Highly *trans*-Stereospecific Isoprene Polymerization by Neodymium Borohydrido Catalysts[†]

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ABSTRACT: Highly stereospecific polymerization of isoprene was achieved using borohydridoneodymium complexes. In combination with stoichiometric amounts of dialkylmagnesium, $Nd(BH_4)_3(THF)_3$ (**1**) and $Cp^{*\prime}Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^{*\prime} = C_5Me_4nPr$) afford very efficient catalysts. The activity reaches 37300 (g of polyisoprene/mol of Nd)/h. Half-lanthanidocene **2** gives rise to polyisoprene, 98.5% *trans*-regular, the highest content yet described for a homogeneous organometallic catalyst. NMR experiments argue for the formation of bimetallic $Nd(\mu\text{-}BH_4)Mg$ active species.

Introduction

Rare-earth complexes have been involved in a great number of reports dealing with conjugated diene polymerization since the 1980s.[1−4] Whereas *cis*-diene polymerization has been to a large extent more studied, *trans*-polymerization has seen a renewed interest only recently, after the pioneer work of Natta.[5] *trans*-1,4-Polydienes,[6] and particularly 1,4-*trans*-polyisoprene, produced naturally as gutta-percha rubber, appear well-suited for the elaboration of high-performance tires.[7] Moreover, *trans*-polymerization may also allow incorporation of α-olefin into a polydiene chain, affording high-value-added copolymers.[8−10]

Lanthanide-based isoprene polymerization catalysts are obtained by the reaction of a lanthanide precursor, selected among readily available carboxylates (versatates),[11] halides,[12,13] or alkoxides,[14] with an Al or Mg cocatalyst. *trans*-Sterospecificity is generally related to the use of Nd/Mg combinations,[15,16] but such catalysts do not allow living polymerization. This had just been achieved by means of an organometallic initiator, $(CMe_2C_5H_4)_2Sm(allyl)MgCl_2(ether)_2LiCl(ether)$,[17] which gives rise to polyisoprene with molecular weights that are well controlled, and quite narrow polydispersity indices (1.5−1.8). The polymer was also 95% *trans*-regular, and it was assumed that such stereospecificity could be related to steric hindrance around the samarium atom in the trimetallic catalyst.

Only recently, lanthanide trisborohydrides, $Ln(BH_4)_3(THF)_3$, have been used as valuable precursors for organometallic syntheses.[18,19] The presence of a borohydride ligand in the coordination sphere of a lanthanide generally ensures the formation of neutral rather than ionic "ate" species, and isolation of adducts containing less coordinated THF than in the chloro homologues. For instance, well-defined early half-lanthanidocenes have been isolated readily from $Ln(BH_4)_3(THF)_3$ (Ln = Sm, Nd) as starting materials.[18,20] These trisborohydrides behave like pseudohalides and display several advantages, in particular their higher solubility in apolar solvents, with respect to that of traditional $LnCl_3(THF)_3$. Also, they are easily available in one step from trichlorides, and the BH_4 ligand affords a typical pattern by ^1H NMR, allowing easier NMR analysis and monitoring, particularly in the case of paramagnetic lanthanides.

It was thus of interest to study the ability of lanthanide borohydrido complexes as precatalysts for isoprene polymerization. We present here a complete study, using inorganic $Nd(BH_4)_3(THF)_3$ (**1**) as an alternative to generic LnX_3 (X = Cl, OR, OCOR), and organometallic half-lanthanidocene $Cp^{*\prime}Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^{*\prime} = C_5Me_4nPr$), both associated with dialkylmagnesium derivatives, for such a purpose. Additional information about the molecular structure of active catalytic species is obtained from NMR experiments.

Results and Discussion

$Nd(BH_4)_3(THF)_3$[21] has been used as a single-component initiator for ϵ-caprolactone polymerization.[22,23] It behaves in that case like a hydride, via ring opening polymerization. In a preliminary paper, we reported that $Nd(BH_4)_3(THF)_3$ (**1**) is active as well toward isoprene, but only in the presence of specific alkylating agents, whereas no activity was observed with **1** alone.[24] The catalyst displayed *trans*-stereospecificity, and among the possible reasons for such a control, the formation of a sterically hindered bimetallic Nd−Mg species allowing only a single coordination of the diene was retained. It was thus of interest to study the influence of a bulky and electron-rich ligand in the coordination sphere of Nd for such catalysis, and we studied the ability of recently prepared $Cp^{*\prime}Nd(BH_4)_2(THF)_2$ (**2**) ($Cp^{*\prime} = C_5Me_4nPr$) for this purpose.[20] The synthesis of this complex, a rare example of monocyclopentadienyl derivatives of early lanthanides, had been achieved straightforwardly from $Nd(BH_4)_3(THF)_3$ according to eq

