscience.

3.2.2.5. Cycloheptatrienyl complexes

In 1997, Ephritikhine showed that the reaction of **4**$_{Nd}$ (as a bis-thf adduct) with K[C_7H_9] (2:3 ratio) gives the neutral compound [(thf)(BH_4)$_2$Nd(μ-η^7:η^7-C_7H_7)Nd(BH_4)(thf)$_2$] (**47**$_{Nd}$), a rare example of cycloheptatrienyl compound of a 4f element (Scheme 36) [74]. This compound can be formally seen as resulting from the metathesis reaction of $K_3[C_7H_7]$ and 2 equiv. of **4**$_{Nd}$.



$$\underset{\mathbf{4_{Nd}}}{2\ Nd(BH_4)_3(thf)_2} + 3\ K[C_7H_9] \xrightarrow[\substack{-\ 3\ KBH_4 \\ -\ 2\ C_7H_{10}}]{\text{toluene}} \underset{\mathbf{47_{Nd}}}{[(thf)(BH_4)_2Nd(\mu\text{–}\eta^7\text{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(thf)_2]}$$

Scheme 36.

The crystal structure of **47_{Nd}** was determined, showing an unprecedented inverse cycloheptatrienyl (*i.e.* two metals bound on the opposite sides of an aromatic hydrocarbon ligand) sandwich structure (Fig. 30). The two neodymium-ring centroid distances were quite identical. The tetrahydroborate ligands were postulated as coordinated in a tridentate fashion, from Nd-B distances, and according to the IR data.

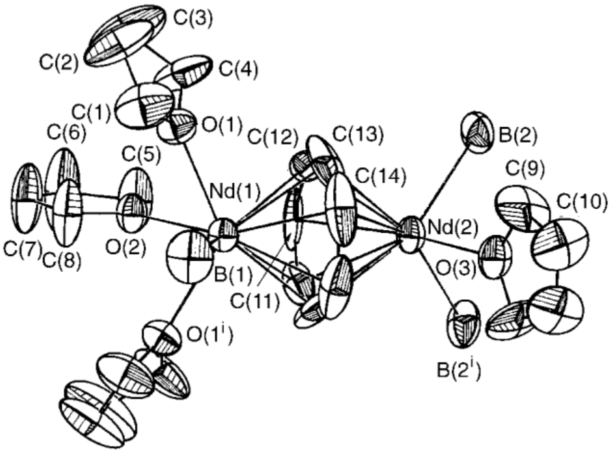
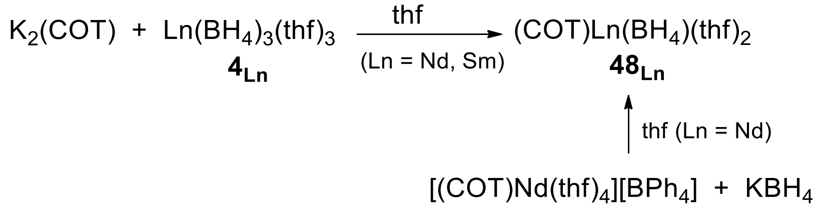


Fig. 30. The crystal structure of complex **47_{Nd}**. Reprinted with permission from Ref. [74]. Copyright 1997 The Royal Society of Chemistry.

3.2.2.6. Cyclooctatetraenyl complexes

Following the strategy of ionic metathesis from **4_{Nd}**, it was shown that K_2COT (COT = η-C_8H_8) reacts straightforwardly with the latter to form $(COT)Nd(BH_4)(thf)_2$ (**48_{Nd}**) [25]. The same compound could be recovered by reaction of the cationic $[(COT)Nd(thf)_4][BPh_4]$ with $K(BH_4)$ in thf (Scheme 37). The samarium analog $(COT)Sm(BH_4)(thf)_2$ (**48_{Sm}**) had already been similarly prepared in the early 1990s and analyzed by ^1H NMR, but further characterizations were not available [75].



Scheme 37.

Crystallization of **48_{Nd}** from benzene led to the dissociation of a thf molecule, with formation of green crystals of $[(COT)Nd(BH_4)(thf)]_2$ (**$48'_{Nd}$**). The peculiar $(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2$ ligation mode of the BH_4 ligand was observed from X-ray structure analysis (Fig. 31), a coordination type that was encountered only once before with the borohydride ligand [76].

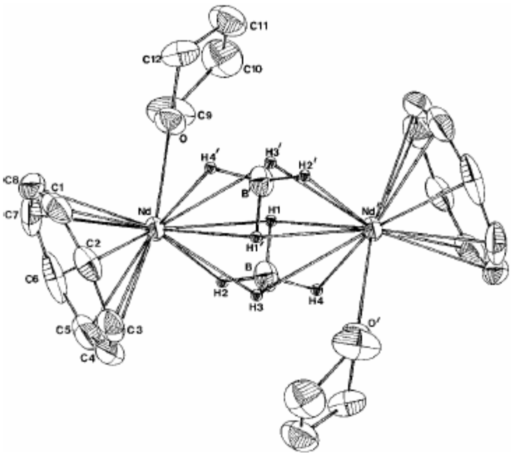


Fig. 31. The crystal structure of complex **48’$_{\mathbf{Nd}}$**. Reprinted with permission from Ref. [25]. Copyright 1998 American Society of Chemistry.

The pyridine-adduct (COT)Nd(BH_4)(C_5H_5N)$_2$ (**48$^{\mathbf{py}}_{\mathbf{Nd}}$**) was mentioned to result from the displacement of the thf ligands by pyridine. This compound was monomeric in this solvent by molecular weight determination [6].

3.2.2.7. Nitrogen-based ligands supported complexes

Simple amido-borohydride complexes were synthesized just recently by Anwander *et al*: the reactions of **4$_{\mathbf{Ln}}$** (Ln = Nd, La) with alkali metal amide M[N(SiMe$_3$)($C_6H_3Pr^i_2$-2,6)] (M = Li, K) produced a diverse range of products, comprising alkali metal-free mono(rare-earth metal) complexes Ln[N(SiMe$_3$)($C_6H_3Pr^i_2$-2,6)]$_2$(BH_4)(thf) (**49$_{\mathbf{Ln}}$**), as well as two “ate” complexes: the mononeodymium {Nd[N(SiMe$_3$)($C_6H_3Pr^i_2$-2,6)]$_2$(BH_4)$_2$}{Li(thf)$_4$} (**50$_{\mathbf{Nd}}$**) and the polymeric {Nd[N(SiMe$_3$)($C_6H_3Pr^i_2$-2,6)]$_2$(μ-BH_4)Li(thf)$_2$(μ-BH_4)}$_n$ (**50’$_{\mathbf{Nd}}$**), depending on the experimental conditions (solvent, alkali metal). The compounds were characterized by NMR and FTIR spectroscopy, elemental and X-ray structure analyses [77].The tridentate coordination mode of the BH_4 moieties in **49$_{\mathbf{Ln}}$** and **50$_{\mathbf{Nd}}$** could be assigned by FTIR spectroscopy and verified through the crystal structure. The solid-state structure of **50’$_{\mathbf{Nd}}$** consisted of polymeric chains of composition {Nd[N(SiMe$_3$)($C_6H_3Pr^i_2$-2,6)]$_2$(μ-BH_4)Li(thf)$_2$(μ-BH_4)}$_n$ with alternating neodymium and lithium metal centers bridged by borohydrido units (Fig. 32, a). From IR data, it was concluded that the borohydrido ligands bind to the neodymium and lithium metal centers in a μ_2-$\eta^{2:2}$ and a μ_2-$\eta^{2:1}$ fashion (Fig. 32, b).

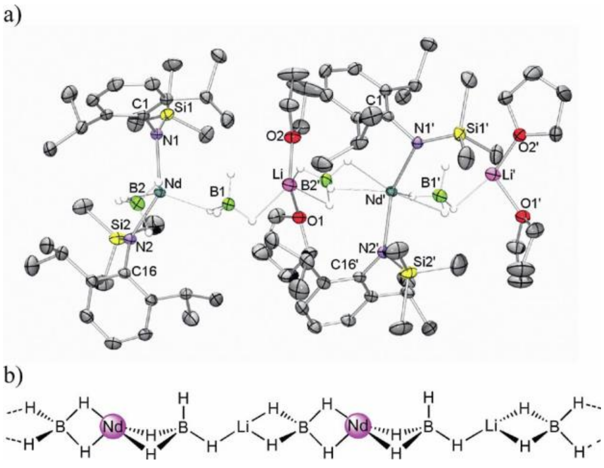
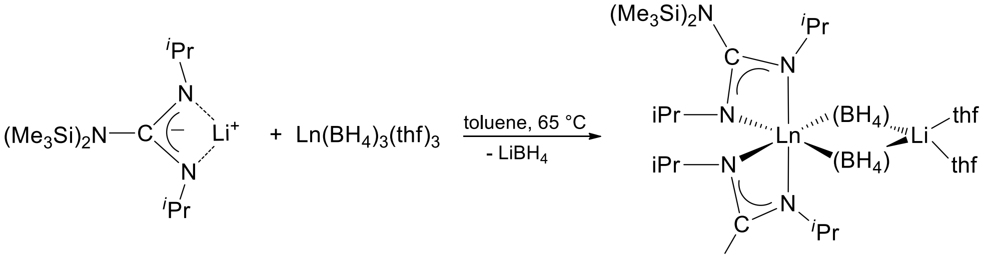


Fig. 32. The crystal structure of complex **50'**$_{Nd}$. Reprinted with permission from Ref. [77]. Copyright 2010 Wiley Interscience.

The bis(benzamidinate) borohydride [(*p*-Tol)C(NSiMe$_3$)$_2$]$_2$Sc(BH$_4$)(thf) (**51**$_{Sc}$) (*p*-Tol = *p*-Me-C$_6$H$_4$) was the first borohydrido complex bearing a nitrogen-based ligand. It was obtained by salt metathesis reaction of the chloro precursor [(*p*-Tol)C(NSiMe)]$_2$ScCl(thf) with NaBH$_4$ [78]. Despite no X-ray data available, a dihapto BH$_4$ ligation mode was deduced from IR data, whereas no conclusive information had been received for its yttrium analog [PhC(NSiMe$_3$)$_2$]$_2$Y(BH$_4$)(thf) [79]. To our knowledge, there is so far no example of a bis(benzamidinate) borohydride that was structurally characterized in the rare earths series.

The reactions of lanthanide tris(borohydrides) **4**$_{Ln}$ with two equiv. of lithium *N*,*N*´-diisopropyl-*N*´-bis(trimethylsilyl)guanidinate in toluene produced the heterobimetallic [(Me$_3$Si)$_2$NC(NPr^i)$_2$]Ln(BH$_4$)$_2$Li(thf)$_2$ complexes (**52**$_{Ln}$: Ln = Sm or Nd) (Scheme 38). X-ray diffraction experiments as well as NMR and IR spectroscopic studies demonstrated that the reactions afforded monomeric "ate" complexes, in which the lanthanide and lithium atoms are linked to each other by two μ_2-$\eta^{2:2}$ bridging BH$_4$, three of four H atoms of the borohydride groups being bridging, with two of these groups serving as μ^2-bridges, while one H atom acts as a μ^3-bridge [80].



52$_{Sm}$, **52**$_{Nd}$

Scheme 38.

It was shown in a subsequent paper [44] that **52**$_{Sm}$ afforded the well-separated ionic compound [{(Me$_3$Si)$_2$NC(NPr^i)$_2$}$_2$Sm(BH$_4$)$_2$]$^-$[Li(dme)$_3$]$^+$ **52'**$_{sm}$ by treatment with dme. The η^3-coordination of the BH$_4$ groups observed by X-ray analysis (Fig. 33) was confirmed by the IR spectrum.

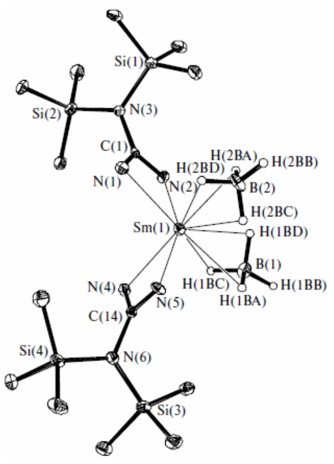


Fig. 33. The crystal structure of complex **52'$_{Sm}$**. Reprinted with permission from Ref. [44]. Copyright 2007 MAIK Nauka/Interperiodica.

A series of lanthanide borohydride complexes supported by bulky guanidinate ligands $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(thf)_2$ (**53$_{Ln}$**: Ln = Nd, Sm, Yb) was synthesized by the reaction of the bis-thf adducts of **4$_{Ln}$** with a twofold molar excess of $[(Me_3Si)_2NC(NCy)_2]Li$ [81]. Initially, the synthesis of such complexes had been investigated by metathesis reactions of the related chloride complexes with $NaBH_4$. However, this method was found to occur with redistribution of guanidinate ligands, yielding finally the monoguanidinate derivative **20$_{Sm}$,** (see section 3.1.2.2) in very low yields [42]. This clearly validates the advantage of metathetic reaction from **4$_{Ln}$** derivatives as starting reagents for further organolanthanide syntheses.
X-ray diffraction studies revealed that compounds **53$_{Ln}$** have similar structures. All three are heterodimetallic "ate" complexes that have two borohydride ligands μ-bridging the lanthanide and lithium atoms. However, despite the fact that both borohydride groups are μ-bridging in all complexes, their coordination modes are different: one group is tridentate with respect to the lanthanide atom, and bidentate with respect to the lithium one, while the second one is μ-$\eta^{2:2}$-bridging in **53$_{Nd}$** and **53$_{Sm}$** but μ-$\eta^{2:1}$-bridging in **53$_{Yb}$** (Fig. 34).

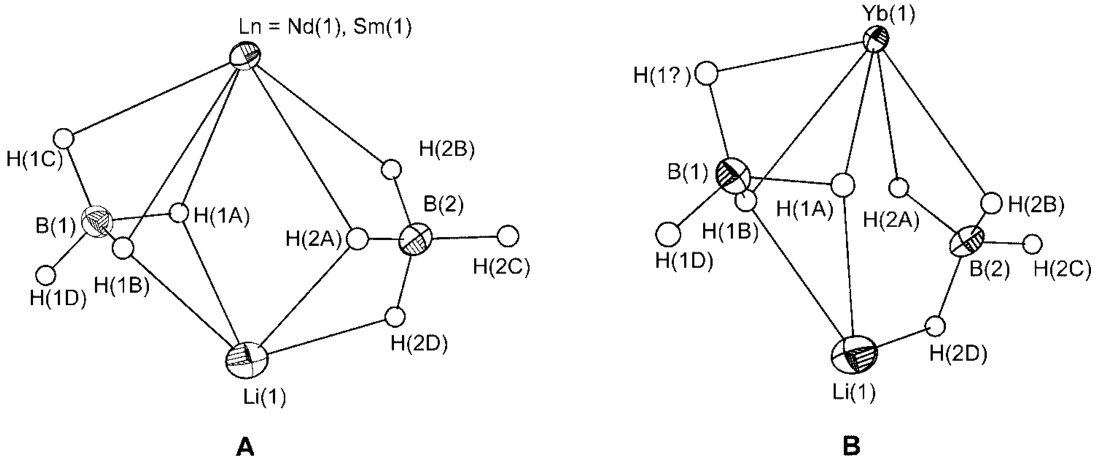
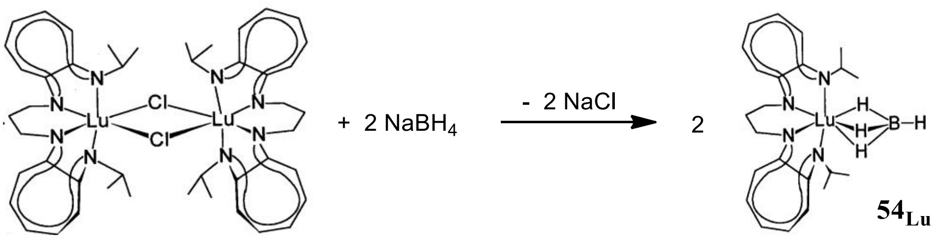


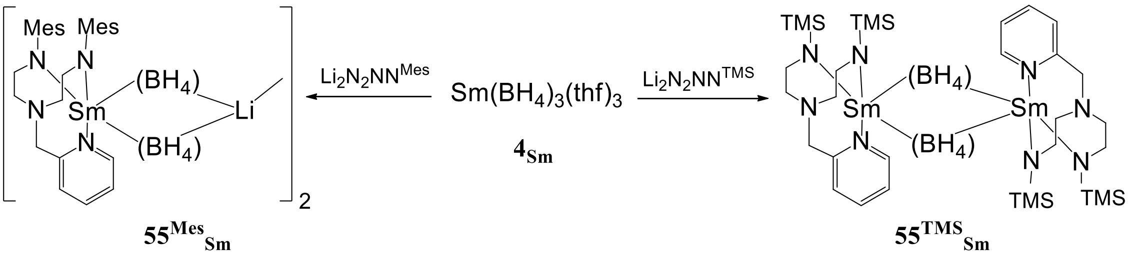
Fig. 34. The coordination modes of borohydride groups in complexes **53$_{Ln}$** (A, Nd, Sm; B, Yb). Reprinted with permission from Ref. [81]. Copyright 2007 Wiley-VCH

The bridged aminotroponiminate complex of lutetium $[(Pr^i)TP]Lu(BH_4)$ (**54$_{Lu}$**) ($(Pr^i)TP$ = 1,3-di(2-(isopropylamino)troponiminate)-propane) was prepared in 2000 by reaction of $NaBH_4$ with the corresponding chloride complex as shown in scheme 39 [82]. The trihapto mode of (BH_4)-bridging was deduced from IR data.



Scheme 39.

Samarium polydentate amide-supported borohydride complexes of the diamide-diamine N_2NN^R ligands (N_2NN^R = (2-C_5H_4N)$CH_2N(CH_2CH_2NR)_2$; **55^{TMS}_{Sm}**, R = TMS or **55^{Mes}_{Sm}**, R = Mes) were described by the group of Mountford [83]. They resulted from the reaction of the trisborohydride samarium precursor with the two lithium salts as depicted in scheme 40.



Scheme 40.

Depending on the substituents, neutral **55^{TMS}_{Sm}**, or anionic **55^{Mes}_{Sm}** compounds were isolated. The structure of **55^{Mes}_{Sm}** was that of an "ate" complex with one residual $LiBH_4$ per samarium (Fig. 35). In this structure, one borohydride is tridentate, the other one bidentate. The lithium atoms are the bridges for the two samarium amido borohydride fragments, and both are linked to three hydrogen atoms of three different BH_4 groups. The molecular structure of **55^{TMS}_{Sm}** was established on the basis of NMR and IR, in adequation with bridging BH_4 groups.

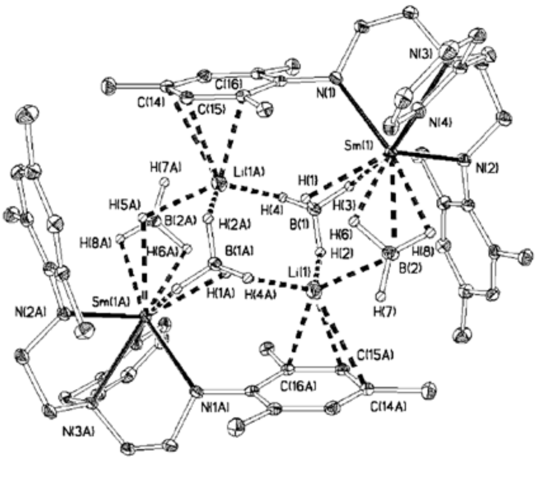
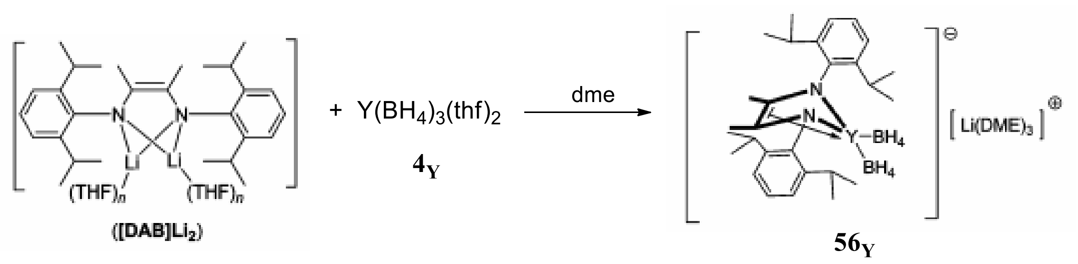


Fig. 35. The crystal structure of complex **55^{Mes}_{Sm}**. Reprinted with permission from Ref. [83]. Copyright 2005 The Royal Society of Chemistry.

The yttrium complex bearing the rigid enediamido dianionic ligand {{DAB}Y$(BH_4)_2$}{Li$(dme)_3$} **56_Y** [DAB^{2-} = (2,6-$C_6H_3Pr^i{}_2$)NC(Me)=C(Me)N(2,6-$C_6H_3Pr^i{}_2$)$^{2-}$] was synthesized by salt metathesis starting from **4_Y** (Scheme 41) [84].



Scheme 41.

Full characterization was achieved by multinuclear NMR and by single-crystal X-ray diffraction studies. The DAB ligand was bonded to the metal center *via* two covalent Y-N bonds, with additional η^2-coordination of the C=C bond to the metal atom (Fig. 36).

