Tuning the catalytic properties of rare earth borohydrides for the polymerisation of isoprene

Fanny Bonnet,[*a,b,c,d] **Chloe E. Jones,**[a,b,c,d] **Sanaa Semlali,**[a,b,c,d]**, Marc Bria,**[a,e] **Pascal Roussel,**[a,b,c,d] **Marc Visseaux,**[* a,b,c,d] **and Polly L. Arnold** [f]

[a] Univ. Lille Nord de France, F-5900 Lille, France

[b] ENSCL, UCCS, CCM, F-59652 Villeneuve d'Ascq, France

[c] USTL, UCCS, CCM, F-59655 Villeneuve d'Ascq, France

[d] CNRS, UMR8181, F-59652 Villeneuve d'Ascq, France

[e] USTL, CCM RMN, F-59000 Villeneuve d'Ascq, France

[f] School of Chemistry, University of Edinburgh, U.K.

E-mail : marc.visseaux@ensc-lille.fr or fanny.bonnet@ensc-lille.fr

Abstract.

Previous results obtained for the *cis*-polymerisation of isoprene with scandium half-sandwich complex $Cp*Sc(BH_4)_2(THF)$ **1a** were extended to its neodymium analog. The X-ray structure of the already reported neodymium monomer compound $Cp*Nd(BH_4)_2(THF)_2$ **1b** is presented. $Cp*Nd(BH_4)_2(THF)_2/[CPh_3][B(C_6F_5)_4]/Al(^iBu)_3$ catalytic system was found to be very active and stereoselective towards isoprene polymerisation, leading to highly 1,4-*cis* polyisoprene up to 92%. The effect on isoprene polymerisation of the addition of a NHC molecule to $Cp*Ln(BH_4)_2(THF)_n$ pre-catalyst ($Cp*= \eta^5-C_5Me_5$, Ln = Sc, n = 1, **1a**; Nd, n = 2, **1b**; Sm, n = 2, **1c**) or to a trisborohydride $Ln(BH_4)_3(THF)_n$ (Ln = Sc, n = 1.5, **2a**; Nd, n = 3, **2b**; Sm, n = 3, **2c**) was also studied. Several NHC ligands were assessed: the classical [1-$C\{(N^tBuCH)\}_2$] (L^1) and functional N-heterocyclic carbenes, two amino-tethered $HNBu^tCH_2CH_2[1-C\{N(CHCH)NR\}]$ (HL^{2-R}) (R = ^tBu, Mes (Mes = 2,4,6-Me_3-C_6H_2)) and the hydroxyl-tethered $HOCMe_2CH_2[1-C\{N(CHCH)N^iPr\}]$ (HL^3). Neodymium-based complex $(L^{2-tBu})Nd(BH_4)_2(THF)_2$ **3** could be isolated and characterized. With some of the catalytic combinations tested, the introduction of the NHC ligand in the coordination sphere of the complex induces a switch of the stereoselectivity of the resulting polymer. Scandium complex **2a**, which produces mainly 1,4-*cis* polyisoprene when associated to a borate activator and

aluminum alkyl, leads to 1,4-*trans* polymer up to 94% regular when HL[2-tBu] carbene is added to the same reaction mixture. This result is the only example of highly *trans*-polyisoprene synthesized with a scandium based catalyst. Coordination of the carbene moiety to the rare earth centre is confirmed by NMR studies on paramagnetic neodymium pre-catalysts.

Introduction.