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Table 1. Selected Experiments of Isoprene Polymerization with Borohydride Complexes Activated with $Mg(nBu)_2$

run[a]	precatalyst	[Mg]/[Nd]	[I]/[Nd]	time (h)	yield (%)	activity[b] ((g_{pol}/mol_{Nd})/h)	$M_{n(exptl)}$[c]	MWD[d]	$M_{n(calcd)}$[e]
1[f]	1	1	600	2.75	69	10 200	27 600	1.57	28 100
2[f]	1	1	1000	2.75	63	15 600	43 000	1.79	42 800
3[f]	1	2	600	2.75	95	14 100	23 600	1.14	19 400
4[f]	1	3	1000	20	91	3100	15 000	1.50	20 600
5	2	0.9	120	2.75	>99	2900	9500	1.15	9100
6	2	0.9	520	2.75	75	9600	26 400	1.26	29 400
7	2	0.9	870	2	73	21 600	56 700	1.18	48 000
8	2	1.2	1180	2	93	37 300	50 500	1.16	62 100
9	2	1.2	520	2.75	89	11 400	29 100	1.21	26 200
10	2	1.7	120	2.75	91	2700	6600	1.27	4400
11	2	52	120	20	60	250	[h]		
12[g]	2	0.9	120	20	>99	400	13400	1.54	9100
13		$Mg(nBu)_2$	135	20	0				

[a] Toluene 0.5 mL; $T = 50$ °C; $Mg(nBu)_2$ (1.0 M, heptane solution). [b] Calculated by {[monomer]/[Nd]}(yield) × 68(time)$^{-1}$. [c] Average number molecular weight, determined by steric exclusion chromatography (THF, polystyrene standards). [d] M_w/M_n. [e] Calculated by {[monomer]/[Mg]}(yield) × 68. [f] Preliminary results, already published.[24] [g] Isoprene/1-hexene = 1/1. [h] Poorly soluble.

1, without the comproportionation usually observed with

$$Nd(BH_4)_3(THF)_3 + KCp^{*\prime} \xrightarrow[\text{2. pentane}]{\text{1. THF/toluene}} Cp^{*\prime}Nd(BH_4)_2(THF)_2 + KBH_4 \quad (1)$$

these elements, particularly with chloride complexes.[25] As expected, **2** combined with equivalent amounts of $Mg(nBu)_2$ displayed good efficiency along with higher *trans*-stereospecificity for isoprene polymerization.

Selected experiments are gathered in Table 1. Runs 1−4 and runs 5−12 were carried out starting, respectively, from **1** and **2**.

Activity. The monomer conversion is mostly quantitative in less than 3 h, depending on the monomer/catalyst ratio and the amount of cocatalyst. The average activity reaches 15 600 (g of polymer/mol of Nd)/h with **1** (run 3), which is in all cases higher than that obtained with neodymium trichloride based catalysts.[13,15,26] With **2** (run 8) a better activity, 37 300 (g of polymer/mol of Nd)/h, is observed, markedly higher than those mentioned in the literature for *trans*-specific similar polymerizations (ranging from 1000 to 10 000 (g of polyisoprene/mol of catalyst)/h). The activities of *cis*-processes, kinetically favored,[27] are 2 orders of magnitude higher.[28,29]

The higher activity of the catalytic system obtained with precatalyst **2** might be ascribed to the smaller quantity of coordinated THF than in **1**. However, a more convincing explanation is the presence of the electron-rich Cp*′ ligand, which favors $\eta^3-\eta^1$ allylic rearrangement, hence allowing faster chain migration.[30]

The **2**/$Mg(nBu)_2$ catalytic system appears less successful in the presence of a large excess of dialkylmagnesium (run 11); a very poorly soluble material, likely cross-linked, is obtained. Obviously the quasi-living character is no longer retained in such conditions. Competition between $Mg(nBu)_2$ and isoprene monomer during the coordination step may account for such a result. A blank test conducted with $Mg(nBu)_2$ alone did not afford any polymer in the same experimental conditions (run 13).

In the presence of a 50/50 isoprene/1-hexene mixture, no incorporation of olefin in the polymer occurred (pure polyisoprene is quantitatively obtained, run 12), and **2**/$Mg(nBu)_2$ catalyst is inactive as well toward 1-hexene homopolymerization in our experimental conditions. Actually, the very few lanthanide catalysts allowing α-olefin polymerization all consist of electronic-deficient complexes.[31] Such a finding may account here for a too important electronic donor environment in $Cp^{*\prime}Nd(BH_4)_2(THF)_2$/$Mg(nBu)_2$ despite the presence of only one cyclopentadienyl ligand.

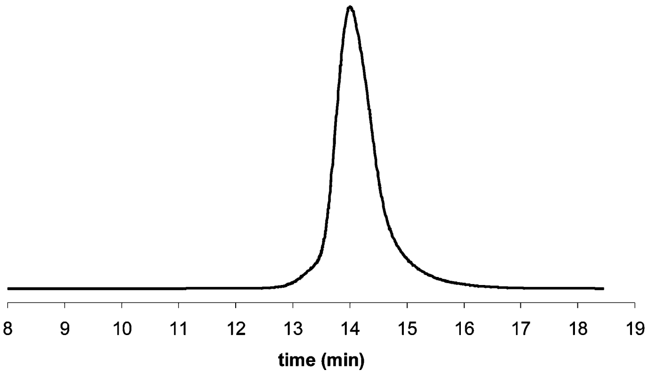


Figure 1. Steric exclusion chromatography trace showing the monomodal character of polyisoprene obtained with $Cp^{*\prime}Nd(BH_4)_2(THF)_2$/$Mg(nBu)_2$ (run 5).