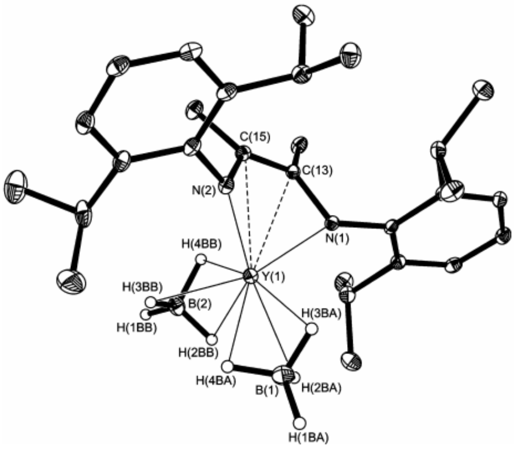
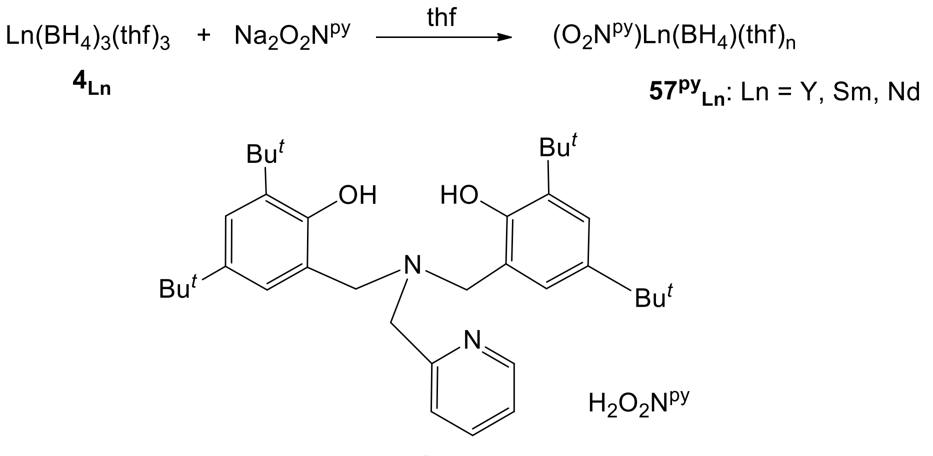


Fig. 36. The crystal structure of the anionic part of complex **56_Y**. Reprinted with permission from Ref. [84]. Copyright 2009 American Chemical Society.

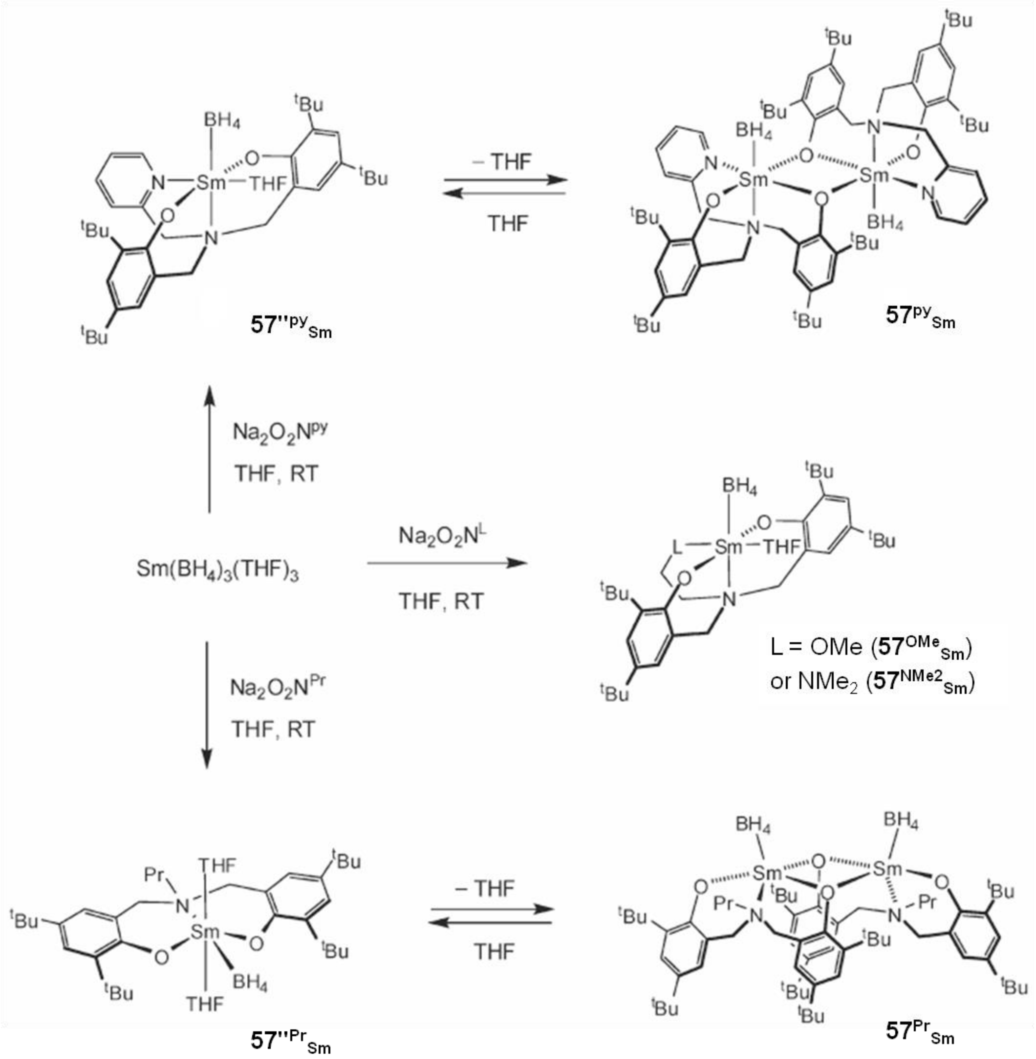
Reaction of the sodium diaminobis(phenoxide) $Na_2O_2N^{py}$ [$H_2O_2N^{py}$ = (2-C_5H_4N)CH_2N{2-HO-3,5-$C_6H_2Bu^t{}_2$}$_2$] with **4_{Ln}** afforded the compounds (O_2N^{py})Ln(BH_4)(thf)$_n$ (**$57^{py}{}_{Ln}$**: Ln = Sm, Y, Nd; n = 0, 0.5, 1, respectively), as illustrated in scheme 42 [85].



Scheme 42.

The coordinated thf molecule in **$57^{py}{}_Y$** and **$57^{py}{}_{Nd}$** could not be removed even upon prolonged drying *in vacuo*. The corresponding pyridine adducts [(O_2N^{py})Ln(μ-BH_4)(py)]$_2$ (**$57'^{py}{}_{Ln}$**: Ln = Y, Sm) were also prepared and characterized.

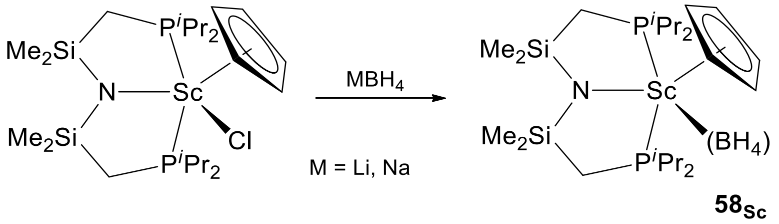
These investigations were just extended to a family of several bis(phenolate)amine-supported samarium borohydride complexes [86]. Reaction of the sodium salt of $H_2O_2N^L$ (O_2N^L = $RCH_2N(CH_2$-2-O-3,5-$C_6H_2Bu^t{}_2)_2$ where R = CH_2OMe, CH_2NMe_2, or Et for L = OMe, NMe_2, or Pr^n, respectively) with **4_{Sm}** gave the borohydride complexes under thf-adduct forms Sm(O_2N^L)(BH_4)(thf) (L = OMe (**$57^{OMe}{}_{Sm}$**), NMe_2 (**$57^{NMe2}{}_{Sm}$**), or py (**$57''^{py}{}_{Sm}$**)) or Sm(O_2N^{Pr})(BH_4)(thf)$_2$ (**$57''^{Pr}{}_{Sm}$**) (scheme 43). Compounds **$57''^{py}{}_{Sm}$** and **$57''^{Pr}{}_{Sm}$** lost thf in vacuo, forming phenolate O-bridged dimers **$57^{py}{}_{Sm}$** and **$57^{Pr}{}_{Sm}$**, respectively. According to the authors, the complex IR spectra of **$57^{py}{}_{Ln}$** compounds initially suggested μ-η^3,η^3-bridging borohydride ligands [85]. But as determined by X-Ray data measurements, the BH_4 ligands in all **$57^{\mathrm{L}}_{\mathrm{Sm}}$** complexes were finally found η^3- terminal, with bridging phenolate in the dimeric structures.



Scheme 43.

3.2.2.8. Heteroleptic complexes

The first heteroleptic ([ZZ'Ln(BH$_4$)], *i.e.* comprising all three different ligands) borohydrido complex of a trivalent rare earth was published by Fryzuk in 2000, who carried out the metathesis of the chloride $(Cp)ScCl[N(SiMe_2CH_2PPr^{i}_2)_2]$ with $LiBH_4$, to afford $(Cp)Sc(BH_4)[N(SiMe_2CH_2PPr^{i}_2)_2]$ (**58_{Sc}**) (Scheme 44) [87]. This compound exhibited ^{1}H NMR data consistent with a *C*s symmetric solution structure. The fluxional exchange process between bridged and terminal hydrogens of the (BH$_4$) moiety was demonstrated by ^{11}B NMR spectroscopy. IR data were found consistent with a borohydride ligand bound in a tridentate fashion, both in solution and in the solid state.



Scheme 44.

Two unique examples of borohydrido derivatives supported by a linked anilidocyclopentadienyl ligand, $(C_5Me_4CH_2SiMe_2NPh)Ln(BH_4)(thf)_2$ (**59_{Ln}**: Ln = Nd, Sm), were recently prepared by means of the "B/A Route", from equimolar amounts of the triborohydrides **4_{Ln}** and *n*-butylethylmagnesium (BEM) in the presence of the related aniline-tethered cyclopentadiene [55]. Despite paramagnetism, their ^1H NMR spectrum could be fully interpretated, as shown Fig. 37.

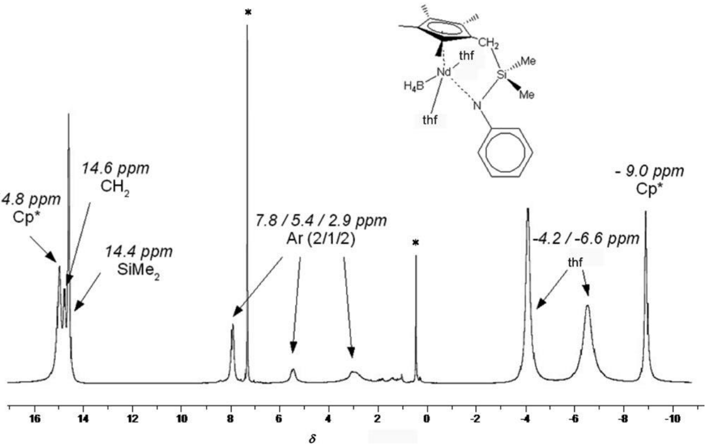


Fig. 37. ^1H NMR spectrum of **59_{Nd}** in C_6D_6 at 300 K (the BH_4 signal appears in the range 30–40 ppm at higher temperatures; * residual C_6D_5H, silicon grease). Reprinted with permission from Ref. [55]. Copyright 2010 Wiley Interscience.

From X-ray structural analysis, both **59_{Ln}** compounds are "$Mg(BH_4)_2$-free", by contrast with other lanthanidocenes prepared using the same strategy (*vide infra*, sections 3.2.2.1 and 3.2.2.4), and the borohydride ligand is bonded in a trihapto terminal mode (Fig. 38).

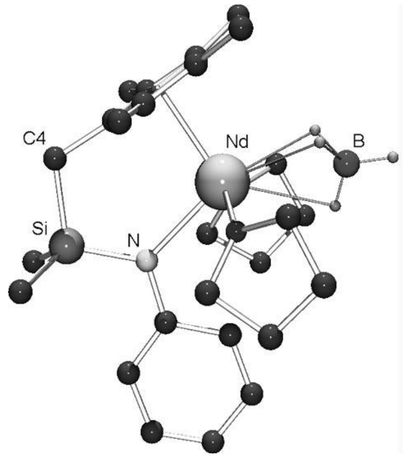
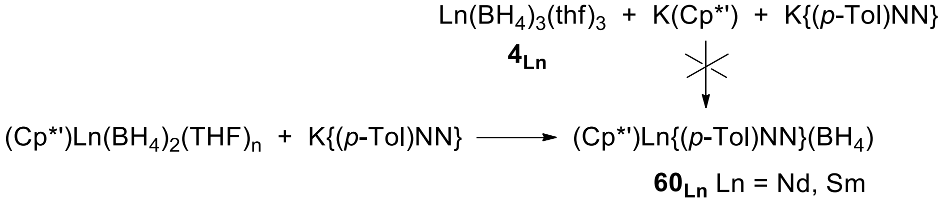


Fig. 38. The crystal structure of the symmetrical subunit of complex **59_{Nd}**. Reprinted with permission from Ref. [55]. Copyright 2010 Wiley Interscience.

The complexes [(Cp*’)Ln{(*p*-Tol)NN}$(BH_4)]_2$ (**60_{Ln}** : Ln = Sm, Nd; Cp*’ = $C_5Me_4Pr^n$; (*p*-Tol)NN = (*p*-Tol)NC(Me)CHC(Me)N(*p*-Tol), were synthesized by a metathetic reaction of their monocyclopentadienyl precursors **17_{Ln}** with the related potassium diketiminate, whereas the one-pot procedure from the trisborohydrides and 1 equiv. of each anionic reagent lead to mixtures of homoleptic products (scheme 45) [88].



Scheme 45.

Both complexes were characterized by ^1H NMR spectroscopy and elemental analysis. The samarium complex, the first trivalent heteroleptic one that could be structurally characterized, is a non solvated dimer. Although hydrogen atoms were not located, the Sm-B distances were found to agree well with bidentate bridging borohydrides. The diketiminate ligand exhibits a typical boat conformation, with a short Sm-C (central carbon atom) bond (Fig. 39).

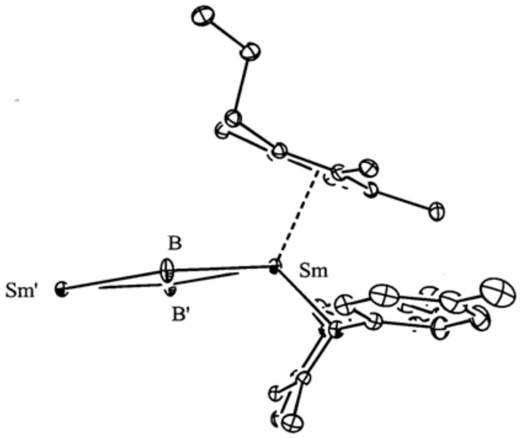


Fig. 39. The crystal structure of complex **60_{Sm}**. Reprinted with permission from Ref. [88]. Copyright 2004 Wiley Interscience.

By contrast, (Cp^{Ph3})Sm{(*p*-Tol)NN}(BH_4) (**61_{Sm}**) was successfully prepared by one-pot ionic metathesis between **4_{Sm}**, $K(Cp^{Ph3})$ and (*p*-Tol)NNK (1:1:1 ratios) in toluene, but no X-ray data were available for this complex [33].

The mixed alkoxo half-metallocene $[(Cp^*)Sc(BH_4)\{\mu\text{-}O(CH_2)_3CH_3\}]_2$ (**62_{Sc}**) was isolated as a by-product of the synthesis of **15_{Sc}** (see section 3.1.2.1), likely resulting from the ring opening of a thf molecule during the reaction [36]. This heteroleptic complex, which was obtained accompanied with **36^{Me}_{Sc}** , was contained in the same unit cell as the latter, in a 2 : 1 ratio, and displays a dinuclear structure with a symmetrical oxo bridge (Fig. 40). The BH_4 unit was terminal tridentate.

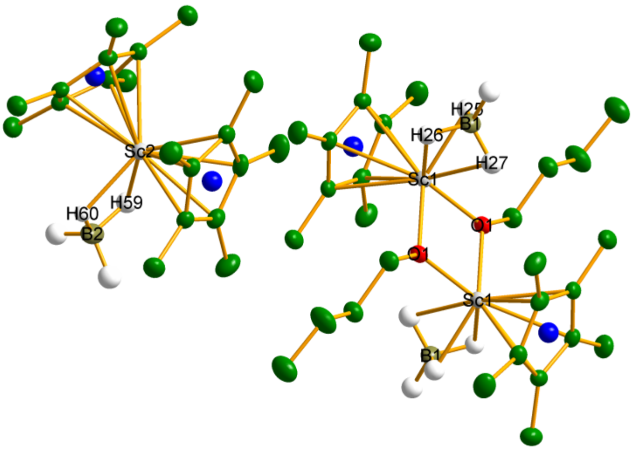
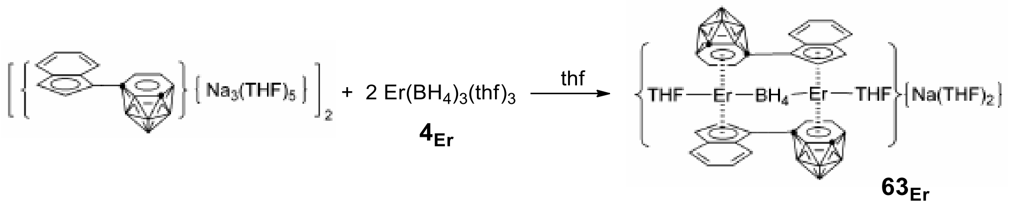


Fig. 40. The crystal structure of complex **62_{Sc}** (right), associated in the unit cell with **35^{Me}_{Sc}** (left). Reprinted with permission from Ref. [36]. Copyright 2009 The Royal Society of Chemistry.

3.3. Tri-substituted "ate" complexes

Reaction of the directly attached carboranyl-indenyl compound 1-(*o*carboranyl)indene $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(thf)_5\}]_2$ with **4_{Er}** in a 1:2 molar ratio in thf gave the BH_4-bridged dinuclear complex $\{[\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(thf)]_2(\mu\text{-}BH_4)\}\{Na(thf)_2\}$ (**63_{Er}**) (scheme 46), which molecular structure was established by a single crystal X-ray analysis. In view of the Er-B distances (BH_4 hydrogens were not located), it was suggested that the BH_4 group was $\mu_2\text{-}\eta^{2:2}$ bonded between two erbium atoms [89].



Scheme 46.

Table 3

Di- and Tri-substituted Organometallic Borohydride Compounds and their Characterization

Compound	Synthesis [a]	NMR	Infra Red	Elem. Anal.	X-ray (H-(BH_4) located)	Reference
$[(Cp^{ttt})_2Dy(BH_4)][K(18\text{-crown-6})]$ (**30**$_{\mathbf{Dy}}$)	F	^1H	-	-	✓ (yes)	[54]
$[(Cp)_2Nd(BH_4)]_2[Mg(BH_4)_2(thf)_4]$ (**31**$_{\mathbf{Nd}}$)	C	^1H	-	✓ (3 thf)	✓ (no)	[55]
$(Cp')_2LnBH_4(thf)$ (Ln = Y, Sm, Lu) (**32**$_{\mathbf{Ln}}$)	A	^1H, ^{13}C	-	✓	-	[56]
$[(Cp')_2Sm(BH_4)]_2$ (**32’**$_{\mathbf{Sm}}$)	A, D, E	-	-	✓	-	[57] [58]
$(Cp^Q)_2Nd(BH_4)$ (**33**$_{\mathbf{Nd}}$)	A, E	^1H	✓	✓	✓ (no)	[60] [61]
$(Cp^{ttt})_2Ln(BH_4)$ (Ln = Dy, Tm) (**34**$_{\mathbf{Ln}}$)	B	^1H	-	✓	✓ (yes)	[54] (Dy), [62] (Tm)
$(Cp^{Ph3})_2Sm(BH_4)(thf)$ (**35**$_{\mathbf{Sm}}$)	B	^1H	-	✓	-	[33]
$(C_5Me_4H)_2Ln(BH_4)(thf)$ (Ln = Y, Sm, Lu) (**36**$^{\mathbf{H}}_{\mathbf{Ln}}$)	A	^1H, ^{13}C	-	✓	-	[56]
$(Cp^*)_2Sc(BH_4)$ (**36**$^{\mathbf{Me}}_{\mathbf{Sc}}$)	D	^1H	-	-	✓ (yes)	[36]
$(Cp^*)_2Ln(BH_4)(thf)$ (Ln = Y, Sm, Lu, Nd) (**36**$^{\mathbf{Me}}_{\mathbf{Ln}}$)	A, B (Nd), C (Nd)	^1H, ^{13}C	✓ (Nd)	✓	✓ (yes: Nd ; no: Sm)	[56], [63] (Nd)
$(C_5Me_4Et)_2Ln(BH_4)(thf)$ (Ln = Y, Sm, Lu) (**36**$^{\mathbf{Et}}_{\mathbf{Ln}}$)	A	^1H, ^{13}C	-	✓	✓ (yes: Y)	[56]
$(C_5Me_4Pr^i)_2Ln(BH_4)(thf)$ (Ln = Y, Sm, Lu) (**36**$^{\mathbf{iPr}}_{\mathbf{Ln}}$)	A	^1H, ^{13}C	-	✓	✓ (yes: Sm)	[56], [64] (Sm)
$(Cp^*)'_2SmBH_4(thf)$ (**36**$^{\mathbf{nPr}}_{\mathbf{Sm}}$)	B	^1H	-	✓	✓ (yes)	[29]
$(Cp^{4i})_2Ln(BH_4)$ (Ln = Nd, Sm) (**37**$_{\mathbf{Ln}}$)	B	^1H, T1 (Sm)	-	✓	✓ (yes)	[7], [65]
$[K(thf)][(P^*)_2Nd(BH_4)_2]$ (**38**$_{\mathbf{Nd}}$)	B	^1H, ^{31}P	-	✓	-	[6]
$[K(18\text{-crown-6})(thf)_2][(P^*)_2Nd(BH_4)_2]$ (**38’**$_{\mathbf{Nd}}$)	B	^1H, ^{31}P	✓	-	✓ (no)	[66]
$(MeOCH_2CH_2C_9H_6)_2Ln(BH_4)$ (Ln = Y, La) (**39**$_{\mathbf{Ln}}$)	A	^1H	✓	✓	✓ (yes)	[67]
$[\textit{rac}\text{-}Me_2C(C_5H_3\text{-}3\text{-}SiMe_3)_2Yb(BH_4)_2][Li(thf)_2]$ (**40**$_{\mathbf{Yb}}$)	A	-	✓	✓	✓ (yes)	[68]
$\textit{meso}\text{-}Me_2Si(C_5H_3\text{-}3\text{-}SiMe_3)_2Yb(BH_4)(thf)$ (**41**$_{\mathbf{Yb}}$)	A	-	✓	✓	✓ (yes)	[69]
$Me_2Si(C_5H_3\text{-}3\text{-}SiMe_3)_2Nd(BH_4)(thf)_2$ (**41**$_{\mathbf{Nd}}$)	B	^1H	-	✓	-	[70]
$[Li(thf)_4][Ln(BH_4)_2\{(C_{13}H_8)CPh_2(C_5H_4)\}]$ (Ln = La, Nd) (**42**$_{\mathbf{Ln}}$)	B	-	Raman	✓	✓ (yes)	[71]
$\{[K(18\text{-crown-6})][(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2]\}_2\cdot dioxane$ (**42’**$_{\mathbf{Nd}}$)	B	-	-	✓	✓ (yes)	[72]
$[Me_2Si(C_5H_4)(C_{13}H_8)Nd(BH_4)_2][Li(thf)].0.5LiBH_4$ (**43**$_{\mathbf{Nd}}$)	B	^1H	-	✓	-	[70]
$\{(Me_2Si\text{-}(C_{13}H_8)_2)Nd(BH_4)_2[Li(thf)]\}_2$ (**44**$_{\mathbf{Nd}}$)	B	^1H	-	✓	✓ (yes)	[73]
$[Me_2Si(2,7\text{-}Bu^t{}_2C_{13}H_6)_2]Nd(BH_4)_2Li(ether)_3$ (**45**$_{\mathbf{Nd}}$)	B	^1H	-	-	✓ (yes)	[73]
$[(CMe_2C_5H_4)_2Ln(BH_4)_2)]_2Mg(thf)_3$ (Ln = Nd, Sm) (**46**$_{\mathbf{Ln}}$)	C	^1H	-	✓ (Nd)	✓ (yes)	[55]
$[(thf)(BH_4)_2Nd(C_7H_7)Nd(BH_4)(thf)_n]$ (n = 2, 3) (**47**$_{\mathbf{Nd}}$)	B	^1H	✓	✓	✓ (n = 3, no)	[74]
$(COT)Ln(BH_4)(thf)_2$ (Ln = Nd, Sm) (**48**$_{\mathbf{Ln}}$)	A (Nd), B	-	✓ (Nd)	✓ (Nd)	-	[25] (Nd), [75] (Sm)
$(COT)Nd(BH_4)(py)_2$ (**48**$^{\mathbf{Py}}_{\mathbf{Nd}}$)	- [b]	^1H	-	-	-	[6]
$[(COT)Nd(BH_4)(thf)]_2$ (**48’**$_{\mathbf{Nd}}$)	B	-	✓ (Nd)	-	✓ (yes)	[25]
$Ln[N(SiMe_3)(C_6H_3Pr^i{}_2\text{-}2,6)]_2(BH_4)(thf)$ (Ln = La, Nd) (**49**$_{\mathbf{Ln}}$)	B	^1H, ^{13}C	✓	✓	✓ (yes)	[77]
$\{Nd[N(SiMe_3)(C_6H_3Pr^i{}_2\text{-}2,6)]_2(BH_4)_2\}\{Li(thf)_4\}$ (**50**$_{\mathbf{Nd}}$)	B	^1H, ^{13}C	✓	✓	✓ (yes)	[77]