Olefin based elastomers are of primary industrial interest as they are used as high-performance materials in high-tech sectors such as tires, sport accessories or adhesives.[1] Among them, *cis*-1,4- and *trans*-1,4-polyisoprenes both exist as natural elastomers issued from Hevea Brasiliensis and Gutta Percha, respectively. They can alternatively be synthesized industrially at high scale by polymerisation of isoprene using stereoselective Ziegler-Natta type polymerisation catalysts.[2,3] In this context, half-sandwich and monosubstituted derivatives of the rare earths have proved to behave as highly valuable catalysts towards the controlled (co)polymerization of conjugated dienes, as highlighted by recent reports.[4-14] Many very efficient catalytic systems suffer however from one main drawback that may hinder their development: the active species are generally based on organometallic derivatives containing sophisticated ligands, which require upstream several synthetic steps for their elaboration.[15] In the search for alternative catalysts that would involve compounds requiring effortless syntheses, we recently demonstrated that the simple borohydrido half sandwich scandium complex Cp*Sc(BH$_4$)$_2$(THF) (**1a**) (Cp* = C$_5$Me$_5$, THF = tetrahydrofuran) is a precatalyst for very active catalytic mixtures towards isoprene *cis*-polymerization.[16] Actually, whereas the patents literature describes efficient catalysts based on paramagnetic neodymium developed by the industry, many catalysts reported in the academic literature are made of scandium, or also lutetium, both diamagnetic, which is an advantage for organometallic syntheses and characterisations, but these latter metals are among the most expensive rare earths. It is thus desirable to identify analogs containing less costly rare earths elements, notably those which belong to the "early" lanthanides family, like neodymium, for use in the area of the controlled polymerization of conjugated dienes. Then, the significant development of their catalytic performances has to be undertaken, and preferably in a simple manner.

In order to improve the efficiency of our systems with this plan in mind, we aimed to examine the influence of the direct addition of a neutral ligand towards the polymerization of isoprene, regarding activity, selectivity, and control of molecular weights. Traditional strategies to switch the regio and the stereoselectivity in conjugated diene polymerization involve adding

alkylaluminum co-catalysts.[17-18] An alternative approach, similar to that of Mountford *et al.*,[19] and Gade *et al.*,[20] and one that is more amenable to rapid catalyst screening, is the use of additional donor ligands. N-heterocyclic carbenes (NHC's) are well suited to the chemistry of rare earths [21,22]and they may stabilize active and/or selective polymerization catalysts from the larger rare earth metals. To our knowledge, the effect of the addition of such ligands has not been assessed in rare earths mediated conjugated dienes polymerization catalysis yet.

We describe in this work our results in isoprene polymerization using simple rare earth based borohydrido catalysts, according to two different strategies. The first part is an extension of our previous results obtained with $Cp*Sc(BH_4)_2(THF)$ (**1a**)/borate/$Al(^iBu)_3$ combinations, to the neodymium analog $Cp*Nd(BH_4)_2(THF)_2$ (**1b**).[16] Since the X-Ray structure of this latter compound was unprecedented, we describe it , as well as this of the hexamer isolated in non polar solvent, in a preliminary section. The second part shows the effect on isoprene polymerisation of the addition of a NHC molecule to bisborohydrides $Cp*Ln(BH_4)_2(THF)_n$ (Ln = Sc, n = 1, **1a**; Nd, n = 2, **1b**; Sm, n = 2, **1c**) and to trisborohydrides $Ln(BH_4)_3(THF)_n$ (Ln = Sc, n = 1.5, **2a**; Nd, n = 3, **2b**; Sm, n = 3, **2c**) as pre-catalysts. Complex $(L^{2-tBu})Nd(BH_4)_2(THF)_2$ **3** bearing $N^tBuCH_2CH_2[1-C\{N(CHCH)N^tBu\}]$ NHC ligand (L^{2-tBu}) was isolated and characterized.

Acronym	Compound
BEM	^nBuEtMg
DBM	$^nBu_2Mg$
TB	$[CPh_3][B(C_6F_5)_4]$
HNB	$[HNMe_2Ph][B(C_6F_5)_4]$
THF	Tetrahydrofuran
DCM	Dichloromethane
CLB	Chlorobenzene
L^1	$1-C\{(N^tBuCH)\}_2$
HL^{2-R} (R = ^tBu, Mes; Mes = 2,4,6-Me$_3$-C$_6$H$_2$)	$HN^tBuCH_2CH_2[1-C\{N(CHCH)NR\}]$
HL^3	$HOCMe_2CH_2[1-C\{N(CHCH)N^iPr\}]$

Results and discussion.