Table 2. Microstructure of Polyisoprenes Synthesized with Borohydrido Catalysts

run	precatalyst[a]	[Mg]/[Nd]	[*trans*-1,4][b] (%)	[*cis*-1,4][b] (%)	[3,4][b] (%)
1[c]	1	1	95.1	3.2	1.7
2[c]	1	1	95.3	3.1	1.6
3[c]	1	2	96.2	1.8	2.0
4[c]	1	3	95.5	2.4	2.1
5	2	0.9	98.5		1.5
6	2	0.9	98.4		1.6
7	2	0.9	98.3		1.7
8	2	1.2	98.1		1.9
9	2	1.2	98.0		2.0
10	2	1.7	96.2	1.0	2.8
11	2	52	57.7	1.0	41.3
12	2	0.9	97.2	1.4	1.4

[a] $Nd(BH_4)_3(THF)_3$ (**1**), $Cp^{*\prime}Nd(BH_4)_2(THF)_2$ (**2**). [b] Determined by ^1H NMR. [c] Preliminary results, already published.[24]

Macromolecular Data. As reported in Table 1, both catalysts display good control of the polymerization process, i.e., M_n values close to theoretical ones, and molecular weight distributions typical of a single-site mechanism. Calculated molecular weights take into account the number of equivalents of Mg cocatalyst added, i.e., the number of chains growing on the metal. SEC analyses were performed against polystyrene standards, but we established that such experimental values were close to the real ones for *trans*-polyisoprenes, since they were in accordance with values

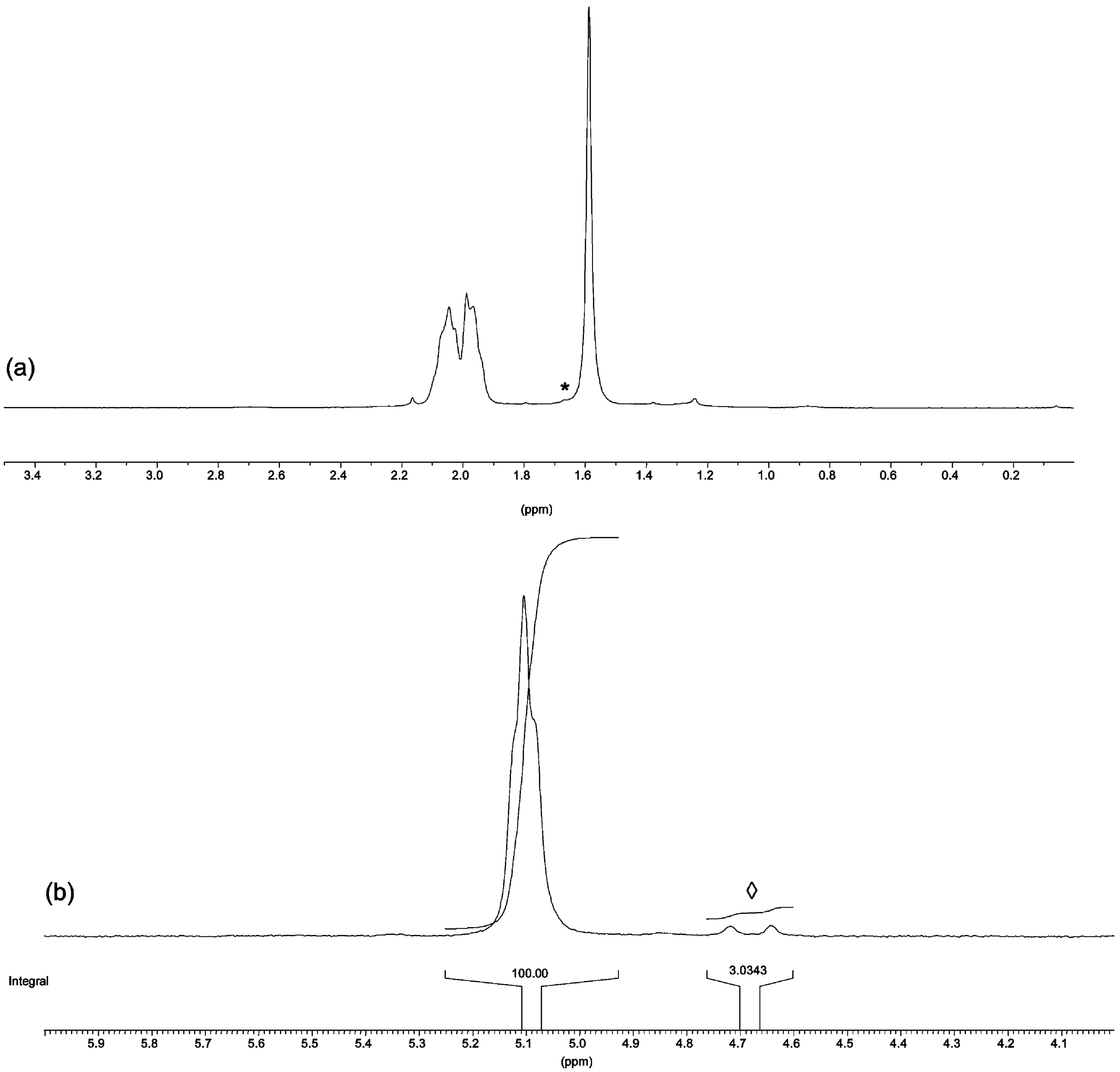


Figure 2. ^1H NMR ($CDCl_3$) spectrum of 98.5% *trans*-polyisoprene, aliphatic region (a), olefinic region (b), showing traces of *cis*-polyisoprene (*) and 3,4-polyisoprene (◊) defects (run 6).