$\{Nd[N(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)]_2(\mu\text{-}BH_4)Li(thf)_2(\mu\text{-}BH_4)\}_n$ (**50’**$_{\mathbf{Nd}}$)	B	^1H, ^{13}C	✓	✓	✓ (yes)	[77]
$[(p\text{-}Tol)C(NSiMe_3)_2]_2Sc(BH_4)(thf)$ (**51**$_{\mathbf{Sc}}$)	A	^1H, ^{13}C	✓	✓	-	[78]
$\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(BH_4)_2Li(thf)_2$ (Ln = Sm, Nd) (**52**$_{\mathbf{Ln}}$)	B	^1H, ^{13}C, ^{11}B, ^7Li	✓	✓	✓ (yes)	[80]
$[\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(BH_4)_2][Li(dme)_3]$ (**52’**$_{\mathbf{Sm}}$)	- [c]	-	✓	✓	✓ (yes)	[44]
$[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(thf)_2$ (Ln = Nd, Sm, Yb) (**53**$_{\mathbf{Ln}}$)	A	^1H, ^{13}C, ^{11}B, ^7Li (Sm)	✓	✓	✓ (yes)	[81]
$[(Pr^i)TP]Lu(BH_4)$ (**54**$_{\mathbf{Lu}}$)	A	^1H, ^{11}B	✓	✓	-	[82]
$[Sm(N_2NN^{TMS})BH_4]_2$ (**55**$^{\mathbf{TMS}}_{\mathbf{Sm}}$)	B	^1H	✓	✓	-	[83]
$[Sm(N_2NN^{Mes})(BH_4)_2Li]_2$ (**55**$^{\mathbf{Mes}}_{\mathbf{Sm}}$)	B	^1H, ^7Li	✓	-	✓ (yes)	[83]
$[\{DAB\}Y(BH_4)_2][Li(dme)_3]$ (**56**$_{\mathbf{Y}}$)	B	^1H, ^{13}C, ^{11}B, ^7Li	✓	✓	✓ (yes)	[84]
$(O_2N^{py})Ln(BH_4)(thf)_n$ [Ln = Y, Nd; n = 0.5, 1, resp.] (**57**$^{\mathbf{py}}_{\mathbf{Ln}}$)	B	^1H, ^{13}C (Y)	✓	✓	-	[85]
$[(O_2N^{py})Ln(BH_4)(py)]_2$ [Ln = Sm, Y] (**57’**$^{\mathbf{py}}_{\mathbf{Ln}}$)	B	^1H, ^{13}C (Y)	✓	✓ (Sm)	-	[85]
$(O_2N^L)Sm(BH_4)(thf)$ [L = OMe (**57**$^{\mathbf{OMe}}_{\mathbf{Sm}}$), NMe_2 (**57**$^{\mathbf{NMe2}}_{\mathbf{Sm}}$), py (**57”**$^{\mathbf{py}}_{\mathbf{Sm}}$)]	B	^1H, ^{11}B	✓	- [f]	✓ (L = OMe, yes)	[86]
$(O_2N^{Pr})Sm(BH_4)(thf)_2$ (**57”**$^{\mathbf{Pr}}_{\mathbf{Sm}}$)	B	^1H, ^{11}B	✓	- [f]	✓ (yes)	[86]
$[(O_2N^L)Sm(BH_4)]_2$ [L = Pr^n, py] (**57**$^{\mathbf{L}}_{\mathbf{Sm}}$)	- [d]	^1H, ^{11}B (L= Pr^n)	✓	✓	✓ (yes)	[85], [86]
$(Cp)Sc(BH_4)[N(SiMe_2CH_2PPr^i_2)_2]$ (**58**$_{\mathbf{Sc}}$)	A	^1H, ^{11}B, ^{31}P	✓	✓	-	[87]
$(C_5Me_4CH_2SiMe_2NPh)Ln(BH_4)(thf)_2$ (Ln = Nd, Sm) (**59**$_{\mathbf{Ln}}$)	C	^1H	-	✓ (Nd)	✓	[55]
$[(Cp^{*\prime})Ln\{(p\text{-}Tol)NN\}(BH_4)]$ (Ln = Sm, Nd) (**60**$_{\mathbf{Ln}}$)	A	^1H	-	✓	✓ (Sm, no)	[88]
$(Cp^{Ph3})Sm\{(p\text{-}Tol)NN\}(BH_4)$ (**61**$_{\mathbf{Sm}}$)	B	^1H	-	✓	-	[33]
$[(Cp^*)Sc(BH_4)\{O(CH_2)_3CH_3\}]_2$ (**62**$_{\mathbf{Sc}}$)	- [e]	^1H	-	-	✓ (yes)	[36]
$\{[\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(thf)]_2(BH_4)\}\{Na(thf)_2\}$ (**63**$_{\mathbf{Er}}$)	B	-	✓	✓	✓ (no)	[89]

[a] See the synthetic methods as defined in the introduction;

[b] from thf displacement by pyridine in **48’**$_{\mathbf{Nd}}$;

[c] from dme treatment of **52**$_{\mathbf{Sm}}$;

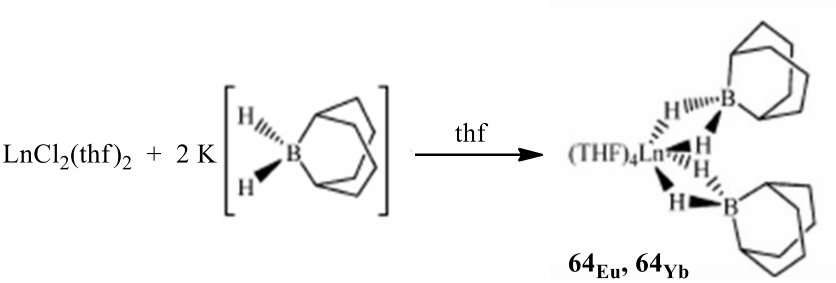
[d] from vacuum treatment of the related thf-adduct;

[e] likely resulting from opening of a thf molecule;

[f] elemental analyses correspond to thf-free compounds.

3.4. Alkylborohydride compounds

Unique examples of well-defined divalent alkylborohydride lanthanide complexes: $(thf)_4Ln\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ (**64_{Ln}**: Ln = Eu, Yb) were synthesized by a metathesis reaction between $LnCl_2(thf)_x$ and $K(H_2BC_8H_{14})$ in thf in a 1:2 molar ratio (Scheme 47) [90].



64_{Eu}, 64_{Yb}

Scheme 47.

Single crystal X-ray analysis established that each dihydroborate fragment is attached in a dihapto mode to the lanthanide metal. Additionally, an agostic interaction between the metal and one of the α-C-H hydrogens from the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit was observed in **64_{Eu}**, but not with **64_{Yb}** (Fig. 41).

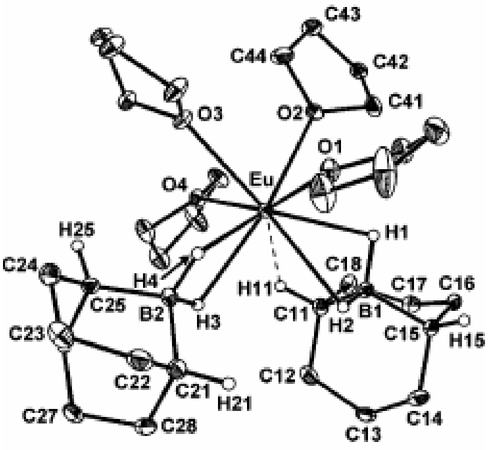


Fig. 41. The crystal structure of complex **64_{Eu}**. Reprinted with permission from Ref. [90]. Copyright 2004 American Chemical Society.

The trivalent trisalkylborohydrides $(Cp')_2Sm(HBEt_3)(L)_2$ (**65^L_{Sm}**) (Cp' = $C_5H_4Bu^t$, L = thf, PMe_3) were obtained from the dimeric chloride $[(Cp)'_2SmCl]_2$ by reaction with a toluene solution of the hydridic reagent $Na(HBEt_3)$, and in the presence of a coordinating molecule: thf or PMe_3 (scheme 48). The molecular structure was established from ^{11}B and ^1H NMR (the paramagnetic NMR Sm-H resonance was located). These compounds were fairly stable in solution but they could not be isolated, due to disproportionation reactions leading invariably to the tris derivative $(Cp')_3Sm$ [58].

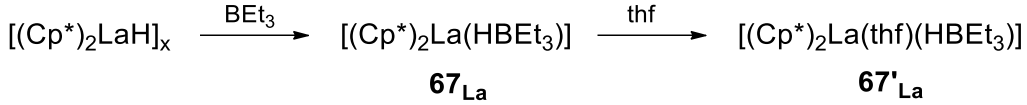
$$[(Cp')_2SmCl]_2 \xrightarrow[\text{thf or } PMe_3]{NaHBEt_3\text{, toluene}} (Cp')_2Sm(HBEt_3)(L)_2$$

65^L_{Sm} L = thf; PMe_3

Scheme 48.

By the similar reaction with the monomeric chloride $(Cp^Q)_2NdCl$, a new product, identified as an alkylborane-supported hydride: $(Cp^Q)_2Nd(HBEt_3)$ (**66_{Nd}**), from NMR characterization (^1H and ^{11}B), was obtained. The Nd-H-B signal was located at 198 ppm in the ^1H NMR spectrum. This hydride was only fairly stable in solution, with further redistribution reactions [60].

A few years later, Evans showed that such alkylborane-supported hydride complexes can be isolated: the reaction of $[(Cp^*)_2LaH]_x$ with BEt_3 afforded straightforwardly the mixed hydridoalkyl borohydrido complex $[(Cp^*)_2La(HBEt_3)]$ (**67_{La}**) and its thf adduct $[(Cp^*)_2La(thf)(HBEt_3)]$ (**$67'_{La}$**), as illustrated on scheme 49 [91].



$$[(Cp^*)_2LaH]_x \xrightarrow{BEt_3} \underset{\mathbf{67_{La}}}{[(Cp^*)_2La(HBEt_3)]} \xrightarrow{thf} \underset{\mathbf{67'_{La}}}{[(Cp^*)_2La(thf)(HBEt_3)]}$$

Scheme 49.

Careful X-ray studies revealed La-Et(B) interactions in both complexes, allowing to better describe them as $[(Cp^*)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$, and $[(Cp^*)_2La(thf)[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$ (Fig. 42). Such interactions were unprecedented in the lanthanide series (with the exception of lanthanoids, *i.e.* yttrium and scandium).

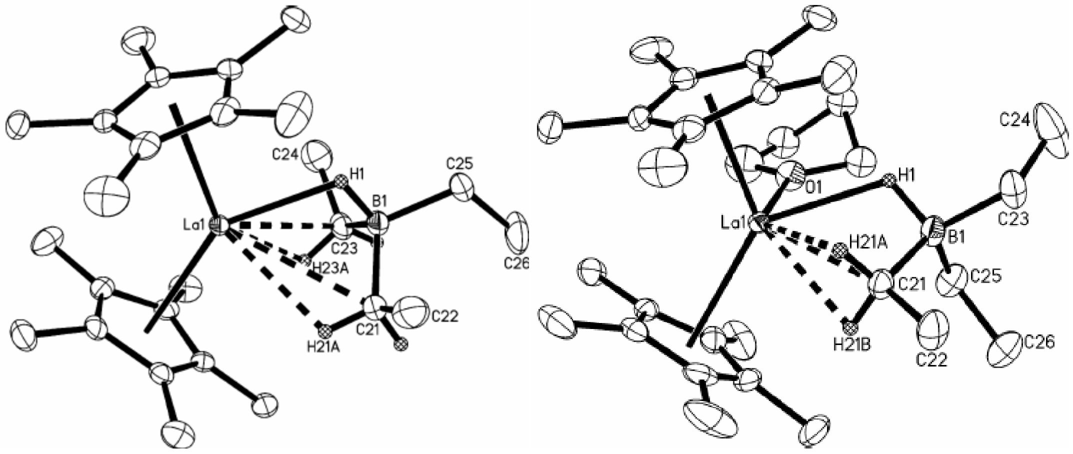
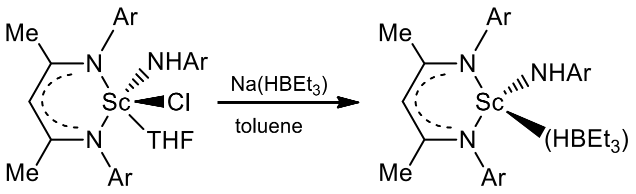


Fig. 42. The crystal structure of complexes **67_{La}** (left) and **$67'_{La}$** (right). Reprinted with permission from Ref. [91]. Copyright 2005 American Chemical Society.

The chloro-anilide complex (Nacnac)ScCl(NHAr)(thf) (Nacnac = $[ArNC(CH_3)]_2CH$, Ar = $C_6H_3Pr^i{}_2$-2,6),was found to react cleanly with $Na(HBEt_3)$ in toluene to yield the thermally stable triethylborohydride adduct $(Nacnac)Sc(NHAr)(HBEt_3)$ (**68_{Sc}**) (Scheme 50) [92]. Variable-temperature ^{11}B NMR spectroscopy indicated the presence of a doublet, but the hydride resonance was not located in the ^1H NMR spectrum.



68_{Sc}

Scheme 50.

The X-ray molecular structure of **68$_{Sc}$** pointed out a bridged hydride ligand confined between the scandium and boron atoms (Fig. 43), with two methylene hydrogens from the ethyl groups of the borane, interacting with the scandium center through agostic interactions.

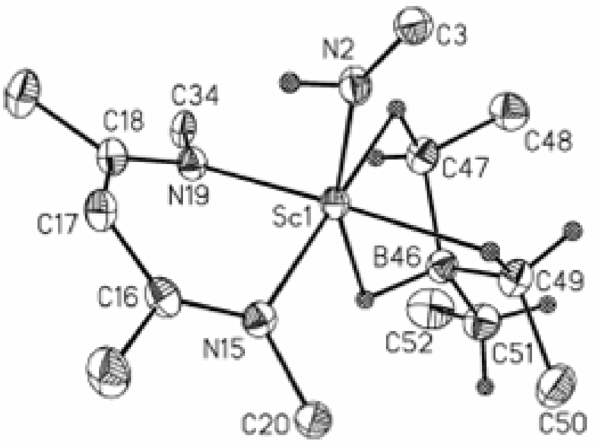


Fig. 43. The crystal structure of complex **68$_{Sc}$**. Reprinted with permission from Ref. [92]. Copyright 2003 American Chemical Society.

The unexpected borohydride Nd(Tp^{Me2})$_2$(H$_2$BEt$_2$) (**69$_{Nd}$**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) was isolated serendipitously from (Tp^{Me2})$_2$NdCl and residual K(H$_2$BEt$_2$) contained in a commercial K(HBEt$_3$) solution [93]. X-ray structure determination of this bis(hydro)bis(ethyl)borato compound showed a Nd–B distance significantly longer than that in neodymium borohydride complexes containing tridentate BH$_4$ ligands, and very close to the value found in the above mentioned **48'$_{Nd}$** [25], thus fully consistent with the bidentate binding mode of the borohydride residue (Fig. 44).

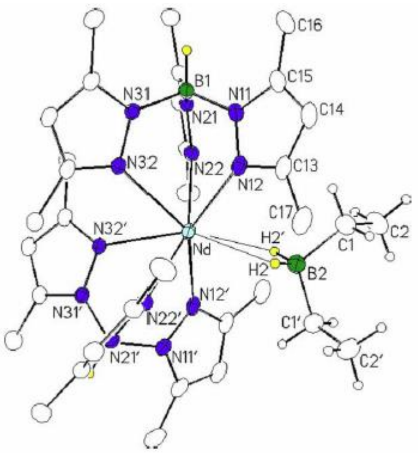
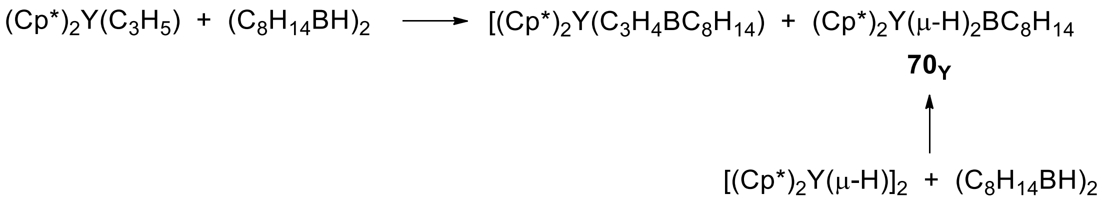


Fig. 44. The crystal structure of complex **69$_{Nd}$**. Reprinted with permission from Ref. [93]. Copyright 2004 Elsevier.

The borohydride (Cp*)$_2$Y[(μ-H)$_2$BC$_8$H$_{14}$] **70$_{Y}$** was isolated as a co-product from the reaction of (Cp*)$_2$Y(C$_3$H$_5$) with 9-BBN, and was alternatively synthesized directly from 9-BBN and the yttrium hydride [(Cp*)$_2$YH]$_2$ (scheme 51) [94].



$$(Cp^*)_2Y(C_3H_5) + (C_8H_{14}BH)_2 \longrightarrow [(Cp^*)_2Y(C_3H_4BC_8H_{14}) + \underset{\mathbf{70_Y}}{(Cp^*)_2Y(\mu\text{-}H)_2BC_8H_{14}} \longleftarrow [(Cp^*)_2Y(\mu\text{-}H)]_2 + (C_8H_{14}BH)_2$$

Scheme 51.

X-ray structure analysis revealed a bidentate bridging mode of the $[(\mu\text{-}H)_2BC_8H_{14}]$ ligand (Fig. 45).

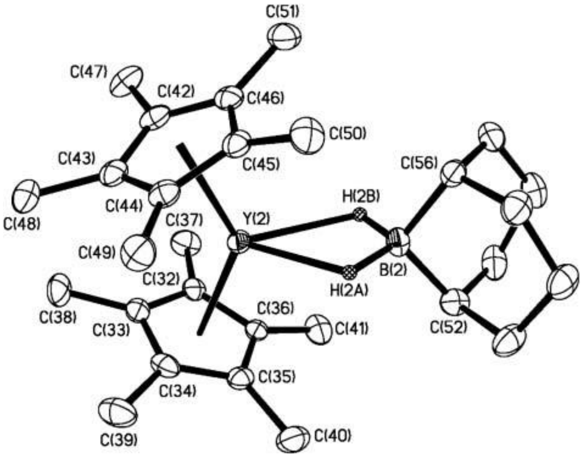


Fig. 45. The crystal structure of complex **70_Y**. Reprinted with permission from Ref. [94]. Copyright 2007 The Royal Society of Chemistry.

Very recently, the synthesis of a new class of highly volatile lanthanide complexes $Ln(H_3BNMe_2BH_3)_3$(thf) (**71_{Ln}**) (all lanthanides except La and Ce), was reported [95]. The *N*,*N*-dimethylaminodiboranate ligand, $H_3BNMe_2BH_3^-$ (DMADB), was considered as a multidentate borohydride ligand that binds to metal centers *via* M-H-B bridges. When sublimed under a dynamic vacuum, it was observed that complexes **71_{Ln}** lose thf to form the corresponding base-free $Ln(H_3BNMe_2BH_3)_3$ **$71'_{Ln}$**. X-ray diffraction studies of the **$71'_{Ln}$** complexes revealed that both nuclearity and hapticity of the $-BH_3$ groups strongly depend on the nature of the rare earth. The yttrium derivative **$71'_Y$** was used as a CVD precursor.