*Structural determination of Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b**.*

Surprisingly, well-defined half-sandwich complexes of the early 4f-metals are rather scarce. Presumably due to their propensity to easily undergo disproportionation, only a small number among them have been structurally described.[23,24] Cp^{R}LnX$_2$ (Cp^R = cyclopentadienyl ligand) compounds can eventually be isolated if the X ligand is sufficiently bulky, for example in (C$_5$H$_5$)La(MBMP)(THF)$_3$ (MBMP = 2,2-methylene-bis(6-*ter*-butyl-4-methyl-phenolate)[25] or Cp*CeX$_2$ (X = 2,6-Di-*ter*-butylphenolate, N(SiMe$_3$)$_2$, CH(SiMe$_3$)$_2$),[26] Cp*LaCH(SiMe$_3$)$_2$,[27] and more recently in Cp*Ln[AlMe$_4$]$_2$ (Ln = La, Nd).[28] When they do not undergo disproportionation, half-sandwich complexes often adopt a cluster or oligomeric arrangement.[29] This was often the case in the borohydride series.[30] However, monoCp borohydrido complexes could be isolated as discrete monomers with bulky Cp^{4i} (Cp^{4i} = η^5-C$_5$H^{i}Pr$_4$).[31] In the Cp* series, the scandium compound was the only one to be structurally characterized,[16] while with larger lanthanides, anionic "ate" [Cp^{R}Nd(BH$_4$)$_3$]$_2$[Mg(THF)$_6$] complexes were also prepared.[32]

Complex Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** was first synthesized by Ephritikhine *et al.* and its molecular structure deduced from ^{1}H NMR, IR spectroscopy, and elemental analysis.[33] We have been able to isolate X-Ray quality crystals of this compound by recrystallization from THF/pentane mixtures and we resolved its molecular structure for the first time (figure 1). In addition and not surprisingly, we noticed that when this **1b** compound is heated in a toluene or a benzene atmosphere, crystals of an unsolvated hexamer [Cp*Nd(BH$_4$)$_2$]$_6$ **1b'**† are obtained. A similar behaviour had been previously observed in the C$_5$Me$_4$^{n}Pr series.[30] Compound **1b** crystallizes as a bis-THF adduct in the P2$_1$/n space group with four molecules in the unit cell. The BH$_4$ ligands are terminal trihapto, whereas previously reported FTIR spectroscopic data indicated the presence of both tridentate and bidentate BH$_4$ ligands.[33] It is likely that the compound isolated by Ephritikhine was a mix between the monomer and oligomeric forms of Cp*Nd(BH$_4$)$_2$(THF)$_x$, in which the [Cp*Nd] units are linked through borohydride bridges. Due to the larger ionic radius of neodymium *vs.* scandium, two THF molecules are necessary to complete the coordination sphere of the metal in the monomeric form, as expected from previous analyses. For comparison, the scandium analog **1a** is a mono-THF adduct in the solid-state, with both borohydride groups acting as tridentate ligands, in accordance with short Sc–B bond lengths (2.345 Å).[16] X-ray crystallographic analysis revealed that both