determined by ^1H NMR for allyl-terminated samples.[8,32] With precatalyst **1**, each equivalent of dialkylmagnesium gives rise to initiation of one single growing chain (runs 1–4). In the presence of two (run 3) or three (run 4) Mg atoms per Nd, two and three chains are initiated on the lanthanide metal, respectively. Addition of a slight stoichiometric default (runs 5–7) or excess (runs 8 and 9) of dialkylmagnesium to precatalyst **2** affords molecular weights close to the expected ones. All these results are in accordance with a quasi-living process, indicating that (i) only one alkyl group per MgR_2 is transferred from the Mg atom to the Nd one to create an active bond and initiate polymerization, and (ii) then most of the Nd–R formed species are active. Such behavior features a main difference with the well-known double-alkyl-transfer reaction in lanthanide/MgR_2 dual-component catalysts.[33]

SEC analysis shows monomodal profiles (in very few cases a slight shoulder at high M_n values could be observed). A typical chromatogram (run 5) is displayed in Figure 1. Especially with a catalyst prepared from **2** (runs 5–10), M_w/M_n values are very close to the ideal value of 1: they are in the 1.15–1.3 range, which confirms the single-site catalyst character deduced from molecular weights.

Upon addition of an excess of magnesium cocatalyst to **2** (1.7 Mg atoms/Nd, run 10), the experimental M_n value (6600) remains higher than the calculated one (4400) for a monoalkylation (i.e., one active R per MgR_2) with 1.7 Mg atoms/Nd. Since double alkylation (i.e., both R groups of MgR_2 active) of Nd by $Mg(n\text{Bu})_2$ should provide molecular weights that would be significantly lower than 4400, this occurrence can be discarded.

Stereospecificity. Both catalysts are *trans*-stereospecific, as long as the amount of $Mg(n\text{Bu})_2$ remains stoichiometric (Table 2). In the presence of 1.7 equiv of dialkylmagnesium per Nd, the *trans*-stereoregularity falls to 96.2% (run 10), whereas no specificity remains when a large excess of cocatalyst is used (run 11), indicating a different polymerization mechanism in the latter case.

$Cp^{*\prime}Nd(BH_4)_2(THF)_2/Mg(n\text{Bu})_2$ affords up to 98.5% *trans*-steroregularity. To our knowledge, such a *trans*-content is the highest one obtained with a homogeneous single-site catalyst. It is noteworthy that the rate of defects with **2** as a precatalyst consists of 3,4-units only