Finally, an anionic tetra(borane-supported)carbene scandium complex, comprising four agostic B-H-Sc interactions was described by Siebert *et al*. [96]. The Sc-H distances were longer in this complex than those determined for a true [Sc](BH_4) borohydride compound [97].

Table 4

Alkylborohydride compounds and their characterization

Compound	Synthesis [a]	NMR	Infra Red	Elem. Anal.	X-ray (H-(BH_4) located)	Reference
$(thf)_4Ln\{(H)_2BC_8H_{14}\}_2$ (Ln = Eu, Yb) (**64**$_{\mathbf{Ln}}$)	A	^1H, ^{11}B (Ln = Yb)	✓	✓	✓ (yes)	[90]
$(Cp')_2Sm(HBEt_3)(L)_2$ (L = thf, or PMe_3) (**65**$^{\mathbf{L}}_{\mathbf{Sm}}$)	A	^1H, ^{11}B (L = thf)	-	-	-	[58]
$(Cp^Q)_2Nd(HBEt_3)$ (**66**$_{\mathbf{Nd}}$)	A	^1H, ^{11}B	-	-	-	[60]
$[(Cp^*)_2La(HBEt_3)]$ (**67**$_{\mathbf{La}}$)	E	^1H, ^{11}B, ^{13}C	✓	✓	✓ (yes)	[91]
$[(Cp^*)_2La(thf)(HBEt_3)]$ (**67’**$_{\mathbf{La}}$)	- [b]	^1H, ^{11}B, ^{13}C	✓	-	✓ (yes)	[91]
$(Nacnac)Sc(NHAr)(HBEt_3)$ (**68**$_{\mathbf{Sc}}$)	A	^1H, ^{11}B, ^{13}C	✓	✓	✓ (yes)	[92]
$[Nd(Tp^{Me2})_2(H_2BEt_2)]$ (**69**$_{\mathbf{Nd}}$)	A	-	-	-	✓ (yes)	[93]
$(Cp^*)_2Y(H_2BC_8H_{14})$ (**70**$_{\mathbf{Y}}$)	E	^1H, ^{11}B	✓	-	✓ (yes)	[94]
$Ln(H_3BNMe_2BH_3)_3(thf)_n$ (all Ln except La and Ce) (n = 1, **71**$_{\mathbf{Ln}}$; n = 0, **71’**$_{\mathbf{Ln}}$)	A	^1H (n = 1: Er; n = 0:Tb), ^{11}B (n = 1: Er; n = 0: Er, Tb)	✓ (n = 1: Er; n = 0: Er, Tb)	✓	✓ (yes: Pr, Sm, Er)	[95]

[a] See the synthetic methods as defined in the introduction;

[b] from conversion of **67**$_{\mathbf{La}}$ in the presence of thf.

4. Reactivity of borohydride complexes

4.1. Borohydride complexes as starting materials for further organolanthanide syntheses

4.1.1. Metathetical reactions from borohydride complexes

$Ln(BH_4)_3(thf)_3$ ($\mathbf{4_{Ln}}$) compounds are not only valuable precursors for the synthesis of borohydrido organolanthanides, they can also be used to prepare tri-substituted organometallic complexes of the rare earths, as an alternative to their trichloride, trisamide, or trisalkyl counterparts. Moreover, any lanthanide organometallic compound bearing a BH_4 ligand is potentially exploitable to prepare molecular compounds by the substitution of the latter.

The trisborohydrides were used as starting materials to prepare several crystalline compounds containing the tris(dithiolene) $Ln(dddt)_3$ unit [98], by reacting together $\mathbf{4_{Ln}}$ (Ln = Nd, Ce) with M_2dddt (M = Na, K; dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate).

Treatment of *in situ* prepared $SmCl(BH_4)_2$ with $K[HB(3,5\text{-}Me_2pz)_3]$ was reported to afford in low yield the pyrazolylborate derivative $[HB(3,5\text{-}Me_2pz)_3]_2SmCl$ instead of the expected monosubstituted $[HB(3,5\text{-}Me_2pz)_3]Sm(BH_4)_2$. This accounts for a rather higher facility to displace a borohydride than a chloride in such complexes [38].

Several mixed ring complexes (COT)Nd(Cp*)(thf), (COT)Nd(P*)(thf), $[(COT)Nd(OEt)(thf)]_2$, $[Na][(COT)Nd\text{-}(SBu^t)_2]$ and $[Na(thf)_2][\{(COT)Nd\}_2(SBu^t)_3]$ were synthesized from the monoborohydride $(COT)Nd(BH_4)(thf)_2$ ($\mathbf{47_{Nd}}$), by reaction with the alkali metal salt of the respective ligand. Protonolysis of the metal-borohydride bond in $\mathbf{48_{Nd}}$ with NEt_3HBPh_4 in thf afforded the cation $[(COT)Nd(thf)_4][BPh_4]$ [99], which constitutes a key reactivity regarding polymerization reactions, as will be demonstrated further in this article.

By mixing a stoichiometric amount of $(Cp^{4i})Sm(BH_4)_2(thf)$ ($\mathbf{18_{Sm}}$) and $LiN(SiMe_3)_2$, a new set of signals revealed the presence of the diamido complex $[(Cp^{4i})Sm\{N(SiMe_3)_2\}_2]$ mixed with ca 50% of unreacted borohydrido half-sandwich. By using the more bulky chelating benzamidinate anion $Li[C_6H_5C(NSiMe_3)_2]$, it was possible to substitute one borohydride ligand of $\mathbf{18_{Sm}}$ [7]. Similarly, the homoleptic complex $La[N(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)]_3$ was prepared in hexane, by reacting amido borohydride $La[N(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)]_2(BH_4)(thf)$ ($\mathbf{49_{La}}$) with 1 equiv. of $K[N(SiMe_3)(C_6H_3Pr^i_2\text{-}2,6)]$ [77].

The amide compounds $Sm(O_2N^L)\{N(SiMe_3)_2\}(OEt_2)_n$ (n = 1, L = OMe or py ; n = 0, L = NMe_2) were prepared by reaction of the borohydrides $Sm(O_2N^L)(BH_4)(thf)$ ($\mathbf{57^L_{Sm}}$) with $KN(SiMe_3)_2$ [86].

The substitution of a borohydride group may also be achieved using an allylic reagent: the reaction of *ansa*-complex $\mathbf{46_{Sm}}$ with a twofold excess of allylLi(dioxane) according to scheme 52 afforded the known bis(allyl) derivative $[(CMe_2C_5H_4)_2Sm(allyl)_2)]^-$ [100,55].

$$[(CMe_2C_5H_4)_2Sm(BH_4)_2)]_2Mg(thf)_3 \xrightarrow{\text{2 Li(allyl)(dioxane)}} [(CMe_2C_5H_4)_2Sm(allyl)_2)]Li(dioxane)(thf)_x$$

$\mathbf{46_{Sm}}$

Scheme 52.

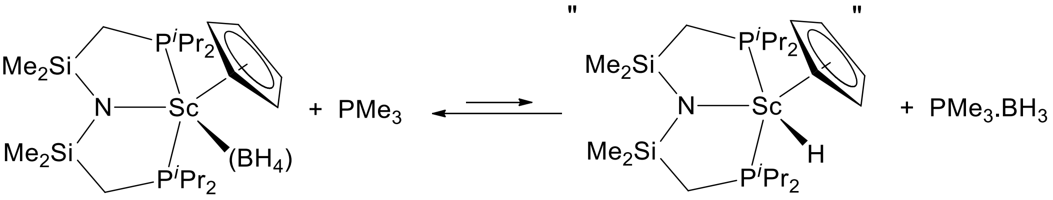
Finally, the reaction of the divalent alkylborohydride **64_{Yb}** with 2 equiv. of $B(C_6F_5)_3$ afforded the solvent-separated ion pair $[Yb(thf)_6][HB(C_6F_5)_3]_2$ by abstraction of a hydride and release of borane, according to scheme 53 [90].

$$\underset{\mathbf{64_{Yb}}}{(thf)_4Yb\{(\mu\text{-}H)_2BC_8H_{14}\}_2} + 2\,B(C_6F_5)_3 \longrightarrow [Yb(thf)_6][HB(C_6F_5)_3]_2 + (HBC_8H_{14})_2$$

Scheme 53.

4.1.2. Hydride formation from borohydride complexes

Extrusion of borane from a borohydride organometallic compound is a well-known reactivity [101] which remains surprinsingly scarce with rare earth derivatives [5]. The sole example reported since 1996 is the reaction of **58_{Sc}** with PMe_3 (scheme 54), which was monitored by $^{11}B\{^1H\}$ NMR spectroscopy [87]. This reaction was found to produce $PMe_3{\cdot}BH_3$ and the putative hydride, $(C_5H_5)Sc(H)[N(SiMe_2CH_2P^iPr_2)_2]$ for which only indirect evidence in solution was given. It was shown that all species exist in solution under equilibrium.

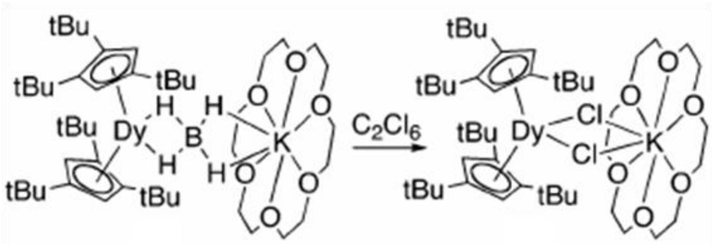


58_{Sc}

Scheme 54.

4.1.3. Redox transformations

Treatment of trivalent $(Cp^{ttt})_2Tm(BH_4)$ (**34_{Tm}**) with K/C_8 afforded the thulliocene $(Cp^{ttt})_2Tm$, whereas the same reaction was unsuccessful with the dysprosium analog **34_{Dy}** [62]. However, in the presence of crown ether, the latter lead to complex **30_{Dy}** (see section 3.2.1). Upon oxidation of **30_{Dy}** by hexachloroethane, a trivalent organodysprosium dichloride "ate" complex was obtained (scheme 55). The divalent borohydride **30_{Dy}** was also shown to reductively couple diphenylacetylene [54].



30_{Dy}

Scheme 55.

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[5] This reaction corresponds to the reverse process of synthetic method E as defined in the introduction.

The carboranyl-indenyl $\{[\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(thf)]_2(\mu\text{-}BH_4)\}\{Na(thf)_2\}$ (**63_{Er}**) generated upon reaction with excess sodium metal the BH_4-free dinuclear complex$\{[\eta^5:\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(thf)]_2\}\{Na_4(thf)_8\}$ [89].

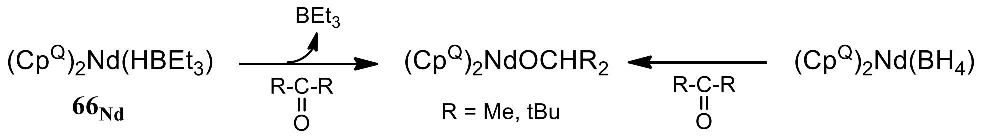
4.2. Stoichiometric organic transformations

Borohydride complexes of the rare earths can display typical hydride behaviour: in most cases, they are able to react with protic compounds like alcohols or silanols, and they can easily reduce ketones, or even open thf. However, they are in general resistant to borane elimination (even if in some cases hydrides could be obtained, but such examples remain scarce), which contrasts with what observed in the chemistry of transition metals [2]. Akylborohydrides are more prone to generate metal hydrides.

The reaction of yttrium tetrahydroborate complex $NaY(BH_4)_4(dme)_4$ (employed as precursor in the syntheses of $(Bu_4N)[Ln(BH_4)_4(dme)_n]$ (**$7a_{Ln}$**) complexes, see section 2.2.3) with triethylcarbinol in thf, yielded the bis(3-ethyl-3-pentoxy)borane $BH[OC(C_2H_5)_3]_2$ [102].

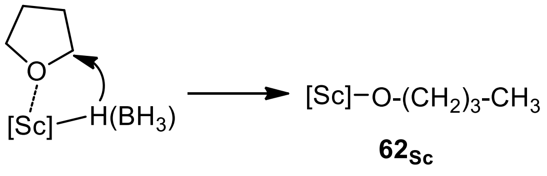
Similarly, it is by acido-basic reaction of **4_{Ln}** (Ln = La, Nd) with dehydroxylated silica and with iminophosphine-aminopyridinyl ligand 2-Pyridyl-$NHPPh_2{=}NC_6H_3$-2,6-Me_2 that were prepared the grafted bis(borohydride) surface compounds $[(\equiv SiO)Ln(BH_4)_2(thf)_{2.2}]$ (**28_{Ln}**) [51] and the bis(borohydrido) neodymium complex **26_{Nd}** [50], respectively.

The ether-tethered $(Cp^Q)_2Nd(BH_4)$ (**32_{Nd}**) and $(Cp^Q)_2Nd(HBEt_3)$ (**66_{Nd}**) complexes can reduce dimethylketone and pivalone, affording the corresponding alkoxides (scheme 56) [60]. A similar reactivity was noticed with complexes $(Cp')_2Sm(HBEt_3)(L)_2$ (**$65^L{}_{Sm}$**) which both react with propanone to afford the corresponding alkoxide $(Cp')_2Sm(OCHMe_2)$ [58].



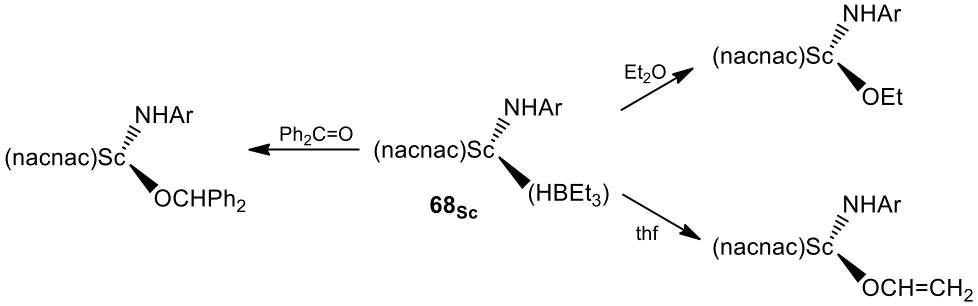
Scheme 56.

The mixed alkoxo half-metallocene $[(Cp^*)Sc(BH_4)\{\mu\text{-}O(CH_2)_3CH_3\}]_2$ (**62_{Sc}**), obtained serendipitously, was probably formed by opening of a thf molecule by a *H*(BH_3) hydride moiety, through activation by the highly oxophilic scandium atom of the parent half-sandwich complex $(Cp^*)Sc(BH_4)_2(thf)$ (**15_{Sc}**) (scheme 57, see also section 3.2.2.8) [36].



Scheme 57.

In a similar manner, heteroleptic alkylborohydride **68_{Sc}** was highly reactive: borane extrusion occured in Et_2O, reacting itself as a Lewis base, to afford the ethoxide (Nacnac)Sc(NHAr)(OEt) through cleavage of the C-O bond of an ether molecule. Tetrahydrofuran was also found to react with **68_{Sc}** to yield the enolate (Nacnac)Sc(NHAr)-($OCH{=}CH_2$). Finally, treatment of **68_{Sc}** with an equimolar amount of benzophenone in toluene afforded the corresponding diphenylmethoxide complex, entailing insertion of the carbonyl functionality into the Sc-H bond (scheme 58) [92].



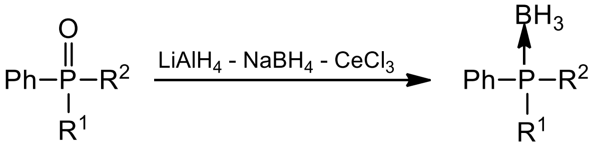
Scheme 58.

4.3. Organic catalysis

Surpringly, apart from polymerization, very little information has been reported regarding the contribution of borohydride compounds of the rare earths towards organic catalysis: as far as we know, three studies were published in this time frame, and one only since 1997.

The first result, already mentioned in the review of Ephritikhine, refers to hydroboration of substituted alkenes with $LiBH_4$ in the presence of catalytic amounts of $NdCl_3$, in which a metal borohydride complex would be the active species [103].

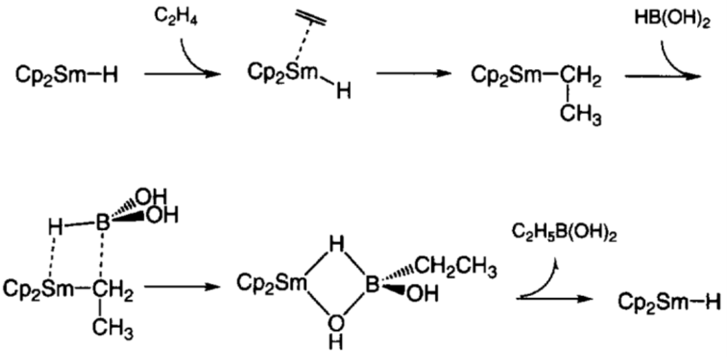
A decade before, a result that passed somewhat unnoticed is the one-pot synthesis of phosphine-boranes from phosphine oxides by a three-component reagent system, $LiAlH_4$-$NaBH_4$-$CeCl_3$, reported by Imamoto *et al.* in 1985. It is noteworthy that the reaction did not proceed in the absence of $CeCl_3$, and therefore trivalent cerium was suspected to "activate" $NaBH_4$, presumably through the formation of Ce-(BH_4) species (scheme 59) [104].



$$Ph{-}\overset{O}{\overset{\|}{P}}(R^1){-}R^2 \xrightarrow{LiAlH_4\text{ - }NaBH_4\text{ - }CeCl_3} Ph{-}\overset{BH_3}{\overset{\uparrow}{P}}(R^1){-}R^2$$

Scheme 59.

A theoretical study, published by Koga *et al.* in 1999, deals with the mechanistic investigation of samarium(III)-catalyzed olefin hydroboration reaction using *ab initio* methods [105]. After ethylene (chosen as a model) insertion, the borane adds to $[(Cp)_2SmC_2H_5]$ to form a putative alkylborohydride complex (scheme 60). It is likely that the same occurs in the organolanthanide-catalyzed cyclization/boration of dienes reported by Molander *et al.* in 2001, although the formation of such intermediate is not discussed therein [106].



Scheme 60.

The reader is encouraged to refer to the review of Beletskaya *et al.* for a specific survey of hydroboration catalysed by metal complexes, which includes a section devoted to the lanthanides, but with no explicit mention of implication of borohydride compounds, except the above mentioned article of Ephritikhine [107].

4.4. Polymerization reactions

Although rare earth borohydrides are known since the 1970s, their introduction in polymerization catalysis is very recent. There is no mention of that kind of reactivity in the review of Ephritikhine, and one can consider that it started less than a decade ago, while it is attracting nowadays a very fast increasing interest. Noteworthy, Marks mentioned in his review the use of borohydride compounds as polymerization catalysts, but these studies were limited to transition metals [8].

Polymerization reactions using rare earth borohydrides are based on the already mentioned reactivity of the BH_4 group, which may behave according to two different reactive pathways, like a hydride, or like a pseudo-halide. Most examples related to the hydride behaviour are connected to the polymerization of polar monomers (with a few exceptions concerning methylmethacrylate), whereas in turn all the instances dealing with non polar monomers involve the pseudo-halide behaviour of the borohydride ligand, thus requiring the addition of an alkylating agent as co-catalyst.

4.4.1. Polar monomers

Polar monomers like cyclic esters, trimethylene carbonate, or acrylates, have been the subject of a growing number of studies involving borohydride derivatives of the rare earths, in homo- and co-polymerization reactions. The complexes used in this frame are listed in the general table 5, which includes the particular activities of each initiator used. Details of the polymerization reactions as well as mechanistic and theoretical studies are presented hereafter.