4

borohydride groups in **1b** act as tridentate ligands, in connection with short Nd–B bond distances in the range 2.648-2.663 Å. By comparison, such distances lay in the range 2.596-3.050 Å in [Cp*Nd(BH$_4$)$_2$]$_6$ hexamer **1b'** (see ESI [‡]). The centroid (Cp*)-Nd distance is 2.43 Å as well as in the "ate" complex [Cp*Nd(BH$_4$)$_3$]$^-$ [32] and in the range 2.442-2.502 Å in [Cp*Nd(BH$_4$)$_2$]$_6$ **1b'** (see ESI [‡]).
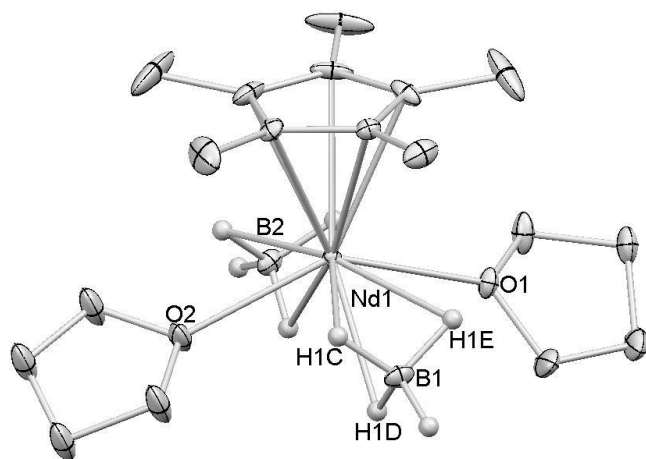
Figure 1. Displacement ellipsoid plot of Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** (30%). Only H-atoms on the borohydride ligand are represented. Selected bong lengths (Å) and angles (°): Nd1-B1 = 2.6486(18); Nd1-B2 = 2.6630(18); Nd1-H1C = 2.428; Nd1-H1D = 2.449; Nd1-H1E = 2.458; Nd1-O1 = 2.5460(11); Nd1-centroid = 2.438; B1-Nd1-B2 = 136.59(6).

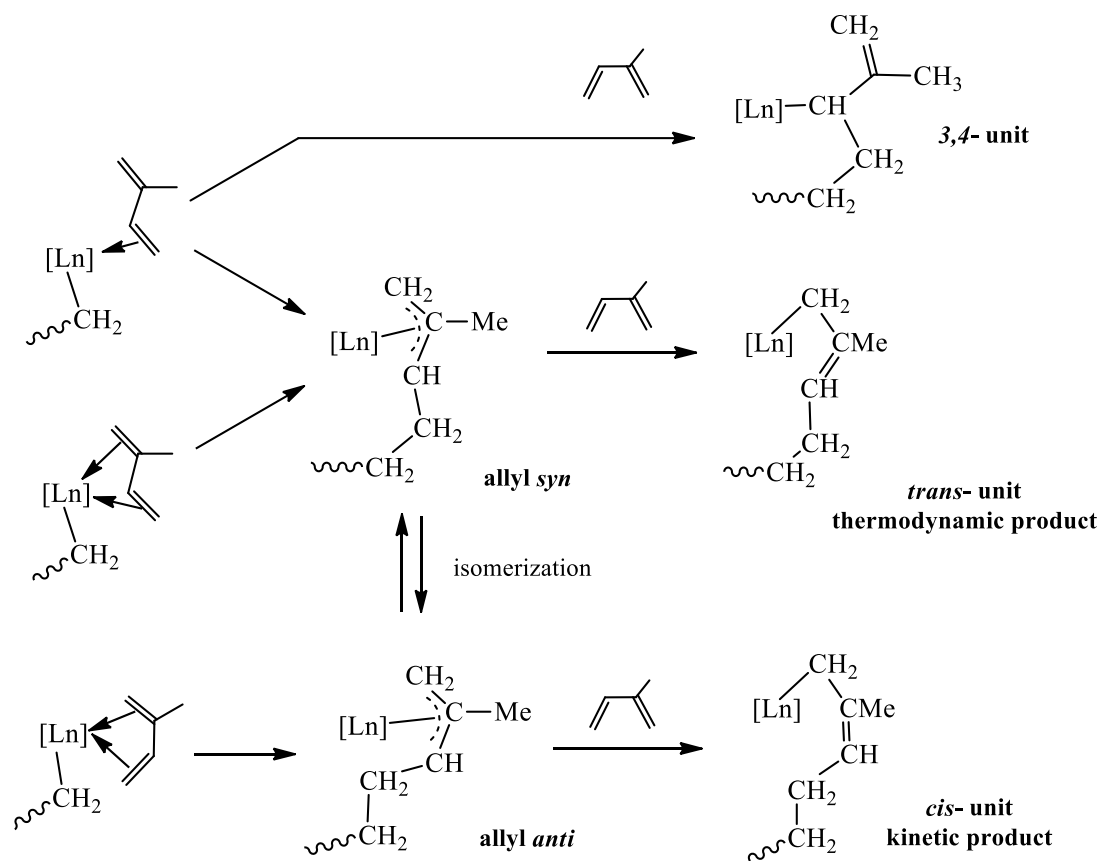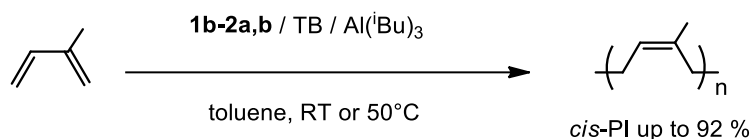*Polymerisation of isoprene with **1b**/borate/Al(ⁱBu)₃.*