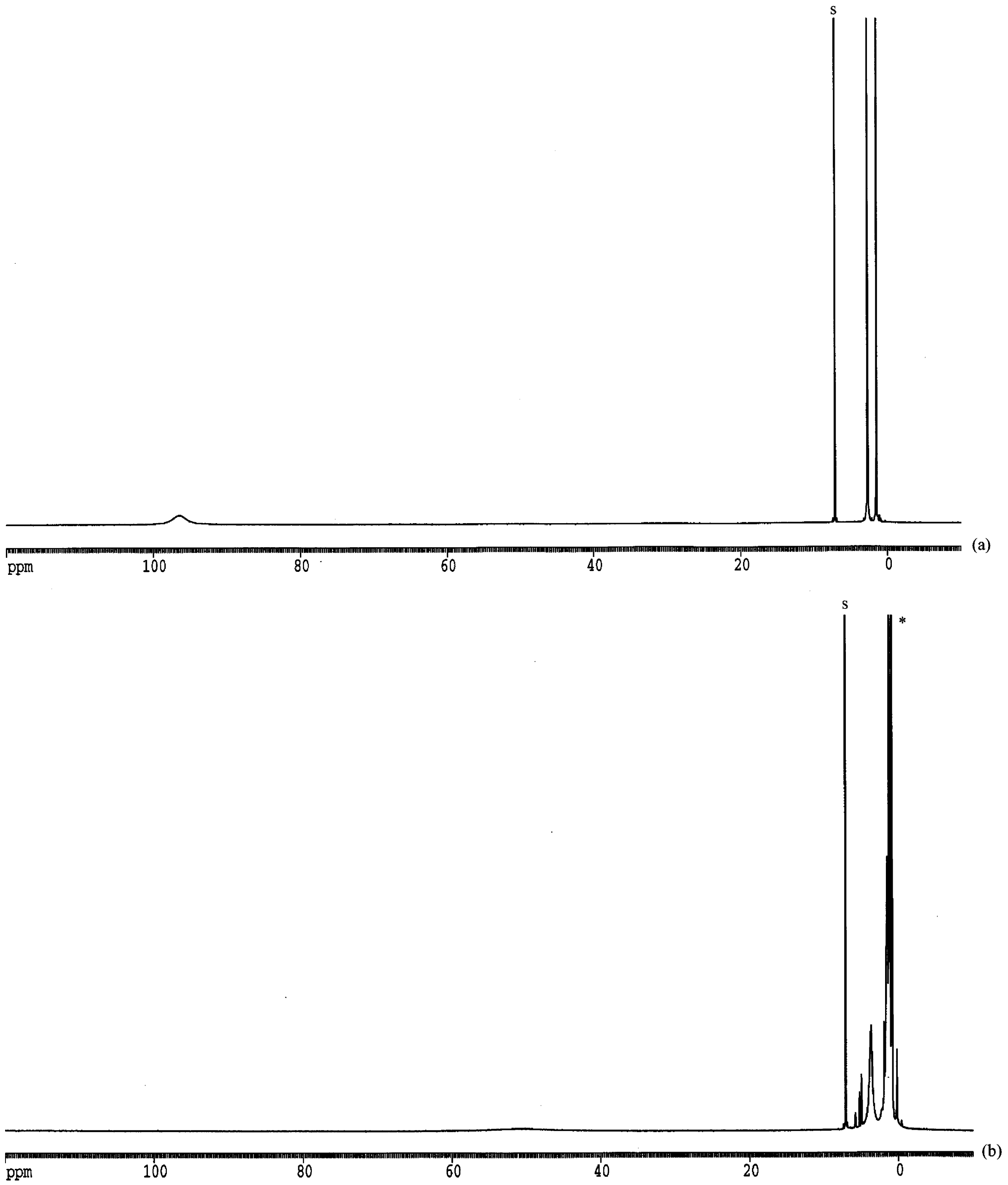


Figure 3. ^{1}H NMR (C_6D_6, 300 K) spectrum of $Nd(BH_4)_3(THF)_3$ alone (a) and after addition of 1 equiv of $Mg(nBu)_2$ (b) (s, C_6D_5H; *, heptane).

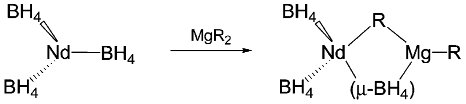
(*cis*-1,4-polyisoprene was detected as traces). A typical ^{1}H NMR spectrum is displayed in Figure 2 (run 6). The DSC thermogram of 98.5% *trans*-polyisoprene (run 5) exhibits a glass transition at $T_g = -71$ °C. The polymer is highly crystalline as expected ($T_m = 47$ °C, $\Delta H = 43$ J g^{-1}), in accordance with the low rate of defects of the polymer.

The microstructure of polyisoprene is 1,4-*trans* at more than 95% with the $Nd(BH_4)_3(THF)_3/Mg(nBu)_2$ system (runs 1−4). Small quantities of 1,4-*cis*- and 3,4-motives (ca. 2−3% each) are also present.

It is generally admitted that *trans*-polymerization can be related to single coordination of the diene monomer to the metal,[27,34,35] when double coordination of the diene is required to afford *cis*-polydiene. According to a recent theoretical study related to hindered permethyllanthanidocene catalysts, the coordination step of the monomer is likely dependent on the steric hindrance around the metal, and as a matter of fact, single η^2 coordination may be preferred.[36] Such an assumption was also made by Spitz and co-workers, who polymerized butadiene with neodymocene catalysts.[37] This feature must be specially taken into consideration in the case of isoprene polymerization; it was invoked to account for the 95% *trans*-specificity obtained with the already mentioned trimetallic ansasamarocene.[17]

One can note that the small amount of 1,4-*cis*-polymer obtained with **1**/$Mg(nBu)_2$ disappears when **1** is replaced by **2**; the bulky $Cp^{*\prime}$ totally prevents η^4 coordination of isoprene to the neodymium atom. Similarly, although

Scheme 1. Formation of the Active Bimetallic Species Nd(μ-BH$_4$)Mg upon Addition of Dialkylmagnesium to Nd(BH$_4$)$_3$(THF)$_3$[a]



[a] Solvent molecules are omitted for clarity.

the *trans*-stereoregularity falls to 96.2% with a Mg/Nd ratio of 1.7 (run 10), the microstructure reveals the presence of a very low quantity of *cis*-polyisoprene (1.0%), which agrees well with a disfavored η^4 coordination, likely due to competition between the monomer and cocatalyst.

Considering the well-known bridging ability of the borohydride ligand in lanthanide chemistry,[20] the *trans*-stereospecificity can be tentatively correlated to the formation of sterically hindered borohydrido-bridged bimetallic Nd/Mg species. Bimetallic Nd/Mg associations have been frequently observed[38–40] or postulated[15,41] when a magnesium derivative is reacted with a lanthanide complex. It was therefore assumed that bridging Ln(μ-BH$_4$)Mg species could be formed, and NMR experiments were undertaken to focus on that point.

^{1}H NMR Experiments. For clarity, the cyclopentadienyl ligand exhibiting numerous signals, these experiments were first conducted with **1**. Figure 3 displays the ^{1}H NMR spectrum of **1** alone (a) and immediately after addition of 1 equiv of Mg(nBu)$_2$ (1.6 M, heptane) (b), both recorded at 300 K. The BH$_4$ signal is shifted from $\delta = 98$ ppm to $\delta =$ ca. 50 ppm. In addition, this new resonance is now very broad, accounting for dynamic exchange between different borohydride groups.