Table 5

Borohydride Rare Earth Complexes Used in Polar Monomer Polymerization

Complex	Lactones	Lactide	MMA	TMC	References (monomer) [a]
$Sm(BH_4)_2(thf)_2$ ($\mathbf{1_{Sm}}$)	✓ (ε-CL)				[13]
$Y(BH_4)_3(thf)_2$ ($\mathbf{4_{Y}}$)	✓ (ε-CL, δ-VL)	✓ (*rac*-LA)			[110] (ε-CL) [111] (δ-VL, *rac*-LA)
$La(BH_4)_3(thf)_3$ ($\mathbf{4_{La}}$)	✓ (ε-CL, δ-VL)	✓ (*rac*-LA)			[109] (ε-CL) [111] (δ-VL, *rac*-LA)
$Pr(BH_4)_3(thf)_2$ ($\mathbf{4_{Pr}}$)	✓ (δ-VL)	✓ (*rac*-LA)			[111]
$Nd(BH_4)_3(thf)_3$ ($\mathbf{4_{Nd}}$)	✓ (ε-CL, δ-VL)	✓ (L-LA, *rac*-LA)	✓		[108], [109], [110] (ε-CL) [111] (δ-VL, *rac*-LA) [115] (L-LA, ε-CL) [33], [116] (MMA)
$Sm(BH_4)_3(thf)_3$ ($\mathbf{4_{Sm}}$)	✓ (ε-CL, δ-VL)	✓ (*rac*-LA)	✓	✓	[109] (ε-CL) [111] (δ-VL, *rac*-LA) [117] (MMA) [116] (TMC)
$[Ln(BH_4)_2(thf)_5]^+[BPh_4]^-$ ($\mathbf{8_{Ln}}$: Ln = Y, La, Nd, Sm)	✓ (ε-CL)				[24]
$Cp^*Sm(BH_4)(thf)_2$ ($\mathbf{11_{Sm}}$)	✓ (ε-CL)				[13]
$Cp^{Ph3}Sm(BH_4)_2(thf)_2$ ($\mathbf{14'_{Sm}}$)			✓ [d]		[33]
$Cp^{*\prime}Ln(BH_4)_2(thf)_2$ ($\mathbf{17_{Ln}}$: Ln = Sm, Nd)			✓ [d]		[33]
$(C_5Me_4$-C_6H_4-*o*-$NMe_2)Sc(BH_4)_2$ ($\mathbf{19_{Sc}}$)			✓ [d]		[41]
$[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(thf)_2$ ($\mathbf{21_{Ln}}$: Ln = Er, Yb)			✓		[43]
$(ArO)Ln(BH_4)_2(thf)_2$ ($\mathbf{27_{Ln}}$: Ln = Yb, Er)			✓		[51]
$[(\equiv SiO)Ln(BH_4)_2(thf)_{2.2}]$ ($\mathbf{28_{Ln}}$: Ln = La, Nd)	✓ (β-BL)				[52]
$[\{CH(PPh_2NSiMe_3)_2\}Ln(BH_4)_2]$ ($\mathbf{29_{Ln}}$: Ln = Y, Lu)	✓ (ε-CL)				[53], [114]
$(Cp^{Ph3})_2Sm(BH_4)(thf)$ ($\mathbf{35_{Sm}}$)			✓ [d]		[33]
$Cp^*_2Sm(BH_4)(thf)_2$ ($\mathbf{36^{Me}_{Sm}}$)	✓ (ε-CL)		✓		[109], [112], [114] (ε-CL)

					[117] (MMA)
$(Cp^{*\prime})_2Nd(BH_4)(thf)$ (**36$^{nPr}_{Nd}$**) [b]			✓ [d]		[33]
$Cp^{4i}{}_2Sm(BH_4)$ (**37$_{Sm}$**)			✓ [d]		[33]
$[(Me_3Si)_2NC(N^iPr)_2]_2Ln(BH_4)_2Li(thf)_2$ (**52$_{Ln}$**: Ln = Sm or Nd)			✓		[80]
$[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(thf)_2$ (**53$_{Ln}$**: Ln = Nd, Sm, Yb)		✓ (L-LA, *rac*-LA)	✓		[81] (LA) [44] (MMA)
$[(N_2NN^{TMS})SmBH_4]_2$ (**55$^{TMS}_{Sm}$**)	✓ (ε-CL)		✓		[83]
$[(N_2NN^{Mes})Sm(BH_4)_2Li]_2$ (**55$^{Mes}_{Sm}$**)	✓ (ε-CL)		✓		[83]
$(O_2N^L)Ln(BH_4)(thf)_n$ (**57$^L_{Ln}$**: Ln = Sm, Y, Nd; L = py, OMe, NMe_2, Pr^n)	✓ (ε-CL)	✓ (L-LA, *rac*-LA)			[85], [86]
$Cp^{*\prime}Ln(BH_4)\{(p\text{-Tol})NN\}$ (**60$_{Ln}$**: Ln = Nd, Sm)			✓ [d]		[33]
$Cp^{Ph3}Sm(BH_4)\{(p\text{-Tol})NN\}$ (**61$_{Sm}$**)			✓ [d]		[33]
[tetrahydroSalen]$Y(BH_4)(dme)$ [b,c]	✓ (ε-CL)				[113]

[a] ε-CL = ε-caprolactone, δ-VL = δ-valerolactone, β-BL = β-butyrolactone, L-LA = (*S*,*S*)-lactide, *rac*-lactide = (*S*,*S*)-LA + (*R*,*R*)-LA, TMC = trimethylene carbonate, MMA = methyl metacrylate;

[b] non isolated, prepared *in situ* from ionic metathesis;

[c] tetrahydroSalen = $[(2\text{-}OH\text{-}C_6H_2Bu^t{}_2\text{-}3,5)CH_2N(CH_3)CH_2]_2$;

[d] in some cases in the presence of Bu^nLi or $Mg(Bu^n)_2$.

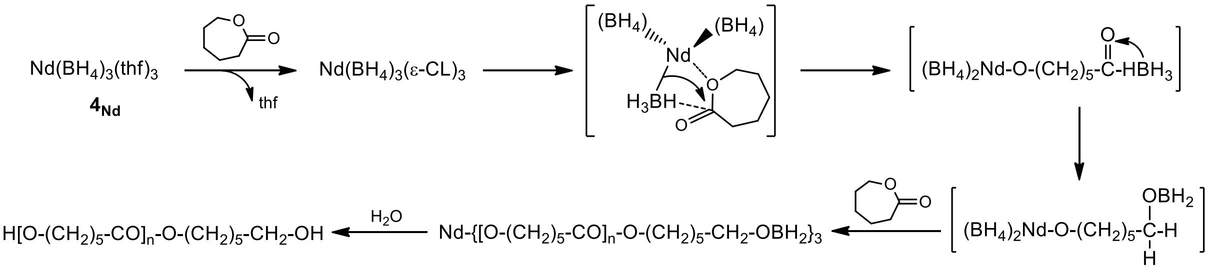
4.4.1.1. Cyclic esters

4.4.1.1.1. Lactones

4.4.1.1.1.1. Trivalent borohydride initiators

4.4.1.1.1.1.1. Non-substituted borohydride initiators

The ring-opening polymerization of ε-caprolactone using a rare earth complex involving a borohydrido group, was firstly reported by Guillaume *et al.* [108,109]. They showed that the trisborohydrides $Ln(BH_4)_3(thf)_3$ (**4_{Ln}**: Ln = La, Nd, Sm) initiate the ring-opening polymerization of ε-caprolactone at room temperature to give, in quantitative yields and in less than fifteen minutes (for monomer/catalyst ratios 100 to 750), α,*ω*-dihydroxytelechelic poly(*ε*-caprolactone) displaying a fairly narrow molar mass distribution (PDI ≤ 1.4). A good agreement between $M_{n(theo)}$ and $M_{n(exp)}$ was observed for low $[monomer]_0/[initiator]_0$ ratios (< 100) whereas a deviation ($M_{n(exp)} < M_{n(theo)}$) was obtained at higher ratios (> 250), indicating the occurrence of some transfer reactions. Regarding the mechanism of the polymerization, the authors postulated that the initiation process consecutively involves i) monomer coordination to the neodymium center, ii) insertion into the Nd−hydride(BH_3) bond and iii) reaction with the (HBH_3) group. The polymerization subsequently proceeds with an alkoxide initiator to finally yield α,ω-telechelic poly(ε-caprolactone) with hydroxy end-groups (scheme 61).



Scheme 61.

An interesting approach was undertaken by Sun *et al.* who described the synthesis of poly(ε-caprolactone)s with various end-capping groups, *via* a one-pot reduction–initiation strategy involving lanthanide trisborohydrides **4_{Ln}** (Nd or Y) in the presence of aldehydes and ketones. Carbonyl compounds were reduced by the lanthanide compounds, which *in situ* triggered the ring-opening polymerization of ε-caprolactone. The end-capping degree was found to reach 100 % with selected carbonyl compounds [110].

The catalytic behavior of a series of **4_{Ln}** derivatives (Ln = La, Pr, Nd, Sm, Y, Yb) was studied for the ring-opening polymerization of another cyclic ester, δ-valerolactone (δ-VL) [111]. The catalytic activities followed the order of the ionic radii: La > Pr > Nd > Sm > Y > Yb. ^1H NMR and Maldi-Tof analyses of the obtained polymers revealed a hydroxy-telechelic structure. The molecular weights of the resulting polymers (M_n up to 15000) were found to increase linearly with conversion and the molecular weights distributions remained relatively narrow (PDI = 1.3 to 1.6) indicating a controlled polymerization process with these systems.

The polymerization of ε-caprolactone was also studied with the cationic borohydrido $[Ln(BH_4)_2(thf)_5]^+[BPh_4]^-$ (**8_{Ln}**) complexes (Ln = Y, La, Nd, Sm) as initiators [24]. All these cationic compounds were found to result in complete conversion within one minute at room temperature leading to narrow PDI's and molecular weights in accordance with more than two growing chains initiated per metal.

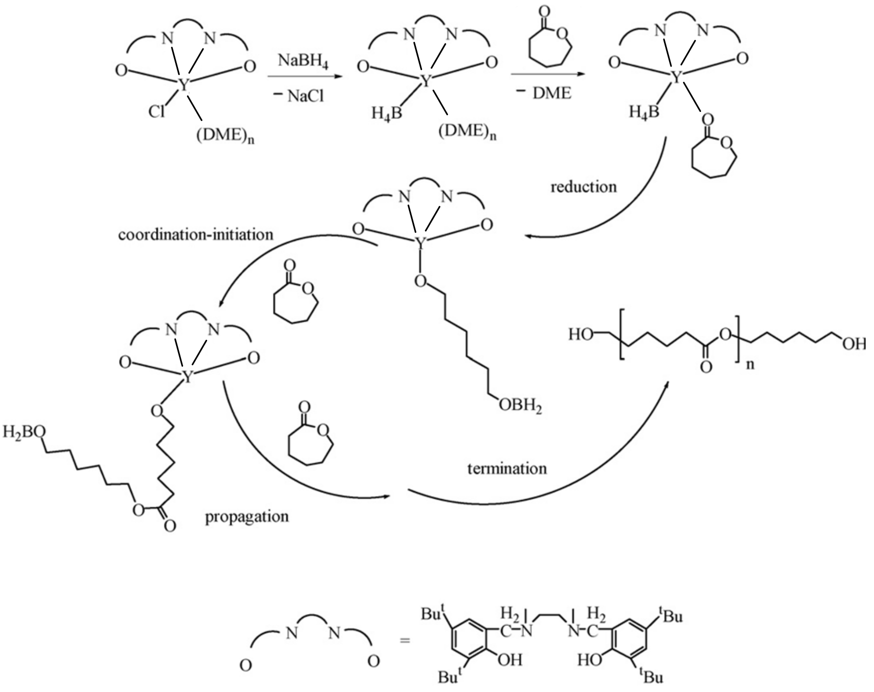
4.4.1.1.1.1.2. Substituted borohydride initiators

Following their studies with the trisborohydrides, Guillaume *et al.* reported the controlled ring-opening polymerization of ε-caprolactone with the lanthanide complex $Cp^*_2Sm(BH_4)(thf)$ (**36^{Me}_{Sm}**). Poly(ε-caprolactone) was obtained in quantitative yield within 30 min at room temperature (monomer/catalyst ratios 50 to 300). The use of this single-site initiator allowed a better understanding of the polymerization mechanism, in particular with the identification of the intermediate adduct $Cp^*_2Sm(BH_4)$(ε-CL). The stereoelectronic contribution of the two Cp* ligands appeared to slow down the polymerization and to limit transesterification reactions *vs*. the trisborohydride **4_{Sm}** [109,112].

Ring-opening polymerization of ε-caprolactone was reported by Bonnet *et al.* using rare earth post-metallocene complexes such as $Ln(O_2N^{py})(BH_4)(thf)_n$ (**57^{py}_{Ln}**, Ln = Sm, Y, Nd). High activities (full conversion within 2 min, for monomer/catalyst ratio ca. 300) with a good control and lack of transesterification reactions were noticed with these systems [84]. This study was recently extended with success to samarium borohydrides **57^{L}_{Sm}** (L = OMe, NMe_2, py, Pr^n, see section 3.2.2.7), to afford linear dihydroxytelechelic poly(*ε*-CL). Overall, the borohydride initiators were superior for the ROP of *ε*-CL when compared to otherwise identical amide initiators in this bis(phenolate)amine series [86].

The same research group reported the polymerization of this monomer with diamide-diamine borohydrido samarium $\{[(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NTMS)_2]Sm(BH_4)\}_2$ (**55^{TMS}_{Sm}**). The complete polymerization of 250 equiv. of ε-caprolactone was performed in a toluene-thf mixture within 1 min at room temperature, affording a polymer with good control over macromolecular data. The mesityl substituted analog **55^{Mes}_{Sm}** was half as active, likely due to the steric encumbrance of the mesityl group [83].

The research team of Sun reported recently the polymerization of ε-CL initiated by *in situ* generated yttrium borohydrido complex stabilized by a tetrahydrosalen ligand. The yttrium chloride precursor $\{[(2\text{-}OH\text{-}C_6H_2Bu^t_2\text{-}3,5)CH_2N(CH_3)CH_2]_2\}_2YCl(dme)$ was reacted with $NaBH_4$ to afford the borohydrido analog which was not isolated, and ε-CL was added subsequently (scheme 62). Poly(ε-caprolactone) was obtained in fair conversions, and quite narrow PDI's (1.13 – 1.71). In the absence of $NaBH_4$ no polymerization took place, showing that the process was initiated by the Y-(BH_4) function [113].

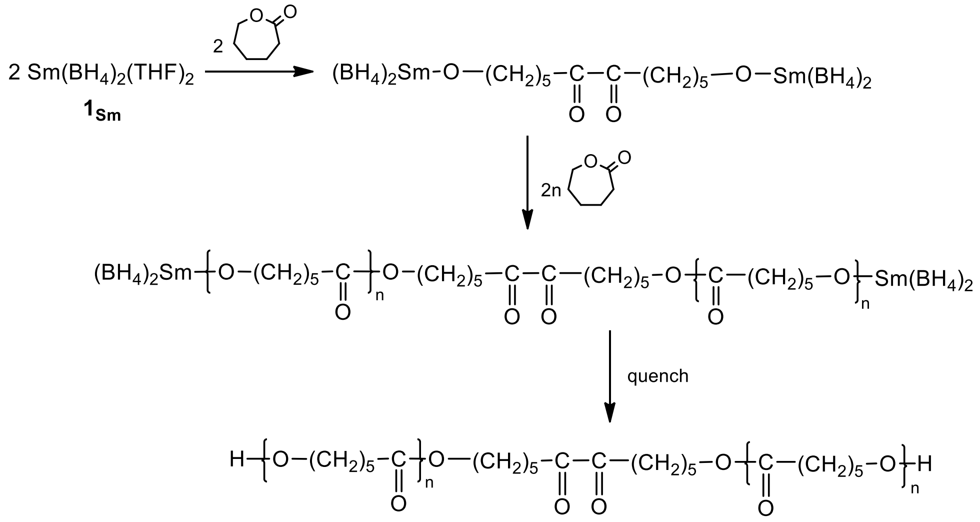


Scheme 62.

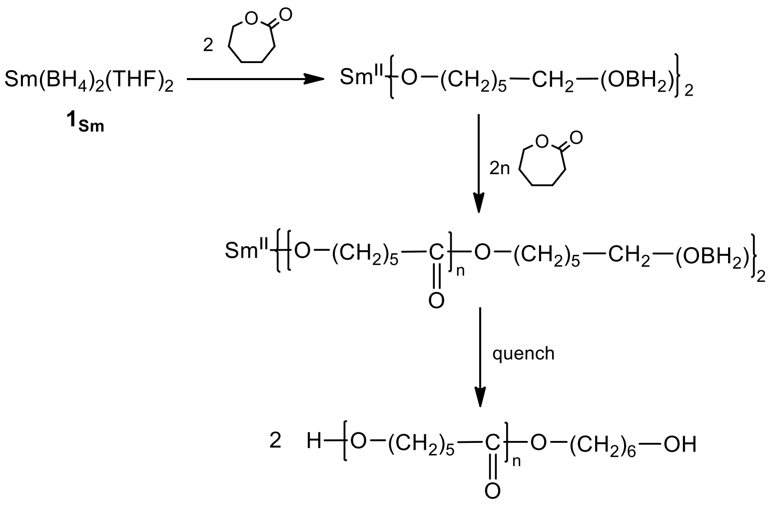
The ring-opening polymerization of β-butyrolactone was performed at room temperature using silica-supported lanthanide-based borohydride $[(\equiv SiO)Ln(BH_4)_2(thf)_{2.2}]$ (**28**$_{\mathbf{Ln}}$: Ln = La, Nd) as catalysts. Best results were obtained with the neodymium compound. The authors reported that the use of these heterogeneous catalysts, though less active than the non-supported precursors **4**$_{\mathbf{Ln}}$, allowed the formation of poly(β-butyrolactone) up to 85% isotactic. By contrast, the **4**$_{\mathbf{Ln}}$ initiators led to an atactic polymer [52].

4.4.1.1.1.2. Divalent borohydride initiators

Polymerization of ε-caprolactone was recently performed with divalent borohydrido complexes $Sm(BH_4)_2(thf)_2$ (**1**$_{\mathbf{Sm}}$) and $Cp^*Sm(BH_4)(thf)_2$ (**11**$_{\mathbf{Sm}}$). These compounds were found to both initiate the polymerization of ε-caprolactone in thf at room temperature in some minutes. The **11**$_{\mathbf{Sm}}$ initiator led to narrow polydispersities (1.2-1.4) and higher activity. Two different initiation mechanisms were proposed on the basis of the experimental molecular weights, and depending on the monomer/catalyst ratio. At low ratios ([ε-CL]/[Sm] = 116), a monoelectronic transfer can be envisaged (scheme 63), with one growing chain per two samarium. At higher ratios ([ε-CL]/[Sm] = 465), at least three polymer chains are initiated, speaking in favour of an additional initiation mechanism by insertion into the Sm(II)-(BH_4) bond (scheme 64) [13].



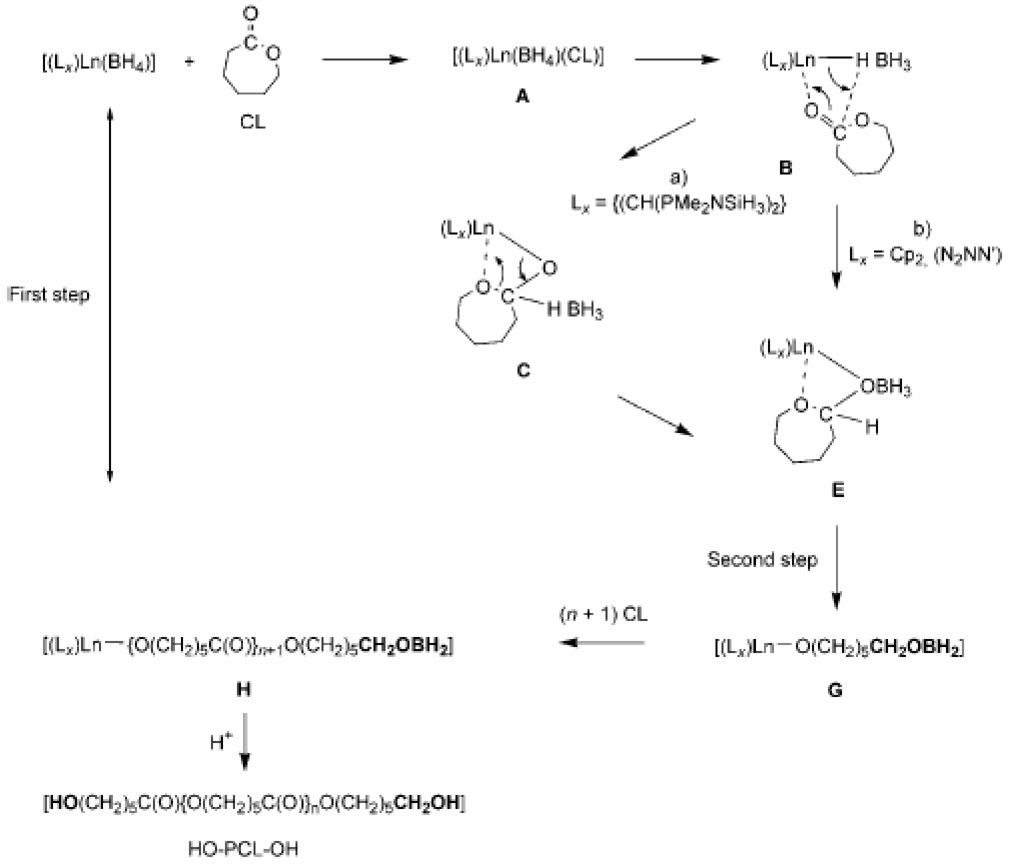
Scheme 63.



Scheme 64.

4.4.1.1.1.3. Theoretical studies

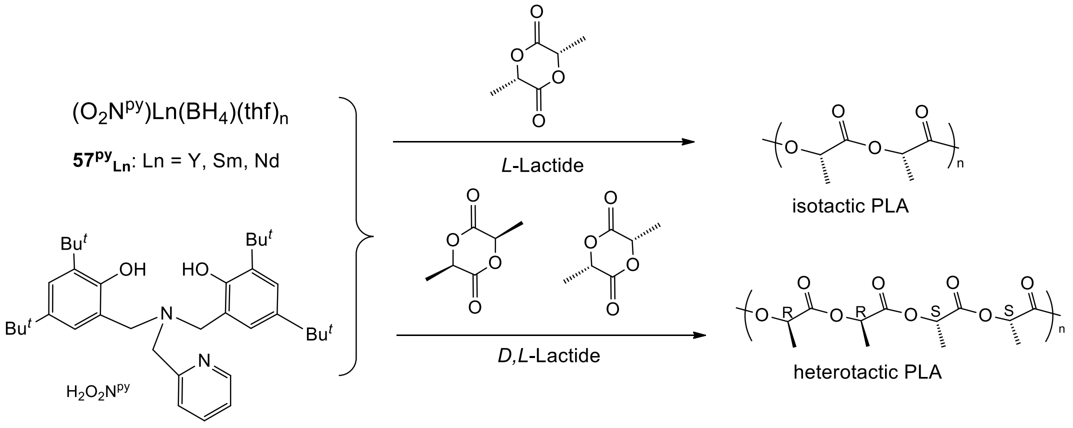
The mechanisms of the polymerization of ε-caprolactone initiated by $Cp^{*}_{2}Sm(BH_4)(thf)$ (**36^{Me}**$_{Sm}$) and by the amido-amino post-metallocenes $[Sm(N_2NN^{R})BH_4]_2$ (**55^{R}**$_{Sm}$) were studied at the DFT level with $[(L_x)Eu(BH_4)]$ compounds as models (L_x = Cp_2 or N_2NN'; N_2NN' = $(2\text{-}C_5H_4N)CH_2N(CH_2\text{-}CH_2NMe)_2$), and then compared to the behavior of the hydride $[Cp_2Eu(H)]$ [114]. For all compounds the reaction proceeded in two steps: a hydride transfer from the rare earth initiator to the carbonyl carbon of the lactone, followed by ring-opening of the monomer. In the last step a difference was observed between the hydride and borohydride complexes, because for the latter the ring-opening was induced by an additional B-H bond cleavage leading to a terminal $-CH_2OBH_2$ group, *via* reduction of the carbonyl group by BH_3 (path b, scheme 65). By comparison, upon reaction of caprolactone with the hydride $[Cp_2Eu(H)]$, the alkoxy–aldehyde complex produced, $[Cp_2Eu\{O(CH_2)_5C(O)H\}]$, is the first formed initiating species. These DFT investigations were considered as fully compatible with previously reported experimental mechanistic studies. Similar investigations initiated by bis(phosphinimino)methanide complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln(BH_4)_2]$ (**29**$_{Ln}$: Ln = Y, Lu), which were modeled as $[(L_x)Eu(BH_4)]$ ($L_x = \{CH(PMe_2NSiH_3)_2\}$), indicate that this type of complex reacts in an unprecedented manner with the first B-H activation being achieved within two steps (path a in scheme 65). This particularity was attributed to the metallic fragment based on the natural bond order analysis [53].