Figure 2. Coordination modes of the isoprene monomer and the stereochemistry of the resulting polyisoprene.

Factors that govern the selectivity in conjugated dienes polymerization are closely connected to the coordination mode of the monomer to the catalyst (see figure 2).[2,3] Whereas *cis*-polyisoprene is mainly formed via the coordination of both double bonds of the isoprene monomer to the metal center in η^4 mode, *trans*-polyisoprene can result either from η^2 or η^4 coordination modes. However, isomerization reaction can occur in between *syn* and *anti* allyl species formed after insertion of the monomer, leading to *cis*-units even in the case of a previous η^2 coordination of the monomer. A 3,4-polyisoprene results from single coordination of the monomer, which is generally accepted as in line with the steric hindrance around the catalyst metal.[34] Thus, by subtle changes of the environment around the catalyst metal, one may possibly be able to tune the selectivity.

We investigated the polymerisation of isoprene using rare earths borohydrides pre-catalysts of three types: half-sandwiches Cp*Ln(BH₄)₂(THF)₂, *in situ* modified trisborohydrides Ln(BH₄)₃(THF)₃/L, and *in situ* modified half-sandwiches Cp*Ln(BH₄)₂(THF)₂/L, L being a

6

N-heterocyclic carbene. The co-catalysts are of two types, Al trialkyl (Al(^{i}Bu)$_3$ = triisobutylaluminum) combined with a borate activator (TB = [CPh$_3$][B(C$_6$F$_5$)$_4$] or HNB = [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]), and Mg dialkyl (BEM = ^{n}BuEtMg; DBM = ^{n}Bu$_2$Mg). Selected results are gathered in table 1 (scheme 1).