We assume that, thanks to the bridging ability of the BH$_4$ group, formation of a Nd(μ-BH$_4$)(μ-R)MgR bimetallic species may occur, which corresponds well to the monoalkylation deduced from macromolecular data. A possible molecular structure is depicted in Scheme 1;

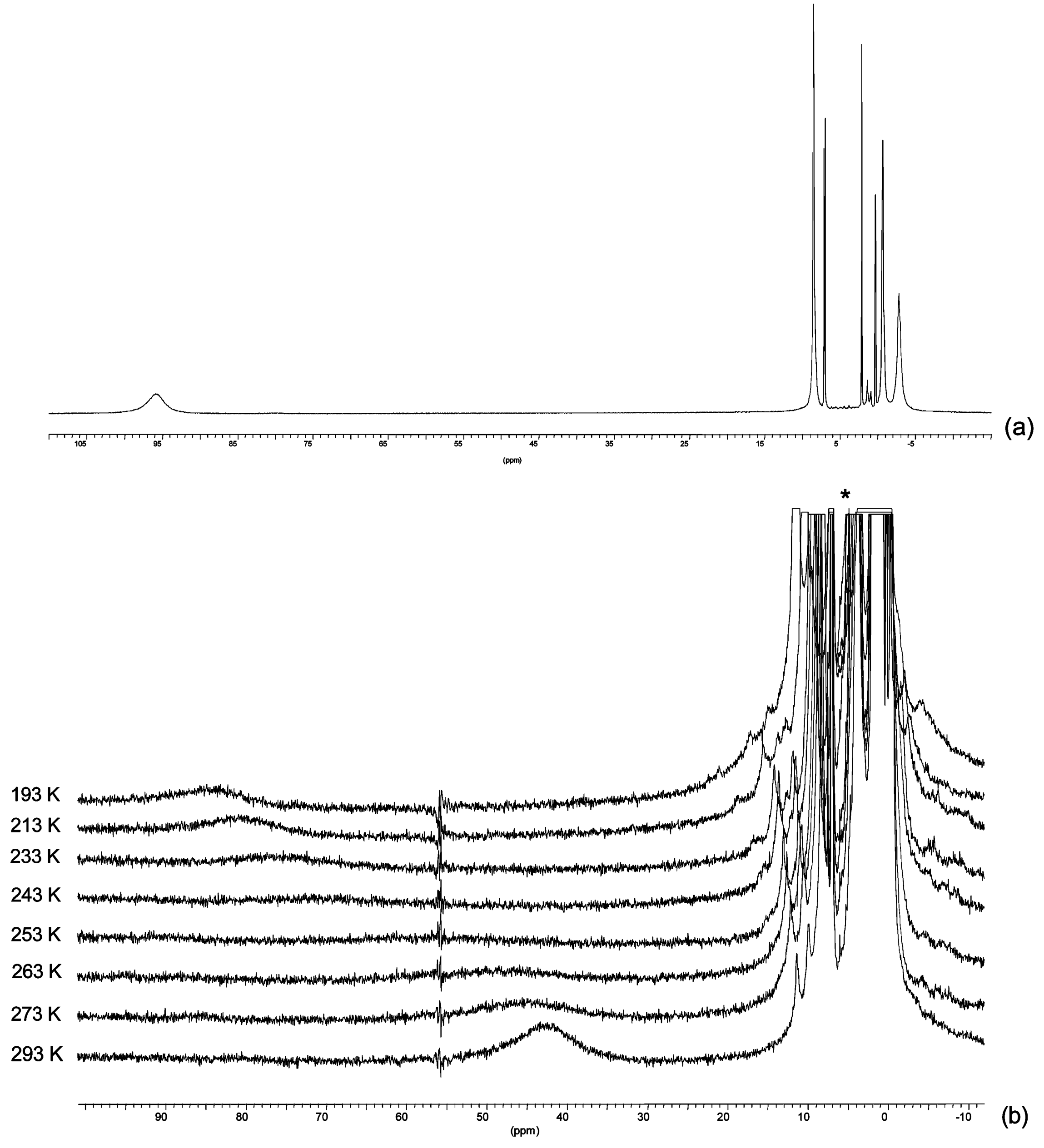
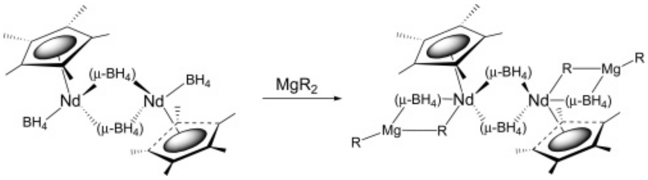


Figure 4. ^{1}H NMR (C$_7$D$_8$) spectrum of Cp*Nd(BH$_4$)$_2$(THF)$_2$ alone (300 K) (a) and after addition of 1 equiv of BEM, recorded at different temperatures (range 193−293 K) (b) (*, hexanes).

Scheme 2. Formation of the Active Bimetallic Species Cp*Nd(μ-BH$_4$)Mg upon Addition of Dialkylmagnesium to Cp*Nd(BH$_4$)$_2$(THF)$_2$[a]



[a] Solvent molecules are omitted for clarity.

the neodymium atom is surrounded by two terminal BH$_4$ groups (Nd(BH$_4$)$_3$(THF)$_3$ is a monomer in the solid state),[21] with the third one bridging to the MgR moiety, leading to a ^{1}H NMR spectrum showing an average BH$_4$ resonance (Figure 3b). No coalescence could be observed at low temperature, indicating fast exchange on the NMR time scale.