Scheme 65.

4.4.1.1.2. Lactide

Ring-opening polymerization of lactide initiated by a borohydride rare earth complex was first described in 2005 by Bonnet *et al.*. They reported the behavior of post-metallocenes $[(O_2N^{py})Ln(\mu\text{-}BH_4)(thf)_n]_2$ (**57^{py}_{Ln}**: Ln = Sm, Y, Nd), which all enable the ring-opening polymerization of *L*-lactide and *rac*-lactide, leading respectively to isotactic and to highly heterotactic (up to 87%) polylactide, with narrow PDI's (1.31-1.73) and fair correlation between experimental (3000-15000) and theoretical M_n values (scheme 66). Complex **57^{py}_{Sm}** was found to provide the best control over the molecular weights, *i.e.* with a low degree of transesterification reactions during the polymerization process [85].



Scheme 66.

In a recent publication, these results were extended to the borohydrides $\mathbf{57^{L}_{Sm}}$ (L = OMe, NMe_2, py, see section 3.2.2.7), which allowed as well the ROP of *rac*-LA, with activity increasing in the order $O_2N^{L} = O_2N^{OMe} \approx O_2N^{py} < O_2N^{NMe2}$. The latter ligand also gave the best control of the ROP, as judged by the PDIs and M_n values. All initiator gave heterotactically enriched poly(*rac*-LA). When compared to otherwise identical amide initiators, the borohydride initiators $\mathbf{57^{L}_{Sm}}$ were superior in terms of control of the polymerization [86]. MALDI-ToF MS analysis of the poly(*rac*-LA) formed with these borohydride complexes showed -CH(Me)CHO, $-CH(Me)CH_2OH$, and -CH(Me)OH end groups, originating from the insertion of the first LA monomer into the $Sm\text{-}BH_4$ moieties. DFT calculations on $Eu(O_2'N^{NMe2})(BH_4)$ ($O_2'N^{NMe2} = Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}O\text{-}C_6H_4)_2$) found two mechanisms for the initial ring-opening step of LA by the borohydride group, giving pathways leading to either aldehyde- or alcohol-terminated poly(lactide)s. Of these two pathways, the one giving α,ω-dihydroxy-terminated polymers was the most favored, in agreement with experiment.

Another illustration of the ring-opening polymerization of *L*- and *rac*-lactide initiated by rare earth post-metallocene borohydrido complexes was reported with guanidinate complexes $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(thf)_2$ ($\mathbf{53_{Ln}}$: Ln = Nd, Sm, Yb). These complexes were found to act as monoinitiators for the ring-opening polymerization of *L*- and *rac*-lactide, providing respectively isotactic (M_n 2000-17000, PDI 1.4-1.6) and atactic (M_n 6000-26000, PDI 1.16-2.99) polylactide, with good control over molecular weights for $\mathbf{53_{Nd}}$ [81].

Ring opening polymerization of *L*-lactide with the simple $\mathbf{4_{Nd}}$ was published by Nakayama and co-workers only in 2007. Hydroxy-telechelic isotactic polylactides were obtained in good yield and narrow molecular weight distributions (1.2-1.6). Efficient chain extension of these polylactides was performed using hexamethylene diisocyanate, affording poly(ester-urethane)s [115]. The same research team extended just recently the polymerization of *rac*-lactide to a large number of $\mathbf{4_{Ln}}$ derivatives (Ln = La, Pr, Nd, Sm, Y, Yb). The activity was strongly dependent on the nature of the metal center, and decreased in the order of the ionic radii of the metals (La > Pr > Nd > Sm > Y > Yb). The molecular weights of the resulting polymers increased linearly with conversion while the molecular weights distributions remained relatively narrow (PDI = 1.2 to 1.4). No information on the stereoselectivity obtained is reported [111].

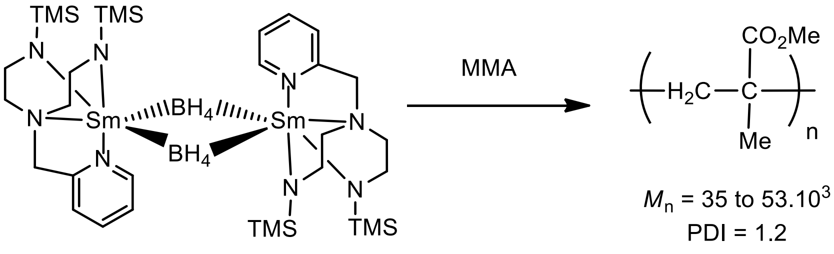
4.4.1.2. Trimethylene carbonate

Guillaume *et al.* showed that poly(trimethylene carbonate) could be synthesized through ring opening polymerization of trimethylene carbonate (TMC) by using the borohydride initiator **4**$_{\mathbf{Sm}}$. A good activity was noticed for that kind of monomer (full conversion in a few hours at room temperature), affording polymers with a regular structure void of ether linkages, along with narrow polydispersity indexes (ranging from 1.2 to 1.4) and molecular weights (M_n 2000-27000) close to the expected values for three growing chains per metal after correction of SEC data. A coordination-insertion mechanism with O-acyl clivage was established on the basis of NMR characterizations of the polymer chain end-functions, supporting the generation of an α-hydroxy,ω-formatetelechelic PTMC. The reduction of the terminal carbonyl group by BH_3 as observed in the case of ε-CL ROP with borohydride initiators (see section 4.4.1.1.1) is presumed here not to occur [116].

4.4.1.3. Methylmethacrylate

4.4.1.3.1. Post-metallocene borohydride initiators

The first instance of a lanthanide borohydride complex initiating the polymerization of methylmethacrylate (MMA) was described in 2005 by Bonnet *et al.* with **55**$^{\mathbf{R}}_{\mathbf{Sm}}$ samarium diamide-diamine (R = TMS, Mes) supported complexes (scheme 67) [83]. Poly(methylmethacrylate) was obtained in good yield with narrow polydispersities. The polymerization was found to occur at a wide range of temperatures, from +25 °C to –78 °C. The microstructure of the poly(methylmethacrylate) was found to depend on the polymerization temperature, and the syndiotacticity increased from 34.8 % at 25 °C to 64.5 % at –78 °C. The chloride related complex remained inactive in the same conditions, speaking in favour of a polymerization initiated by the BH_4 group, hence excluding the occurrence of insertion into the Sm-N bond.



55$^{\mathbf{TMS}}_{\mathbf{Sm}}$

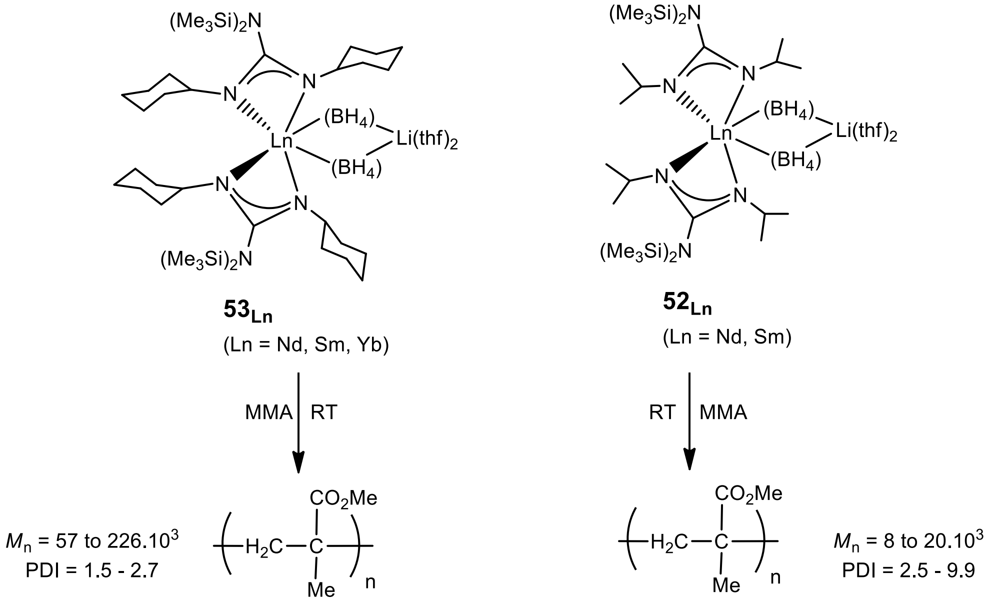
Scheme 67.

The polymerization of MMA was studied one year later with aryloxide lanthanide borohydrido complexes $(ArO)Ln(BH_4)_2(thf)_2$ (**27**$_{\mathbf{Ln}}$: Ln = Yb, Er) [51]. These complexes displayed moderate activities leading to high molecular weights PMMAs, but no data were available regarding the molecular weight distributions. The activity of these systems was shown to strongly depend on the polymerization temperature, with the highest activity at 0 °C. The stereoregularity analysis showed that the polymers obtained were syndiotactic-rich (ca. 60%); only little variations of the tacticity with temperature and time were observed.

Mono(guanidinate)-supported lanthanide borohydrides $[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(thf)_2$ **22**$_{\mathbf{Ln}}$ (Ln = Yb, Er) displayed moderate catalytic activity for the polymerization of MMA, leading to polymers with molecular weights up to ca. 40000 g/mol with somewhat large molecular weights distributions [44]. The erbium complex was more active than its ytterbium parallel. Increasing the reaction temperature negatively impacted the polymerization activity, along with the decrease of the molecular weights. No study of the microstructure of the polymers was reported.

Using the same guanidinate ligand, Trifonov *et al.* studied the activity of the "ate" di-substituted derivatives $[(Me_3Si)_2NC(NCy)_2]_2Ln(BH_4)_2Li(thf)_2$ **53**$_{\mathbf{Ln}}$ (Ln = Nd, Sm, Yb) for the polymerization of MMA [45]. These complexes were moderately active at room temperature, conversion *vs*. time showing a linear character at lower degrees of conversion, and the activity decreased in the order Sm > Nd > Yb. Complexes **53**$_{\mathbf{Sm}}$ and **53**$_{\mathbf{Yb}}$ led to similar molecular weights (57000 g/mol) with quite rather narrow PDI's (1.53 and 1.63 respectively). In contrast, **53**$_{\mathbf{Nd}}$ afforded PMMA with much higher molecular weight of (M_n = 226000 g/mol) along with a broader mass distribution of 2.72. NMR analysis of the final polymers revealed that the percentage of syndiotactic triads reaches 52 % with **53**$_{\mathbf{Sm}}$ and **53**$_{\mathbf{Yb}}$, but this value dropped down to 32% with **53**$_{\mathbf{Nd}}$ (scheme 68, left).

The same group described a similar work using a slightly different version of the guanidinate ligand bearing *iso*-propyl substituents [80]. A moderate activity was observed with **52**$_{\mathbf{Ln}}$ (Ln = Sm, Nd) at room temperature, leading to poly(methyl methacrylate)s with much higher PDI's (2.52 to 9.95) and no stereoregularity (scheme 68, right).



Scheme 68.

Surprisingly, it is only in 2008 that the simple **4**$_{\mathbf{Ln}}$ (Ln = Sm, Nd) were thoroughly investigated towards the polymerization of MMA. The activity of these initiators was quite low, and affording poly(methylmethacrylate) with molecular weights much higher than the calculated ones, and rather broad distributions (up to 2.7), which was attributed to a poor initiation efficiency by the authors. Rather syndiotactic PMMA's were obtained with an average percentage of *rr* diads of 55% [117]. Preliminary studies had been undertaken with **4**$_{\mathbf{Nd}}$ in 2006 by Visseaux *et al.* [33]. It was shown that this compound initiated the polymerization of MMA in the presence of $(2,6\text{-Bu}^t\text{-4-Me-}C_6H_3O)_2AlEt$ as an activator [118], at 0 °C. In these conditions, the yield was low (10 % in 3 h) but the polymer formed was 81 % syndiotactic. Studies were then conducted with various alkylating agents as co-catalysts, enabling a conversion up to 95 %, with stereoselectivities up to 92% *mm* or 75 % *rr*, depending on the experimental conditions.

4.4.1.3.2. Half-metallocene and metallocene borohydride initiators

The polymerization of MMA initiated by a series of Cp-substituted borohydrido lanthanide complexes was reported in 2006. The catalytic systems employed were made of lanthanide based (Ln = Sm or Nd) half-metallocenes (**17_{Nd}**, **17_{Sm}**, **$14'_{Sm}$**) or metallocenes (**35_{Sm}**, **36^{nPr}_{Nd}**, **37_{Sm}**, **60_{Sm}**, **60_{Nd}**, **61_{Sm}**) bearing bulky substituted cyclopentadienyl ligands such as Cp*', Cp^{4i}, Cp^{Ph3}, and/or diketiminate, eventually associated to variable quantities of alkylating agent (Bu^nLi or $MgBu^n_2$) [33]. Quantitative conversions and syndiotactic polymer (> 80 % *rr*) were observed with metallocenes **35_{Sm}** and **37_{Sm}**. With Bu^nLi as an additional co-catalyst and in non polar medium, highly isotactic polymer (up to 95.6 %) was formed. In thf, syndiotactic-rich PMMA was obtained whatever the nature of the co-catalyst. In many cases, molecular weights were higher than expected, likely due to faster propagation *vs.* initiation reactions.

Guillaume *et al.* also reported later the polymerization of methylmethacrylate initiated by the samarocene $Cp^*_2Sm(BH_4)(thf)$ **36^{Me}_{Sm}**. The polymerization was found to proceed at ambient temperature to give rather syndiotactic polymer (up to 67% *rr* diads) with molar masses higher than expected and quite broad molar mass distributions (1.2 to 2.4), which was attributed to a poor initiation efficiency [117].

The single component borohydrido complex $(C_5Me_4\text{-}C_6H_4\text{-}o\text{-}NMe_2)Sc(BH_4)_2$ **19_{Sc}** was just recently reported to act as an efficient initiator towards MMA polymerization [42]. It showed high activity towards the bulk polymerization of methyl methacrylate without specific control, but showed high iso-selectivity (*mm* = 80%) when the polymerization was performed in benzene medium, and switched to syndio-selectivity (*rr* = 74% at -20 °C) in polar thf medium. Besides and worth to be noted, the chloride analog was inert. The binary catalyst system of **19_{Sc}** /$MgBu^n_2$ had similar catalytic performances when compared with **19_{Sc}** in thf medium, but provided enriched syndio-control in benzene solution that was in contrast to the iso-control of **19_{Sc}**. Surprisingly, **19_{Sc}** upon activation with *n*BuLi displayed an extremely high activity (1.1 x 10^6 $g.mol_{Sc}^{-1}.h^{-1}$) and afforded syndiotactic PMMA (*rr* = 75%) at low polymerization temperature (-20 ◦C) in thf.

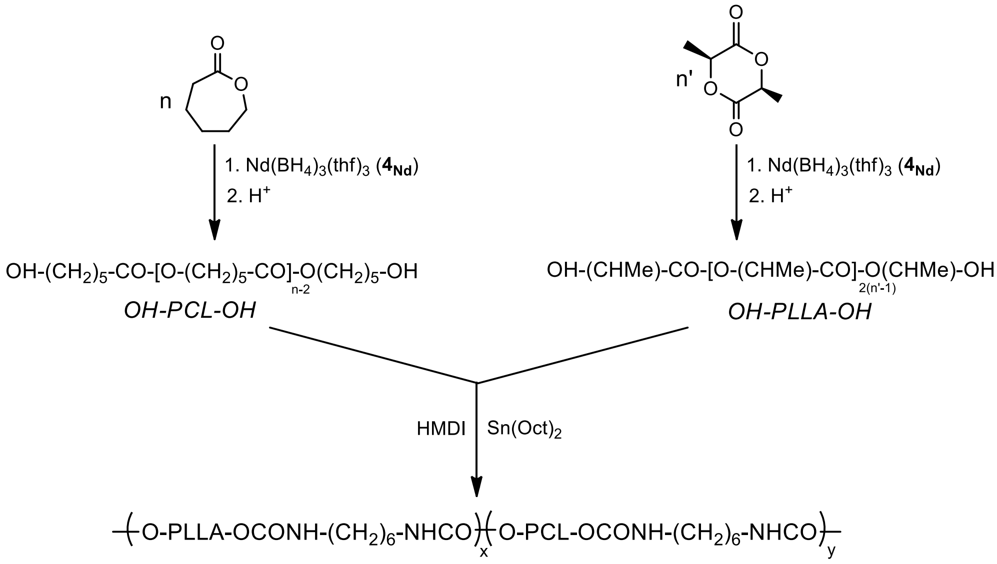
4.4.1.3.3. Theoretical studies

The mechanism of the polymerization of MMA with borohydrido complexes was studied by Maron *et al.* by performing DFT calculations on a bis(cyclopentadienyl)europiocene as model. They showed that the reaction of $[(Cp)_2Eu(BH_4)]$ with MMA leads to the formation of the borate complex $[(Cp)_2Eu\{(OBH_3)(OMe)C{=}C(Me)_2\}]$, *via* the enolate $[(Cp)_2Eu\{O(OMe)C{=}C(Me)_2\}]$. Similar computational results were obtained for the reaction of $[Eu(BH_4)_3]$ and MMA with all of the products showing extra stabilization. This borate-enolate intermediate was considered as the active species in the polymerization of MMA initiated by the borohydride precursors [117]. Enolate formation was, however, less energetically favored than observed *in silico* for the reaction of the hydride $[(Cp)_2Eu(H)]$ with

MMA, hence rationalizing the much higher degree of control of the process in the latter case, as initially observed experimentally by Yasuda et al. with $(Cp^*_2SmH)_2$ [119].

4.4.1.4. Copolymers of polar monomers

Nakayama *et al.* described the random copolymerization of ε-CL and *L*-LA with the trisborohydride $\mathbf{4_{Nd}}$. With an equimolar feeding ratio of the co-monomers, very few ε-CL monomer (up to 7.7 %) was incorporated in the PLA chain. Using the same catalytic system, attempts at the block copolymerization of these two monomers by sequential addition of ε-CL and *L*-LA, led to a block copolymer with *L*-LA content of only 5%. However, multiblock PLLA-*co*-PCL copolymers could be obtained by coupling the two hydroxy-telechelic homopolymers OH-PLLA-OH and OH-PCL-OH, previously synthesized by ROP using complex $\mathbf{4_{Nd}}$ (see section 4.4.1.1.2), with hexamethylene diisocyanate (HMDI) in the presence of $Sn(Oct)_2$ (scheme 69) [115].



Scheme 69.

The same group achieved just recently the random copolymerization of δ-VL with either *L*-LA or ε-CL using $\mathbf{4_{La}}$. In the first case, a small amount of δ-VL (6.2 mol %) was incorporated in the PLA chain of the resulting copolymer, starting from equimolar ratios of both co-monomers. In the second one, δ-VL content in the resulting poly(VL-*co*-CL) copolymer was found to reach up to 63 mol %. An attempt of block co-polymerization by sequential additions of δ-VL followed by *L*-LA failed [111].

Block copolymerization of ε-CL with *L*-LA or *rac*-LA was performed with $[(O_2N^{py})Nd(\mu\text{-}BH_4)(thf)]_2$ ($\mathbf{57^{py}_{Nd}}$) as initiator, with first addition of ε-CL. PCL-*block*-P(*L*-LA) (mol% content 23/77) and PCL-*block*-P(*rac*-LA) (mol% content 27/73) were obtained. The block copolymerization by adding *L*-LA first, or the random copolymerization with an equimolar feeding ratio of the two co-monomers, afforded only pure poly(*L*-LA) [85].

Trimethylene carbonate (TMC) and ε-caprolactone were copolymerized using $\mathbf{4_{Sm}}$ to afford both random poly(TMC-*co*-CL) and block poly(TMC-*block*-CL) copolymers. It was found that if ε-caprolactone is introduced first, dihydroxytelechelic HO-PTMC-*block*-PCL-OH polymers are formed, whereas introduction of TMC first or simultaneous addition of the co-monomers leads to (hydroxyformate)telechelic HC(O)O-PTMC-*block*-PCL-OH analogs. In either random or sequential copolymerizations, the ratios of each monomer in the copolymers were close to the initial feed [116].

Di- and triblock polyester-polyacrylate copolymers PCL-*block*-PMMA and PMMA-*block*-PCL-*block*-PMMA were obtained by combined ring-opening polymerization and atom transfer radical polymerization. The procedure consisted in the esterification of the hydroxy group(s) of α,ω-dihydroxytelechelic poly(ε-caprolactone) OH-PCL-OH, previously synthesized from ring-opening polymerization using $\mathbf{4}_{\mathbf{Sm}}$, by means of 2-bromoisobutyryl bromide, and leading to Br-PCL-Br. These bromopolyesters were then used as macroinitiators to synthesize the corresponding di- and triblock copolymers, *via* atom transfer radical polymerization of methylmethacrylate [120].

4.4.2. Non polar monomers

As mentioned before, borohydride rare earths based pre-catalysts need the presence of an alkylating agent as co-catalyst, hence generating a Ln-R moiety by displacement of one BH_4 group, to activate non polar monomers. As far as we know, there are no examples of borohydride complexes enabling the polymerization of non polar monomers by themselves, by contrast to what observed with polar monomers. The use of BH_4 as a leaving group rather than halide has been claimed as an advantage regarding the selectivity in some cases, whereas catalytic activities appear often at least comparable, as will be presented hereafter.

The complexes involved in this section are gathered in the general table 6, which includes the particular behaviour of each compound used, in the presence of a given co-catalyst. Details of the polymerization reactions as well as mechanistic studies are presented hereafter.