1b-2a,b / TB / Al(^{i}Bu)$_3$

toluene, RT or 50°C

cis-PI up to 92 %

**Scheme 1.** Isoprene polymerisation with **1b-2a,b** / trityl borate / Al(^{i}Bu)$_3$ ternary systems (table 1)

Regarding the half-sandwiches, we previously showed that Cp*Nd(BH$_4$)$_2$(THF)$_2$ (**1b**) with 1 equiv MgR$_2$ cocatalyst affords a catalyst for highly *trans*-selective isoprene polymerisation (> 98%).[14] Cp*Sc(BH$_4$)$_2$(THF) (**1a**) is inactive under the same conditions, but combined with a borate as the mixture Cp*Sc(BH$_4$)$_2$(THF)/[CPh$_3$][B(C$_6$F$_5$)$_4$]/Al(^{i}Bu)$_3$ it yields polyisoprene 97% *cis*-regular with excellent activity.[16] Complex **1b** also gives *cis*-rich polymer when associated to TB and triisobutyl aluminum. The best *cis*-rate (91.7 %, run 1.12) is obtained at high monomer loadings ([monomer]/[catalyst] = 6000) and with 2[CPh$_3$][B(C$_6$F$_5$)$_4$]/10Al(^{i}Bu)$_3$. It is noteworthy that with 1 equiv trityl borate the resulting catalyst is poorly active (19 % yield in 7 h, run 1.1), at 50 °C, while less than 5 equiv Al co-catalyst per borate activator affords rather lower selectivity (run 1.2). In order to get catalyst efficiency at this temperature, the best combination is **1b**/2[CPh$_3$][B(C$_6$F$_5$)$_4$]/10Al(^{i}Bu)$_3$, but to generate *cis*-selective polymerisations, ambient temperature conditions are needed, which is detrimental to the overall activity. At room temperature, high loadings of monomer (≥ 2000 equiv) are necessary to produce polymer, otherwise the catalyst remains inactive (runs 1.8, 1.9). It has to be mentioned that experiments 1.8 and 1.9 were carried out with dried samples of **1b** which had probably formed BH$_4$-bridged clusters of **1b'** type, through loss of coordinated THF molecules (see below).[30] This could account for the results. Room temperature conditions allow a more controlled process, since PDI (polydispersity index) values are in the range 1.7-2.0 (runs 1.10-1.12); they increase to values up to 3.8 when the temperature is raised to 50 °C. At this temperature full conversion is attained in less than 15 min. High molecular weights (superior to 10^5) can be obtained with this catalytic system (runs 1.6, 1.12). When **1b** is synthesized *in situ*,[32] higher *cis*-rate (80.6 *vs* 69.6 %, runs 1.4 and 1.3,

respectively) is obtained but to the detriment on the polymer yield (66 % *vs* 100 %). Replacement of the initiating trityl borate by HNB (HNB = [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]) gives rise to the formation of a polymer that is 92% *cis*-selective but with very low activity (run 1.18). However, this is notable since it is a rare example of *cis*-polymerisation at elevated temperature with rare earth borohydrido based catalytic systems.[35]

In chlorinated solvents, two distinct behaviors are observed: polymerisation takes place within minutes in CH$_2$Cl$_2$ (runs 1.13-1.14) very similarly as [CPh$_3$][B(C$_6$F$_5$)$_4$] does alone (run 1.24), to result to insoluble material. A similar trend was reported with pre-catalyst **1a** with similar catalytic combinations;[16] such observations account for a likely cationic process, which is known to favor cross-linking with polydienes and hence poorly soluble polymer. In chlorobenzene (runs 1.15-1.17), good conversions are produced in a few hours, but the *cis*-rate is inferior to that obtained in toluene.

The formation of the neodymium cationic species resulting from the reaction of **1b** either with [CPh$_3$][B(C$_6$F$_5$)$_4$] or [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$][16,36] was established by ^{1}H NMR experiments (see experimental section). When one equivalent of [CPh$_3$][B(C$_6$F$_5$)$_4$] is added to **1b** in THF-*d$_8$*, formation of a single product is observed with δ(BH$_4$) = 100.3 ppm (initially at 67.9 ppm in **1b**) and δ(Cp*) = 8.96 ppm (initially at 7.46 ppm in **1b**) likely corresponding to [Cp*Nd(BH$_4$)(THF)$_x$][B(C$_6$F$_5$)$_4$]. When the reaction was conducted with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] instead of [CPh$_3$][B(C$_6$F$_5$)$_4$], slightly different chemical shifts were observed (δ(BH$_4$) = 100.4 ppm and δ(Cp*) = 9.21 ppm) along with the formation of free amine PhNMe$_2$ (scheme 2). Attempts to crystallize this cationic species failed due to its high reactivity. When THF was used, the solution became viscous as the species polymerizes the solvent. Other attempts in solvents such as toluene or benzene also failed as the species forms insoluble oil in these solvents.[37]
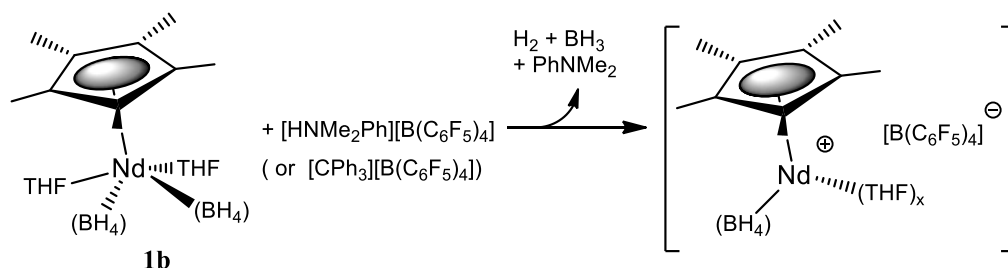
Scheme 2. Probable formation of cationic [Cp*Nd(BH$_4$)(THF)$_x$][B(C$_6$F$_5$)$_4$] from **1b**