Similar experiments were carried out with half-neodymocene Cp*Nd(BH$_4$)$_2$(THF)$_2$ (**3**) (Cp* = C$_5$Me$_5$, giving only one signal for the Me groups, the electron donating ability being similar to that of **2**). One equivalent of butylethylmagnesium (BEM; 20% in hexanes) is added, and a blue precipitate that is partially soluble is formed. Figure 4 displays the ^{1}H NMR spectrum of **3** (a), and that of the same complex after addition of BEM (b). The initial BH$_4$ signal (δ = 96 ppm (a)) is shifted to ca. 43 ppm at 293 K, which is an uncommonly low value for a borohydrido-half-neodymocene ((C$_5$*i*Pr$_4$H)-Nd(BH$_4$)$_2$(THF); δ = 114 ppm[18]). The same as for **1**, the BH$_4$ resonance is very broad, typical of a dynamic exchange between different borohydride groups. A variable-temperature NMR study was undertaken (Figure 4b); this time coalescence occurs, at 253 K, and one BH$_4$ resonance is clearly depicted since 213 K (the second one is probably masked in the diamagnetic zone). Dynamic exchange between BH$_4$ groups, slower than with **1**, arises from the presence of the bulky Cp* in the coordination sphere of the neodymium atom.

In Scheme 2 is depicted a possible bimetallic Nd(μ-BH$_4$)Mg compound resulting from the reaction of **3**, represented under associated form,[42] with 1 equiv of dialkylmagnesium. The Nd atom bears two different BH$_4$ ligands: a pure Nd(BH$_4$) one, and the other one bridging to the Mg moiety. Association of that Nd/Mg compound, likely in an oligomeric form, may account for the poor solubility observed in the NMR solvent. Note however that, in isoprene medium, the in situ formed Nd/Mg catalyst is perfectly soluble.

Comparison with Similar Dual-Component Catalysts. In Table 3 are compared the performances of catalysts prepared from **1** and **2** to the results obtained with NdCl$_3$(THF)$_3$, Cp*Nd(BH$_4$)$_2$(THF)$_2$ (**3**), heteroleptic {Cp*′[C(*p*-tol)NMe]$_2$Nd(BH$_4$)}$_2$ (**4**),[43] and (C$_5$*i*Pr$_4$H)Sm-(BH$_4$)$_2$(THF) (**5**)[18] in analogous conditions.

All complexes show a high rate of *trans*-specificity. Catalyst prepared from **2** remains the most active and is the most *trans*-stereospecific, closely followed by **4**, the latter showing only a moderate activity, correlated with the high steric hindrance due to the diketiminate ligand.[44] We could not obtain, with **3**, a conversion and an activity as high as with **2**, though the latter provides also more than 98% *trans*-regular polymer. It is noteworthy that the hyperbulky C$_5$*i*Pr$_4$H ligand in **5** is not as efficient as C$_5$Me$_4$*n*Pr to ensure the steric hindrance, allowing the *trans*-stereospecificity. But in the case of **5**, the cocatalyst used was *n*BuLi.

We observed that combination of NdCl$_3$(THF)$_3$ with 1 equiv of Mg(*n*Bu)$_2$ affords a quite *trans*-stereospecific catalyst of low activity. Similar behavior was previously reported for the NdCl$_3$(TBP)$_3$/MgR$_2$ system (TBP = tributyl phosphate).[13,15] To improve the activity of NdCl$_3$-based catalysts, Porri added (allyl)MgCl to NdCl$_3$(THF)$_3$–he obtained in situ prepared allyl-lanthanide complexes—arguing that σ-Ln−C compounds were too unstable.[45] The enhancement of activity observed for Nd(BH$_4$)$_3$(THF)$_3$/Mg(*n*Bu)$_2$ against NdCl$_3$-(THF)$_3$/Mg(*n*Bu)$_2$ may be here attributed to the higher solubility of the trisborohydride. Nd(BH$_4$)$_3$(THF)$_3$, much more easily available and handled, appears then as a valuable alternative to alkyl- and allyllanthanide catalysts. The use of MgR$_2$ as alkylating reagent is required to afford *trans*-polyisoprene, whereas in combination with *n*BuLi or AlEt$_3$, Nd(BH$_4$)$_3$(THF)$_3$ gives rise to the formation of irregular polyisoprene.[24]

The low activity of **4**/Mg(*n*Bu)$_2$ might be ascribed to the high steric environment around the metal,[44] leading to a probable competition between internal and monomer coordination. Also, molecular weight distribution (2.01) shows that the process is not as controlled as with **2**/Mg(*n*Bu)$_2$.

Experiments conducted with Sm(BH$_4$)$_3$(THF)$_3$ were totally unsuccessful irrespective of the alkylating agent used. This is a rare difference of catalytic behavior between Nd and Sm, both belonging to the same early lanthanide group. Complex **5** is however an example of a borohydrido complex of samarium (and the sole one reported) that provides as well good activity and 95% *trans*-content.

Finally, **2**/Mg(*n*Bu)$_2$ is clearly the first catalytic system to simultaneously satisfy requirements of high conversion, well-controlled and narrow distribution of macromolecular weights, and high 1,4-*trans*-content. The half-lanthanidocene framework appears particularly well-suited for the efficient *trans*-polymerization of conjugated dienes.