Table 6

Borohydride Rare Earth Complexes Used in non Polar Monomer Polymerization

Pre-catalyst	Ethylene (E)	Isoprene (I)	Butadiene (B)	Styrene (S)	Co-polymer	Co-catalyst ^{a}	References
$Sc(BH_4)_3(thf)_2$ ($\mathbf{4_{Sc}}$)				✓		BEM	[14]
		✓		✓		TB/$Al(Bu^i)_3$	[36]
$Y(BH_4)_3(thf)_2$ ($\mathbf{4_{Y}}$)				✓		BEM	[14][123]
$La(BH_4)_3(thf)_3$ ($\mathbf{4_{La}}$)		✓				BEM	[123][126]
				✓		BEM	[130][14]
$Nd(BH_4)_3(thf)_3$ ($\mathbf{4_{Nd}}$)		✓				$Al(Et)_3$, BEM, MgR_2 ^{b}	[122][123][124][126]
		✓				HNB/$Al(Bu^i)_3$	[28]
				✓		BEM	[130][14]
$Sm(BH_4)_3(thf)_3$ ($\mathbf{4_{Sm}}$)				✓		BEM	[130][14]
$La(BH_4)_2Cl(thf)_{2.6}$ ($\mathbf{2_{La}}$)				✓		BEM	[14]
$Sm(BH_4)_2(thf)_2$ ($\mathbf{1_{Sm}}$)				✓		$Al(Bu^i)_3$	[13]
				✓		HNB or TB/$Al(Bu^i)_3$	[13]
$CpNd(BH_4)_3[Mg(thf)_6]$ ($\mathbf{13_{Nd}}$)		✓				BEM	[32]
				✓		BEM	[127]
$Cp^{Ph3}Nd(BH_4)_3[Mg(thf)_6]$ ($\mathbf{14_{Nd}}$)		✓				BEM	[32]
				✓		BEM	[127]
$Cp^*Sc(BH_4)_2(thf)$ ($\mathbf{15_{Sc}}$)		✓		✓	✓ (I/S)	TB/$Al(Bu^i)_3$	[36]
$Cp^*La(BH_4)_2(thf)_2$ ($\mathbf{15_{La}}$)				✓		BEM	[14][126]
		✓			✓ (I/S)	BEM	[37]
$Cp^*Nd(BH_4)_2(thf)_2$ ($\mathbf{15_{Nd}}$)		✓				BEM	[39][126]
				✓		BEM	[131][14]
	✓				✓ (I/E)	$LiAl(Bu^n)(Oct^n)_3$	[121]
					✓ (I/S)	BEM	[37][131][133]
$Cp^*La(BH_4)_3[Mg(thf)_6]$ ($\mathbf{16_{La}}$)		✓		✓		BEM	[127]
$Cp^*Nd(BH_4)_3[Mg(thf)_6]$ ($\mathbf{16_{Nd}}$)		✓				BEM	[32][39]
				✓		BEM	[127]
$Cp^{*\prime}Nd(BH_4)_2(thf)_2$ ($\mathbf{17_{Nd}}$)		✓				$Mg(Bu^n)_2$	[125]
$Cp^{4i}Sm(BH_4)_2(thf)$ ($\mathbf{18_{Sm}}$)		✓		✓		Bu^nLi	[7]

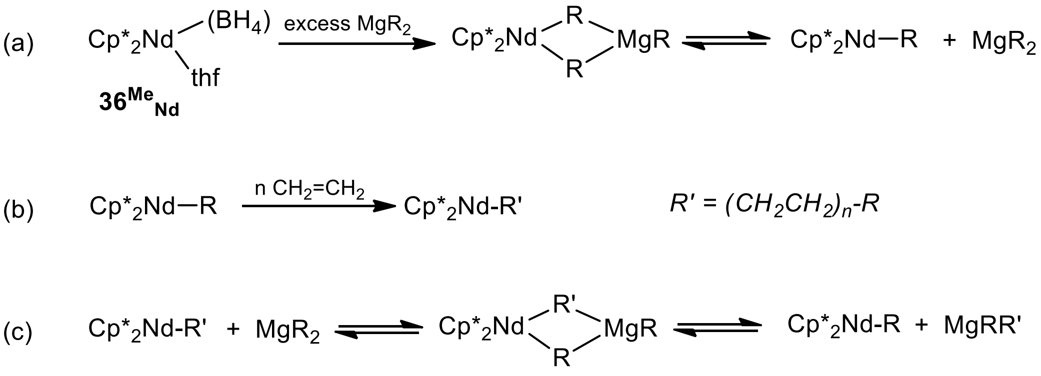
Cp^{4i}Nd(BH$_4$)$_2$(thf) (**18**$_{\mathbf{Nd}}$)		✓		✓		Bu^{n}Li	[7]
(DIP$_2$-pyr)Nd(BH$_4$)$_2$(thf)$_2$ (**25**$_{\mathbf{Nd}}$)			✓ ✓			MMAO B or HNB/Al(Et)$_3$	[49] [49]
[(Cp)$_2$Nd(BH$_4$)]$_2$[Mg(BH$_4$)$_2$(thf)$_4$] (**31**$_{\mathbf{Nd}}$)		✓					[55]
Cp*$_2$Nd(BH$_4$)(thf) (**36**$^{\mathbf{Me}}_{\mathbf{Nd}}$)	✓	✓				BEM	[63]
Me$_2$Si(3-Me$_3$Si-C$_5$H$_3$)$_2$NdBH$_4$(thf)$_2$ (**41**$_{\mathbf{Nd}}$)	✓				✓ (E/B)	Bu^{n}Li/Al(Bu^i)$_3$, Mg(Bu^n)(Oct^n)	[70]
[Me$_2$Si(C$_5$H$_4$)(C$_{13}$H$_8$)Nd(BH$_4$)$_2$][Li(thf)].0.5LiBH$_4$ (**43**$_{\mathbf{Nd}}$)	✓		✓		✓ (E/B)	Bu^{n}Li/Al(Bu^i)$_3$, Mg(Bu^n)(Oct^n)	[70]
{(Me$_2$Si(C$_{13}$H$_8$)$_2$)Nd(BH$_4$)$_2$[Li(thf)]}$_2$ (**44**$_{\mathbf{Nd}}$)					✓ (E/B)	Mg(Bu^n)(Oct^n)	[73]
[Me$_2$Si(2,7-Bu$^t{}_2$C$_{13}$H$_6$)$_2$]Nd(BH$_4$)$_2$Li(ether)$_3$ (**45**$_{\mathbf{Nd}}$)					✓ (E/B)	Mg(Bu^n)(Oct^n)	[73]
[(CMe$_2$C$_5$H$_4$)$_2$Ln(BH$_4$)$_2$)]$_2$Mg(thf)$_3$ (Ln = Nd, Sm) (**46**$_{\mathbf{Ln}}$)		✓					[55]
(C$_5$Me$_4$CH$_2$SiMe$_2$NPh)Ln(BH$_4$)(thf)$_2$ (Ln = Nd, Sm) (**59**$_{\mathbf{Ln}}$)		✓					[55]
[Cp*'Ln{(*p*-Tol)NN}(BH$_4$)]$_2$ (**60**$_{\mathbf{Nd}}$)		✓				Mg(Bu^n)$_2$	[88]

[a] BEM = Bu^{n}EtMg, TB = [CPh$_3$][B(C$_6$F$_5$)$_4$], HNB = [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], B = B(C$_6$F$_5$)$_3$;

[b] R = Bu^n, Hex^n, CH$_2$SiMe$_3$, allyl.

4.4.2.1. Ethylene

The first borohydrido rare earth based catalyst reported in the literature for the polymerization of ethylene is based on neodymocene $Cp^{*}_2Nd(BH_4)(thf)$ (**36^{Me}_{Nd}**) associated to *n*-butylethylmagnesium (BEM) [63]. This catalytic system polymerises ethylene with high activity (up to 4800 $kg.mol^{-1}.h^{-1}$) and it compares well with its halide analog $Cp^{*}_2NdCl_2Li(OEt_2)_2$. Polyethylene with narrow polydispersity indexes and low average molecular weights ranging from 2500 to 5100 g/mol is produced, in accordance with a reversible chain transfer reaction occurring between neodymium and magnesium, as shown in scheme 70. The system was still active even in the presence of large excesses of thf (50 equiv.).



Scheme 70.

Soon after were reported by Spitz *et al.* two other examples of ethylene polymerization catalysts based on borohydrido neodymocenes: the *ansa*-complexes $Me_2Si(C_5H_3\text{-}3\text{-}SiMe_3)_2Nd(BH_4)(thf)$ (**41_{Nd}**) and $[Me_2Si(C_5H_4)(C_{13}H_8)Nd(BH_4)_2][Li(thf)].0.5LiBH_4$ (**43_{Nd}**) were efficient when combined with $Mg(Bu^n)(Oct^n)$ or $Bu^nLi/Al(Bu^i)_3$, with an activity up to 1500 $kg.mol^{-1}.h^{-1}$ and average molecular weights ranging from 1200 to 7500 g/mol [70].

Very recently, it was reported that half-neodymocene $Cp^{*}Nd(BH_4)_2(thf)_2$ (**15_{Nd}**) also enables the polymerization of ethylene when combined with lithium *n*-butyl-tri-*n*-octyl-aluminate **(**90 °C, P = 2 bar, initial activity: 275 $kgmol^{-1}h^{-1}$) [121].

4.4.2.2. Conjugated dienes

Isoprene was the first dienic monomer to be studied in polymerization experiments involving borohydride rare earths catalysts, and most studies are related to this monomer, whereas a little number of reports are dealing only with butadiene-1,3. Most catalytic systems are stereoselective and to summarize, the results in terms of selectivity with conjugated dienes are gathered in table 7.

Table 7
Selectivity in borohydrido lanthanide-based catalysts for the polymerization of conjugated dienes

Catalytic system [a]	*cis*-1,4 (%) [b]	*trans*-1,4 (%) [b]	reference
4_{Sc}/TB/$Al(Bu^i)_3$	55.2	- [c]	[36]
4_{La}/BEM	5.3	92.8	[122][125]
4_{Nd}/$Al(Et)_3$	61.5	38.3	[121][123]

4$_{\mathbf{Nd}}$/Mg(Bu^n)$_2$	1.8	96.2	[121][123]
4$_{\mathbf{Nd}}$/BEM	- [c]	97.7	[122][125]
4$_{\mathbf{Nd}}$/Mg(Hex^n)$_2$	- [c]	96.2	[122]
4$_{\mathbf{Nd}}$/Mg(CH$_2$SiMe$_3$)$_2$	- [c]	86.1	[122]
4$_{\mathbf{Nd}}$/Mg(allyl)$_2$	- [c]	96.3	[122]
4$_{\mathbf{Nd}}$/HNB/Al(Bu^i)$_3$	92.0	3.4	[28]
13$_{\mathbf{Nd}}$/BEM	0	95.2	[32]
14$_{\mathbf{Nd}}$/BEM	0	96.2	[32]
15$_{\mathbf{Sc}}$/TB/Al(Bu^i)$_3$	97.2	- [c]	[36]
15$_{\mathbf{La}}$/BEM [d]	0	98.5	[37][125]
15$_{\mathbf{Nd}}$/BEM	0	98.0	[37][125]
15$_{\mathbf{Nd}}$/Mg(Bu^n)$_2$	0	98.2	[124]
16$_{\mathbf{La}}$/BEM	0.5	97.6	[126]
16$_{\mathbf{Nd}}$/BEM	0	98.2	[39]
17$_{\mathbf{Nd}}$/Mg(Bu^n)$_2$	0	98.5	[124]
18$_{\mathbf{Nd}}$/Bu^{n}Li	- [c]	95	[7]
18$_{\mathbf{Sm}}$/Bu^{n}Li	- [c]	95	[7]
24$_{\mathbf{Nd}}$/HNB/Al(Et)$_3$ [e]	75.2	23.3	[48]
24$_{\mathbf{Nd}}$/B/Al(Et)$_3$ [e]	83.9	13.1	[48]
26$_{\mathbf{Nd}}$/HNB/Mg(Bu^n)$_2$	1.3	97.2	[50]
31$_{\mathbf{Nd}}$/BEM	1.0	90.0	[55]
36$^{\mathbf{Me}}_{\mathbf{Nd}}$/BEM	- [c]	87	[63]
46$_{\mathbf{Nd}}$/BEM	1.0	92.5	[55]
59$_{\mathbf{Nd}}$/BEM	0.3	85.2	[55]
60$_{\mathbf{Nd}}$/Mg(Bu^n)$_2$	0	98.4	[88]

[a] Most selective results obtained for isoprene polymerization, TB = [CPh$_3$][B(C$_6$F$_5$)$_4$], HNB = [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], B = B(C$_6$F$_5$)$_3$;

[b] 3.4 % deduced by difference;

[c] data not available;

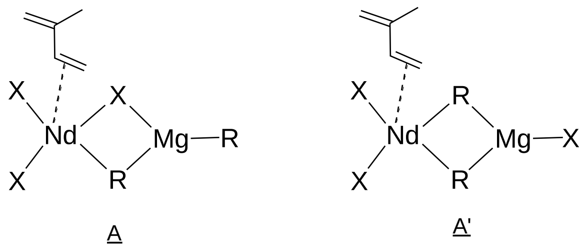
[d] see ref [125] for a full study in the presence of various Chain Transfer Agents;

[e] butadiene polymerization.

4.4.2.2.1. Isoprene

4.4.2.2.1.1. Trisborohydride-based catalysts

The first instance in this frame was reported in 2004 using Nd(BH$_4$)$_3$(thf)$_3$ (**4**$_{\mathbf{Nd}}$) associated to an aluminum or magnesium alkyl co-catalyst. The catalytic system was moderately active and non selective with AlEt$_3$ as co-catalyst. When **4**$_{\mathbf{Nd}}$ was combined with MgRR' (R = Bu^n, R' = Bu^n, Et), the resulting catalyst was active (monomer/catalyst = 1000, full conversion in 2 h at 50 °C) and *trans*-stereospecific, yielding polyisoprene up to 97.7% 1,4-*trans* regular [122,123]. The polymerization showed a *quasi* living character, which was established by a two-step polymerization. Complexes **4**$_{\mathbf{La}}$, **4**$_{\mathbf{Sm}}$ and **4**$_{\mathbf{Y}}$ were tested in the same conditions. The lanthanum derivative was less active and selective (25 % yield in 24 h, % *trans*-1,4 = 92.8 %) and the two other precursors showed no activity. Kinetic studies on the neodymium catalyst showed a first-order reaction rate. The authors attributed the molecular structure of the catalytic species to a bimetallic Ln-Mg one, on the basis of ^{1}H NMR experiments (scheme 71).

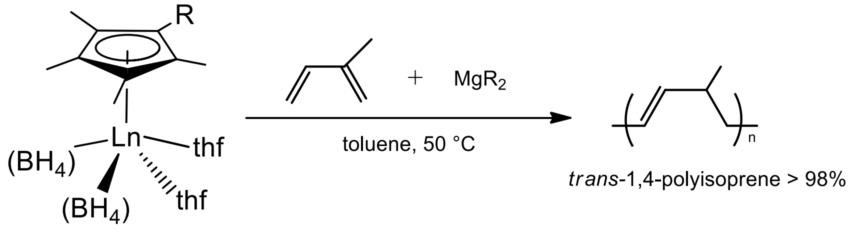


Scheme 71.

The microwave activation of isoprene polymerization with the above-mentioned catalysts $\mathbf{4_{Nd}}$/MgR$_2$ (R = Bu^n) and $\mathbf{4_{Nd}}$/AlEt$_3$ was studied [124]. It was shown that such activation leads to an enhancement in the reactivity, the selectivity being only slightly modified. According to the authors, the observed acceleration implies a mechanism involving a transition state that is significantly more polar than the initial state. At high temperatures, a depolymerization effect under microwave irradiation during the course of the reaction was noticed.

4.4.2.2.1.2. Half-lanthanidocene and related catalysts

Following the results obtained with the $\mathbf{4_{Ln}}$ derivatives, Visseaux *et al.* assessed the borohydrido half-neodymocene Cp*'Nd(BH$_4$)$_2$(thf)$_2$ ($\mathbf{17_{Nd}}$) associated to stoichiometric amounts of Mg(Bu^n)$_2$ for the same polymerization reaction. The introduction of the Cp*' ligand in the coordination sphere of the metal increased the *trans*-1,4 ratio up to 98.5 % and activities were significantly enhanced. A controlled polymerization character was observed with narrow polydispersities and formation of polymers with molecular weights matching well with theoretical values, on the basis of monomer/catalyst ratios. Formation of a bridging Nd(μ-BH$_4$)Mg active species was deduced from ^{1}H NMR experiments [125]. Similar results were observed with Cp*Ln(BH$_4$)$_2$(thf)$_2$ ($\mathbf{15_{Ln}}$, Ln = La, Nd) as pre-catalysts in the same experimental conditions (scheme 72) [37].

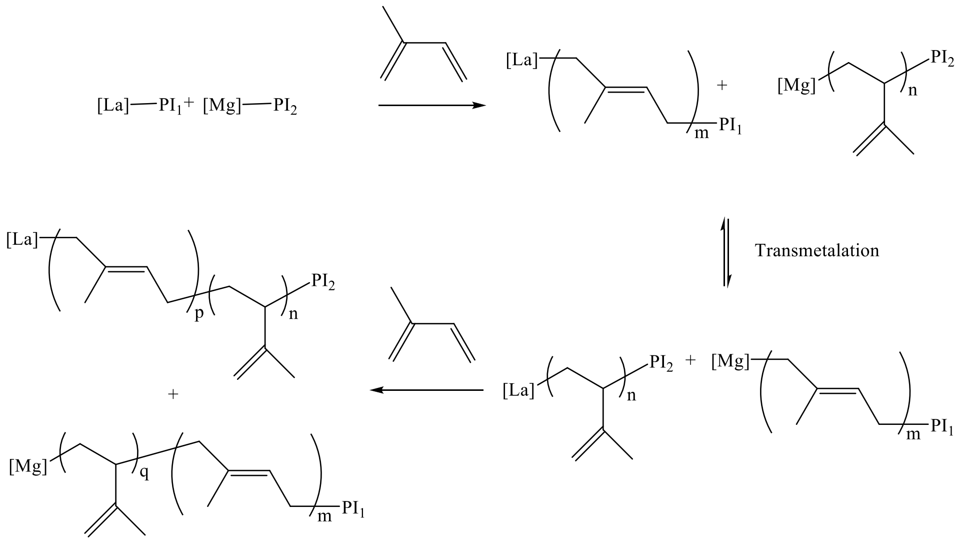


$\mathbf{15_{Ln}}$, $\mathbf{17_{Nd}}$

Ln = La, Nd; R = Me, Pr^n

Scheme 72.

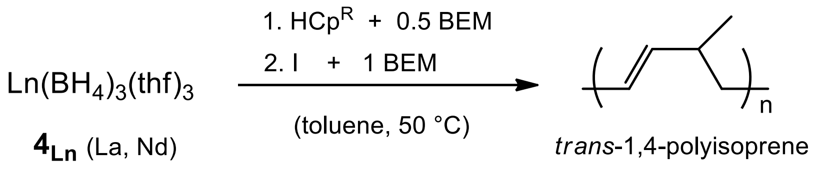
A study was conducted with the latter complexes in the presence of an excess of magnesium co-reagent [126]. Good agreement between the calculated molecular weights (considering two growing chains per Mg) and the measured ones, along with narrow PDI's, was found, highlighting a lanthanum Catalyzed polyisoprene Chain Growth (CCG) on magnesium, which was reported for the first time for this monomer. A transmetalation process was demonstrated to occur efficiently between the borohydride complex and magnesium dialkyl. A gradual decrease of the 1,4-*trans* stereoselectivity of the reaction is observed at the benefit of 3,4-selectivity with increasing quantities of magnesium dialkyl. This was partially attributed to the possible growth of 3,4-polyisoprene units onto the magnesium atom (scheme 73). By combining dialkylmagnesium and trialkylaluminum to the half-lanthanocene **15**$_{\mathbf{La}}$, unprecedented 1,4-*trans* stereospecific reversible coordinative chain transfer polymerization of isoprene was demonstrated.



Scheme 73.

This trend that borohydrido half-lanthanidocenes give rise to *trans*-selective catalysts had already been mentioned by Barbier-Baudry *et al.* as early as 2000: complexes $(Cp^{4i})Ln(BH_4)_2(thf)$ (**18**$_{\mathbf{Ln}}$: Ln = Sm, Nd) associated to Bu^nLi were active for the polymerization of isoprene affording a quantitative yield of mainly (95 %) *trans*-1,4-polyisoprene in 5 h at 50 °C (M_n = 90000 g/mol, M_w/M_n = 1.5) [7].

More recently, bimetallic ionic half-lanthanidocenes $[(Cp^R)Ln(BH_4)_3]_2[Mg(thf)_6]$ **13**$_{\mathbf{Nd}}$, **14**$_{\mathbf{Nd}}$, **16**$_{\mathbf{Nd}}$, and **16**$_{\mathbf{La}}$, all synthesized by the “B/A route”, were tested as well towards isoprene polymerization. With BEM as alkylating reagent, they afforded active catalysts leading in all cases to *trans*-1,4-polyisoprene (up to 98.2 %), along with fair control over macromolecular data, results being almost equivalent using Cp, Cp* or Cp^{Ph3} substituted complexes [32,39,127]. Catalysis tests were also performed by synthesizing the complexes *in situ*, without isolating them (scheme 74). The performances were close from those obtained with neutral or ionic Ln/Mg isolated half-lanthanidocenes.



Scheme 74.

To our knowledge, $[N(C_6H_3\text{-}2,6\text{-}Me_2)PPh_22\text{-}pyr\text{-}N(BH_3)]Nd(BH_4)_2(thf)_2$ (**26**$_{\mathbf{Nd}}$) is the sole non-Cp bis-borohydrido complex that could initiate the living polymerization of isoprene.

Highly regular *trans*-1,4-polymer (97.2 %) is obtained with fair activity (1000 equiv. monomer in 6 h at 50 °C) when the pre-catalyst is combined with organoborate $[PhMe_2NH][B(C_6F_5)_4]$ and $MgBu^n_2$ [50].