The catalytic system $Nd(BH_4)_3(THF)_3$(**2b**)/$[CPh_3][B(C_6F_5)_4]$/$Al(^iBu)_3$ displays good *cis*-selectivity (90 %) at room temperature, along with satisfactory activity (run 1.21). These data are not far from the ones noticed with the half-neodymocene **1b**. We had already established that **2b** can behave as an efficient catalyst for isoprene *cis*-polymerisation: the **2b**/$[HNMe_2Ph][B(C_6F_5)_4]$/$Al(^iBu)_3$ combination yielded more than 90 % *cis*-polyisoprene, but the activity what significantly lower than with trityl borate as activator.[36]

The comparison of the results presented in table 1 with those obtained with the related scandium catalyst (*ie* **1a**/$[CPh_3][B(C_6F_5)_4]$/$Al(^iBu)_3$)[16] calls for the following comments: i) under similar conditions, both activity and *cis*-selectivity remain inferior with neodymium; ii) whereas the optimum precatalyst/activator/cocatalyst ratios were 1/2/20 with scandium, it seems that 1/2/10 ratio conditions are more preferable in the case of neodymium; iii) activities of the same magnitude order (up to ca 4000 kg PI/molcatalyst/h) can then be reached with both catalysts, but the scandium one allows a better *cis*-selectivity. Moreover, it is noteworthy that **2a** did not produce *cis*-PI when combined with $[CPh_3][B(C_6F_5)_4]$/$Al(^iBu)_3$, whereas **2b** does.

Table 1. Isoprene polymerisation with half-sandwich based catalysts combined with borate/alkylaluminum compounds