Table 3. Influence of the Molecular Structure of the Catalyst for Isoprene *trans*-Polymerization

catalytic system[a]	[I]/[Nd]	activity ((g$_{pol}$/mol$_{Nd}$)/h)	M_n	MWD	*trans*-specificity (%)	ref
1/1 Mg(*n*Bu)$_2$	600	15 600	43 000	1.79	95.3	24
2/1.2 Mg(*n*Bu)$_2$	1180	37 300	50 500	1.16	98.1	this work
2/0.9 Mg(*n*Bu)$_2$	120	2900	9500	1.15	98.5	this work
3/1.2 Mg(*n*Bu)$_2$	160	700	9700	1.22	98.2	this work
4/1 Mg(*n*Bu)$_2$	600	1100	15 400	2.01	98.4	43
5/1.5 *n*BuLi	1000	13 000	90 000	1.5	95.0	18
NdCl$_3$(THF)$_3$/1 Mg(*n*Bu)$_2$	460	340			89.5	24

[a] Nd(BH$_4$)$_3$(THF)$_3$ (**1**), Cp*′Nd(BH$_4$)$_2$(THF)$_2$ (**2**), Cp*Nd(BH$_4$)$_2$(THF)$_2$ (**3**), {Cp*′[C(*p*-tol)NMe]$_2$Nd(BH$_4$)}$_2$ (**4**), (C$_5$*i*Pr$_4$H)Sm(BH$_4$)$_2$(THF) (**5**).

Conclusion

Borohydrido complexes of neodymium have been found to be very efficient toward isoprene polymerization catalysis in the presence of equimolar amounts of dialkylmagnesium cocatalyst. $Cp^{*\prime}Nd(BH_4)_2(THF)_2/Mg(nBu)_2$ and $Nd(BH_4)_3(THF)_3/Mg(nBu)_2$ are both *trans*-stereospecific, up to 98.5% with the former catalyst. As far as we know, this is the best result yet obtained with an organometallic catalyst. Quasi-living character is observed, with extremely narrow polydispersity and formation of polymers whose molecular weight corresponds well to the monomer/catalyst ratios. Monomodal distribution is typical of a single-site character. *trans*-Stereospecific character of these catalysts is tentatively attributed to the formation of $Nd(\mu\text{-}BH_4)Mg$ bridging active species on the basis of ^1H NMR experiments. Further studies are in progress.

Experimental Section

Materials. The solvents were dried on sodium−benzophenone ketyl and deoxygenated by distillation immediately before use. All solids were handled in an argon-filled glovebox (Jacomex). Isoprene (99%, Aldrich) was dried first on calcium hydride and then on 3A molecular sieves and distilled just before use. BuLi (1.6 M, hexane) and $Mg(nBu)_2$ (1.0 M, heptane) were purchased from Aldrich. BEM (20%, hexanes) was purchased from Texas Alkyl. $Nd(BH_4)_3(THF)_3$,[21] $Cp^*Nd(BH_4)_2(THF)_2$,[19] and $Cp^{*\prime}Nd(BH_4)_2(THF)_2$[20] were synthesized from $NdCl_3(THF)_3$[21] as reported in the literature.

Polymerization Procedure. In a typical polymerization (run 5 is given as an example), 20 mg (0.041 mmol) of catalyst precursor **2** was weighed in a glovebox, in a 20 mL flask. Dry toluene (0.5 mL), $Mg(nBu)_2$ (0.036 mL, as a 1.0 M solution in heptane), and freshly distilled isoprene (0.5 mL, 5 mmol) were added in this order via syringes into the flask. The reaction mixture was magnetically stirred at 50 °C for 2 h and 45 min. The polymerization reaction was terminated as follows: the viscous mixture was diluted in standard toluene (1 mL), and the resulting solution was poured into ethanol. The white polymer was filtered out, and dried under vacuum for 24 h. Yield: 338 mg (99.3%). SEC: $M_n = 9500$, PDI = 1.15. ^1H NMR: 98.5% *trans*-1,4, 1.5% 3,4.

Measurements. ^1H and ^{13}C NMR were recorded on a Bruker Avance 300 at 300 K in $CDCl_3$ solutions. Steric exclusion chromatography analyses were carried out in THF as eluent at 20 °C (1 mL/min) using a Gynkotek P580A apparatus equipped with two PLgel 5 μm MIXED-C 300 × 7.5 mm Polymer-Labs divinylbenzene columns (range 200−200 000 000) and with a PLgel 5 μm 300 × 7.5 mm Guard column, and an IOTA2 refractive index detector. Absolute values of molecular weights were calculated against polystyrene standards, without correction due to the lack of Mark−Houwink constants for *trans*-regular polyisoprene in the literature. differential scanning calorimetry (DSC) measurements were performed on a TA Instruments 2920 DSC apparatus. An indium standard was used for calibration. Samples of ca. 10 mg were scanned under a nitrogen flow (60 $mL\cdot min^{-1}$, ramp rate 10 $°C\cdot min^{-1}$). Temperatures were determined on the second scan to ensure identical thermal histories, as the inflection point of the corresponding heat capacity jump (T_g), and as the endothermic maximum (T_m).

NMR Experiments. In a typical experiment, precatalyst **1** (10 mg) was weighed inside the glovebox, in an NMR tube equipped with a stopcock (Young). The solvent was added (C_6D_6 or C_7D_8 for variable-temperature analysis), and then the desired amount of dialkylmagnesium (heptane or hexanes solution). The blue solution turned to yellow-green and then yellow-brown within 30 min. A small amount (less than 10%) of olefin was present in the ^1H NMR spectrum. After 24 h at room temperature, the tube's contents were brown, and NMR analysis showed olefins as the major products. In the case of precatalyst **2**, progressive formation of a slightly soluble blue compound was observed. No olefins were detected in the spectrum, even after several hours.

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