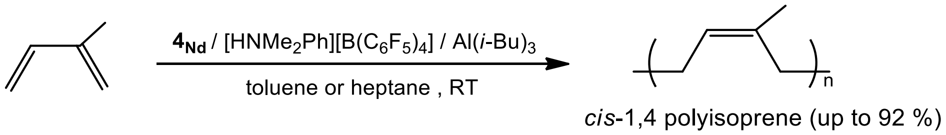
4.4.2.2.1.3. Disubstituted borohydride catalysts

Genuine heteroleptic half-lanthanidocenes $[(Cp^{*\prime})Ln\{(p\text{-Tol})NN\}(BH_4)]_2$ (**60$_{Ln}$**: Ln = Sm, Nd) afforded in the presence of $Mg(Bu^n)_2$ much less active catalysts than their half-lanthanidocenes bisborohydrido congeners, but they were still highly *trans*-1,4 selective (up to 98.4 % *trans*-1,4 units) [88].

Unexpectedly, since bisCp* lanthanide complexes are supposed to be inert towards conjugated dienes polymerization [128], the neodymocene **36^{Me}_{Nd}** associated to BEM was found to produce polyisoprene. The activity remained low (56 % conversion in 90 h at 50 °C) and the polyisoprene obtained was *trans*-1,4 at 87% [63]. With less sterically demanding ligands, it was found that $[(Cp)_2Nd(BH_4)]_2[Mg(BH_4)_2(thf)_4]$ (**31$_{Nd}$**), $[(CMe_2C_5H_4)_2Nd(BH_4)_2)]_2Mg(thf)_3$ (**46$_{Nd}$**), and $(C_5Me_4CH_2SiMe_2NPh)Nd(BH_4)(thf)_2$ (**59$_{Nd}$**) also enable isoprene polymerization in the presence of BEM, to afford *trans*-regular polymer as well [55].

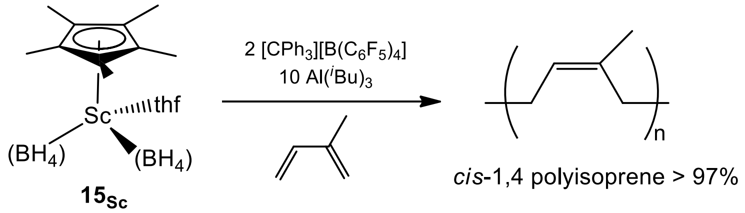
4.4.2.2.1.4. Cationic catalysts

Visseaux *et al* showed that ionic $[Nd(BH_4)_2(thf)_5][B(C_6F_5)_4]$ (**9$_{Nd}$**) associated to $Al(Bu^i)_3$ is a highly active catalyst for the *cis*-polymerization of isoprene. More interestingly the synthesis of the cationic species by the *in situ* reaction of **4$_{Nd}$** with $[HNMe_2Ph][B(C_6F_5)_4]$, followed by addition of $Al(Bu^i)_3$, led to a better control in terms of macromolecular data: at room temperature, 90 % yield was obtained within 30 min, affording *cis*-1,4-polyisoprene up to 92% with high M_n (up to 121000 g/mol) and narrow PDIs (scheme 75). In the presence of large excesses of aluminum co-catalyst, the authors evidenced the occurence of transfer reactions to aluminum during the polymerization process [28].



Scheme 75.

Catalytic systems based on cationic borohydrido scandium compounds were also assessed toward isoprene polymerization. Pre-initiators **4$_{Sc}$** or **15$_{Sc}$** upon treatment with 1 or 2 equiv. of $[Ph_3C][B(C_6F_5)_4]$ and 10 to 20 equiv. of $Al(Bu^i)_3$, showed high activities for the polymerization of isoprene. The process was not controlled in terms of selectivity starting with **4$_{Sc}$**, whereas activation of half-sandwich **15$_{Sc}$** in the same conditions afforded polyisoprene with up to 97.2 % *cis*-1,4 stereoregularity. The control of the polymerization was improved at lower temperature. The half-scandocene generated according to an *in situ* strategy led to the same results in terms of catalytic performance (scheme 76) [36].



Scheme 76.

The experimental preference for *cis*-1,4 polymerization of isoprene by cationic $[Cp^*ScR]^+$ active species was investigated and rationalized by theoretical DFT studies. The activation barrier for the *cis*-1,4 poly-insertion was 10 kcal.mol^{-1} lower than for *trans*-1,4 insertion. This difference in energy barrier was correlated to the difference of diene coordination to the metal fragment. The low steric hindrance in conjunction with the high acidity of the metal was reported to account for strongly favouring, kinetically and thermodynamically, *cis*- insertion over *trans*- insertion, although the *cis*- coordination to the metal center was calculated as slightly less favorable than the *trans*- one. Hence, according to the authors, the selectivity of the reaction was controlled by stereo-electronic factors [129].

Finally, it is worth to be noted that the *β*-diketiminate-supported complex $L^1Y(BH_4)_2(thf)$ (**23Y**) described by Cui *et al.* was inactive towards isoprene polymerization when activated with $[PhNHMe_2][B(C_6F_5)_4]$ and $Al(Bu^i)_3$ [46].

4.4.2.2.2. Butadiene-1,3

In contrast to isoprene polymerization, very few reports involving rare earth borohydrido catalysts are related to butadiene polymerization. In a study devoted to ethylene-butadiene copolymerization (see further), Boisson *et al.* reported that the *ansa*-derivative $[Me_2Si(C_5H_4)(C_{13}H_8)Nd(BH_4)_2][Li(thf)].0.5LiBH_4$ (**43Nd**) was active towards butadiene homopolymerization as well, in combination with $Mg(Bu^n)(Oct^n)$, affording *trans*-1,4-polybutadiene (> 95%) with M_n = ca 8000 gmol^{-1} and quite broad PDI [70].

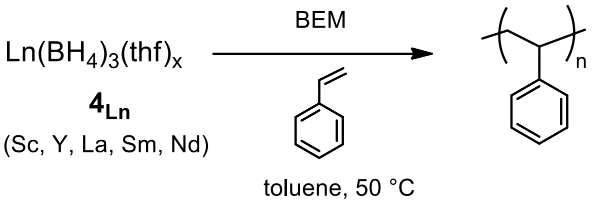
Just recently, Roesky *et al.* reported that the pyrrolyl-supported post-metallocene $(DIP_2\text{-}pyr)Nd(BH_4)_2(thf)_2$ (**24Nd**) activated by $B(C_6F_5)_3$ or $[PhNHMe_2][B(C_6F_5)_4]$ and combined with $Al(Et)_3$ afforded polybutadiene with a very high activity (up 2.36 kg.mmol^{-1}.h^{-1}). Molecular weights higher than 10^5 but broad distributions were obtained, along with *cis*-1,4 content of 83.9 % when $B(C_6F_5)_3$ was used. The same pre-catalyst associated to MMAO was found to afford polybutadiene with a lower activity [48].

4.4.2.3. Styrene

4.4.2.3.1. Trivalent borohydride catalysts

4.4.2.3.1.1. Trisborohydride-based catalysts

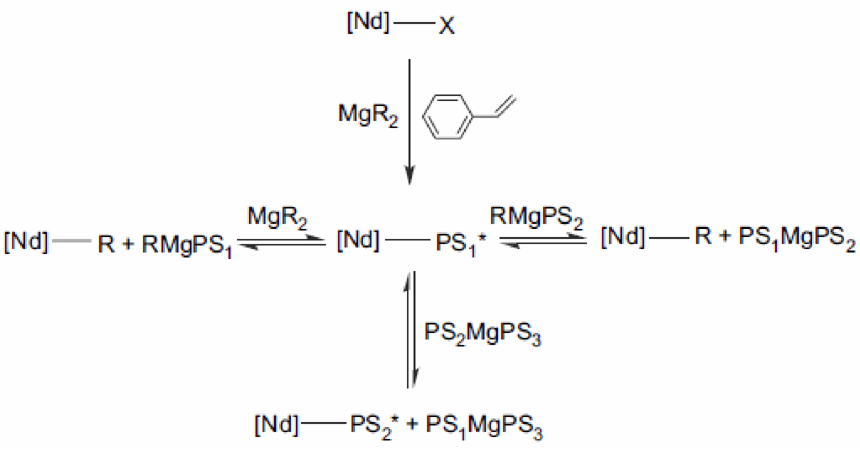
The trisborohydrides **4Ln** (Ln = Sc, Y, La, Sm, Nd) associated to BEM are also efficient catalytic systems for the polymerization of styrene (scheme 77). The reaction needs several hours to be complete at 50 °C. The activity was correlated to the nature of the metal center, following the order La > Nd > Sm > Y > Sc (table 11) [130,14]. The polystyrene produced was atactic. Efficient chain transfer between the lanthanide (lanthanum or neodymium) and magnesium in the presence of an excess of BEM was noticed. Occurrence of simultaneous *β*-H elimination, based on Maldi-Tof analysis of the obtained polystyrenes, was reported by the authors. The mixed chloro-borohydrido lanthanum complex $La(BH_4)_2Cl(thf)_{2.6}$ (**2$_{La}$**) was also tested as pre-catalyst and was efficient for transmetallation reactions as well [14].



Scheme 77.

4.4.2.3.1.2. Half-lanthanidocene catalysts

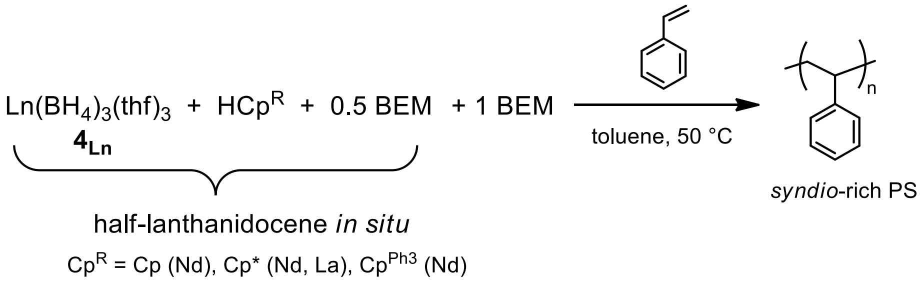
When associated to BEM, the mono-substituted $Cp^*Ln(BH_4)_2(thf)_2$ (**15$_{Ln}$**: Ln = La, Nd) afford efficient catalysts towards styrene polymerization. The introduction of the Cp* ligand in the coordination sphere of the metal significantly improves the control over macromolecular data (narrow PDI's: 1.2-1.3) and allows to produce *syndio*-rich polystyrene (85 %) [131]. The occurrence of transmetallation was established by increasing the Mg/Nd ratio. The reaction was slower in such situation but narrow polydispersity and control over the molecular weights are preserved in the course of the transfer reactions (scheme 78) [14]. Moreover, the selectivity was unchanged in these conditions.



Scheme 78.

Half-lanthanidocenes $(Cp^{4i})Ln(BH_4)_2(thf)$ **18$_{Ln}$** (Ln = Sm, Nd) associated to Bu^{n}Li affording *syndio*-rich (75% *rr* diads) polystyrene in high yield with $M_n = 3.10^5$ gmol^{-1} and PDI = 1.6 [7].

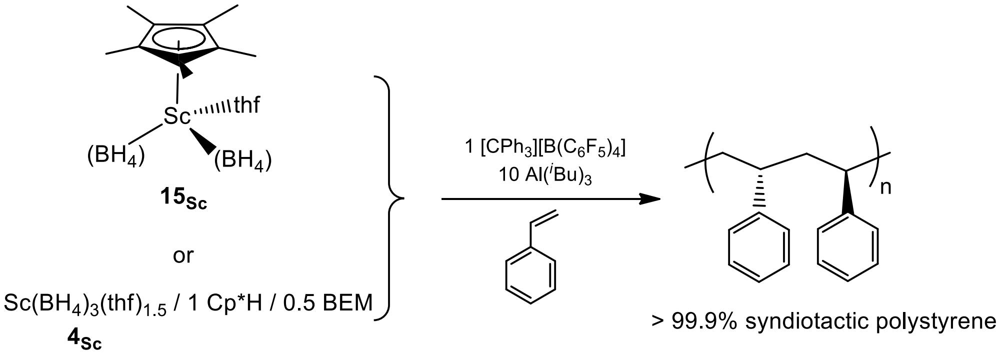
The influence of the nature of the cyclopentadienyl substituents on the polymerization activity was evaluated *via* an *in situ* method. Bimetallic ionic half-lanthanidocenes synthesized *via* the "B/A route", bearing Cp (**13$_{Nd}$**), Cp^{Ph3} (**14$_{Nd}$**), and Cp* (**16$_{Ln}$**, Ln = La, Nd) ligands, were activated with BEM, and they afforded active catalysts for the polymerization of styrene. Polymers with M_n up to 10000 g/mol and molecular weight distributions ranging from 1.1 to 2.5 were formed. The influence of the nature of the cyclopentadienyl ring on the activity was in the order Cp ~ Cp^{Ph3} > Cp*, which suggests an influence of the electron donating ability rather than steric requirements. Catalytic tests were also performed by synthesizing half-sandwich complexes without isolation (*in situ* "B/A route"), immediately followed by BEM activation, as represented in scheme 79. The activities were close from those obtained when the pre-catalysts were isolated and subsequently activated. *Syndio*-rich polystyrene was obtained in all cases, but this value did not reach the level obtained (85%) with isolated **15**$_{\text{Nd}}$ [127].



Scheme 79.

4.4.2.3.1.3. Cationic catalysts

Scandium trisborohydride **4**$_{\text{Sc}}$ associated to $[Ph_3C][B(C_6F_5)_4]$ and $Al(Bu^i)_3$ was reported to initiate the polymerization of styrene, leading to atactic polystyrene in good yield in a controlled manner (PDI = 1.72). Activated in the same conditions, the half-scandocene derivative **15**$_{\text{Sc}}$ was found to display much higher activity (up to 199 kg.mol^{-1}.h^{-1}) and pure syndiotactic polystyrene (*s*PS, *rrrr* > 99.9%) was obtained in all cases without any solvent fractionation. More interestingly, a polymerization reaction conducted *via* the *in situ* "B/A route" synthesis of **15**$_{\text{Sc}}$, by reaction of **4**$_{\text{Sc}}$ with Cp*H in the presence of half an equivalent of BEM, afforded 95 % of pure syndiotactic polystyrene (scheme 80)[36].



Scheme 80.

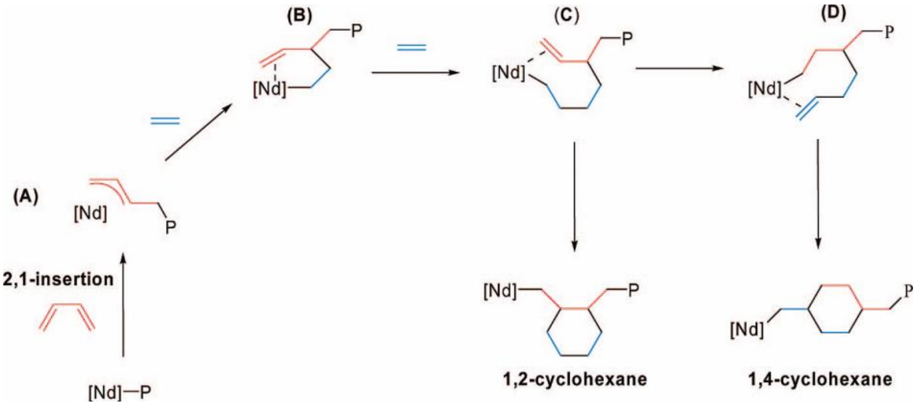
4.4.2.3.2. Divalent borohydride catalysts

Polymerization of styrene was performed using divalent borohydride **1**$_{\text{Sm}}$ as initiator in the presence of triisobutylaluminum. The activity was moderate (60 % yield in 24 h at 50 °C) but narrow PDI values were obtained (1.20-1.99). No improvement of the reaction was noticed in the presence of borate activators. The more sterically crowded divalent half-sandwich **11**$_{\text{Sm}}$ remained inactive towards styrene polymerization in the same conditions [13].

4.4.2.4. Copolymers of non polar monomers

Boisson *et al* reported the copolymerization of ethylene with butadiene using *ansa*-neodymium complexes **41**$_{\text{Nd}}$ or **43**$_{\text{Nd}}$, both associated to $Mg(Bu^n)(Oct^n)$ or $Bu^nLi/Al(Bu^i)_3$ as co-catalysts. Alternating copolymers poly[ethylene-*alt*-(*trans*-1,4-butadiene)] were obtained with all initiators with highest activities close to 500 kg.mol^{-1}.h^{-1}. In all cases, NMR studies showed that the butadiene insertion in the copolymers was in the *trans*-1,4 configuration (> 97%) [68]. Similar results were obtained with [$Me_2Si(3\text{-}Me_3Si\text{-}C_5H_3)(C_{13}H_8)$]$Nd(BH_4)$(thf), which was not characterized, and just mentioned in a patent [132].

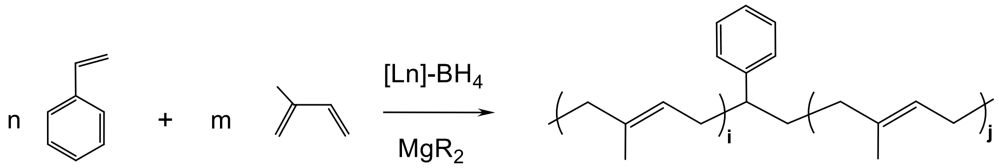
Following these results, the same research group reported that mixed *ansa*-(cyclopentadienyl)(fluorenyl) derivatives **44Nd** and **45Nd** in combination with (Bu^n)(Oct^n)Mg were efficient for the cyclo-copolymerization of ethylene with butadiene. The catalyst prepared from **44Nd** provided elastomers with a polyethylene skeleton incorporating unsaturated groups and *trans*-1,2-cyclohexane rings (up to 44 mol %) that were formed *via* an intramolecular cyclization. When precursor **45Nd** was used, it was shown that the *tert*-butyl substitution of fluorenyl ligands influenced the microstructure of the copolymers since in addition to 1,2-cyclohexane rings, *trans*-1,4-cyclohexane rings were formed (scheme 81)[73].



Scheme 81.

The statistical co-polymerization of isoprene with ethylene was performed recently using borohydrido half-sandwich complex **15Nd** associated to lithium *n*-butyl-tri-*n*-octyl-aluminate. According to NMR analysis, the obtained oligomer (M_n = 2000 g/mol) was made of a *trans*-1,4-polyisoprene structure containing 25 mol % of inserted ethylene units [121].

Unprecedented poly[(*trans*-1,4-isoprene)-*co*-styrene] was synthesized using borohydrido rare earth systems based on the combination of **4Ln** (Ln = La, Nd) or **15Nd**, associated to BEM. The copolymers exhibited molecular weights ranging from 15000 to 66000 g/mol along with quite narrow molecular weight distributions (<1.6), with up to 30% styrene inserted (80/20 styrene/isoprene feed) in a highly *trans*-1,4-polyisoprene structure (96-98%). With **15Nd** a slight increase of the amount of styrene inserted together with narrower molecular weight distributions, in comparison with the trisborohydrides, were noticed. NMR analyses showed that only one styrene moiety was inserted between two *trans*-1,4-polyisoprene blocks (scheme 82) [133].



Scheme 82.

The influence of the quantity of co-catalyst towards the composition of the statistical poly(isoprene-*co*-styrene) copolymer was further studied. It was shown that transmetallation between magnesium and the lanthanide occurs during the copolymerization, leading to the possibility to tune the composition of the copolymer by changing the Mg/Nd ratio rather than the co-monomers feed. Using this strategy, the amount of styrene inserted in the copolymer was increased by a factor 3 using ten equivalents of BEM instead of one, for the same monomer feed. However, this was detrimental to the selectivity (*trans*-1,4-isoprene units dropped from 98 % to 84 % for 1 and 10 equiv. of BEM, respectively) [37].

Statistical copolymerization of isoprene and styrene was carried out with the **15_{Sc}** / $[CPh_3][B(C_6F_5)_4]$ / $Al(Bu^i)_3$ catalytic combination, leading to the formation of a statistical poly(isoprene-*co*-styrene) copolymer, mainly composed of *cis*-1,4-polyisoprene (94.6 %) with 4.8 mol% inserted styrene moieties [36].

Finally, a block copolymer poly[styrene-*block*-(*trans*-1,4-isoprene)] (PDI = 1.2) was synthesized with **15_{Nd}**/BEM, by successive addition of isoprene and styrene, taking advantage of the living character of this catalyst upon isoprene polymerization. The polyisoprene block was highly *trans*-1,4 regular (98%) according to NMR analysis [131].

5. Conclusion

This survey intends to illustrate the richness and the continuous growing potential of the chemistry of borohydride compounds of the rare earths. A great variety of well-defined coordination and organometallic complexes were obtained during the last fifteen years in this frame. The borohydride ligand is not only well comparable with the chloride one, with analogous molecular structures, in the trivalent oxidation state as in the divalent one, but it also gives access to original derivatives when halide analogs cannot be obtained. In particular, it has been shown that borohydrido complexes seem to be less prone to redistribution reactions, especially with the lanthanides belonging to the early series. This structural diversity is obviously strongly connected to the versatility of the borohydride ligand that can adapt itself (and its hapticity) not only depending on the kind of other ancillary ligands but also on the nature of the rare earth element. Furthermore, it is now clearly established that the trisborohydrides can be advantageously employed as an alternative to the traditional other lanthanide precursors for the preparation of organolanthanide compounds.

Analytically, the data gathered in this manuscript clearly demonstrate that NMR spectroscopy has now become one of the essential tools to identify borohydride compounds. Indeed, and this goes against conventional wisdom, despite the paramagnetism of several lanthanides, most authors nowadays publish and give an interpretation of NMR data.

In terms of reactivity, borohydride compounds of the rare earths are today considered as a valuable option for polymerization reactions. They can initiate reactions towards polar monomers by themselves, and they have as well proved to reach at least the same level of efficiency as halides, as pre-catalysts towards non polar monomers. Alkylborohydrides have also been addressed in this review since they display a reactivity that can be found similar to that of tetrahydroborato compounds.

Regarding other fields of organic transformations, it is likely that subsequent efforts will be devoted in the next future to further develop innovative applications, in asymmetric catalysis for instance, through the use of specifically designed chiral lanthanide complexes containing a borohydride group.

The development of a chemistry based on borohydride derivatives of the rare earths is thus of the highest interest, and one can anticipates that important progresses and successes are yet to be achieved in this fascinating area.

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