Run [a]	precatalyst	[I]/[Ln]	[B]/[Ln] [b]	Solvent [c]	T	t (h)	yield (%) / A [d]	Mn_{exp} (g/mol) [e]	PDI [e]	Mn_{th} (g/mol) [f]	cis/trans/3,4(%) [g]
1.1	**1b**	2100	1 TB	tol	50	7	19 / 4	16,400	3.8	27,100	84.7/9.7/8.9
1.2 [h]	**1b**	1000	2 TB	tol	50	2	58 / 20	18,800	1.7	39,400	51.7/39.4/8.9
1.3	**1b**	1000	2 TB	tol	50	24	100 / 3	34,200	2.6	68,000	69.6/21.0/9.4
1.4	**1b** [i]	1000	2 TB	tol	50	19	66 / 2.4	23,700	2.7	44,800	80.6/15.5/3.9
1.5	**1b**	2100	2 TB	tol	50	15 min	100 / 571	38,800	2.2	142,800	73.4/20.0/6.6
1.6	**1b**	3000	2 TB	tol	50	15 min	95 / 775	142,300	2.9	193,800	77.4/15.8/6.8
1.7	**1b**	4000	2 TB	tol	50	3 min	73 / 3971	50,700	2.5	198,600	77.2/17.2/5.6
1.8	**1b**	500	2 TB	tol	RT	24	0/ -	-	-	-	-
1.9	**1b**	1000	2 TB	tol	RT	24	0 / -	-	-	-	-
1.10	**1b**	2000	2 TB	tol	RT	2	30 / 20	48,700	1.7	40,500	84.7/10.7/4.6
1.11	**1b**	3000	2 TB	tol	RT	1	41 / 84	38,100	1.7	83,600	85.0/11.1/3.9
1.12	**1b**	6000	2 TB	tol	RT	3	39.5 / 54	104,500	2.0	161,200	91.7/2.2/6.1
1.13	**1b**	1000	2 TB	DCM	RT	1 min	66 / 2700	ins	ins	-	ins
1.14 [h]	**1b**	1000	2 TB	DCM	RT	2 min	53 / 1080	ins	ins	-	ins
1.15	**1b**	1000	2 TB	CLB [k]	RT	5	100 / 14	50,300	2.3	68,000	62.0/36.0/2.0
1.16	**1b**	2000	2 TB	CLB [j]	RT	2	85 / 58	66,700	2.1	115,600	73.0/23.0/4.0
1.17	**1b**	3000	2 TB	CLB [j]	RT	1	81 / 165	112,700	2.8	165,200	74.0/23.0/3.0
1.18	**1b**	2000	1 HNB	tol [j]	50	69	75 / 0.7	43,600	2.2	102,000	92.0/2.0/6.0
1.19	**1b**	1000	2 HNB	tol	50	96	15 / 0.1	4,500	1.9	10,200	61.0/31.3/7.7
1.20	**1b**	1000	1 HNB	tol	50	65	100 / 1	48,800	2.4	68,000	60.6/35.4/4.0
1.21	**2b**	500	2 TB	tol	RT	30 min	100 / 68	24,700	2.5	34,800	90.0/4.3/5.7
1.22	**2b**	4000	2 TB	tol	50	20	8 / 1.1	nd	nd	-	nd
ref [15]	**2a**	420	1 TB	tol	RT	10 min	97.0 / 166	15,500	1.9	27,700	55.2/40.8/4.0
1.23	**2a**	420	2 TB	tol	RT	1 min	100 / 1714	42,500	3.0	28,600	69.7/27.9/2.4
1.24	-	1000	2 TB	tol	RT	1 min	44 / -	ins	ins	-	ins

[a] Run typically conducted with ca 5 μmol Ln precatalyst (Ln = Sc, Nd)/borate/10Al(iBu)$_3$, ins: insoluble; nd: not determined; [b] TB = [CPh$_3$][B(C$_6$F$_5$)$_4$], HNB = [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]; [c] 0.5 mL, Tol = toluene, DCM = dichloromethane, CLB = chlorobenzene; [d] average activity (kg PI/mol Ln/h); [e] determined by SEC against polystyrene standards; [f] Mn_{th} = [I]/[Nd] x yield x 68; [g] from ^{1}H and ^{13}C NMR; [h] 5 Al(iBu)$_3$; [i] in situ prepared with **2b**/0.5 BEM/Cp*H (BEM = ^{n}BuEtMg); [j] 1 mL; [k] 2.5 mL.

Polymerisation of isoprene in the presence of NHC ligands.

We then decided to examine the result of the addition of a neutral ligand to the borohydride derivatives studied previously, towards isoprene polymerization efficiency. Several NHC ligands were assessed: the classical $[1-C\{(N^tBuCH)\}_2]$ (L^1) and functional N-heterocyclic carbenes, two amino-tethered $HN^tBuCH_2CH_2[1-C\{N(CHCH)NR\}]$ (HL^{2-R}) (R = ^tBu, Mes (Mes = 2,4,6-Me$_3$-C$_6$H$_2$))[38] and the hydroxyl-tethered $HOCMe_2CH_2[1-C\{N(CHCH)N^iPr\}]$ (HL^3, also represented under a zwitterionic form)[39] (scheme 3). Such molecules were chosen as potentially capable to coordinate either to the rare centre or to the magnesium atom, due to the carbene moiety.[21] In addition, HL^{2-R} and HL^3 are prone to afford anionic ligation to the metal via deprotonation. Selected results are gathered in table 2.
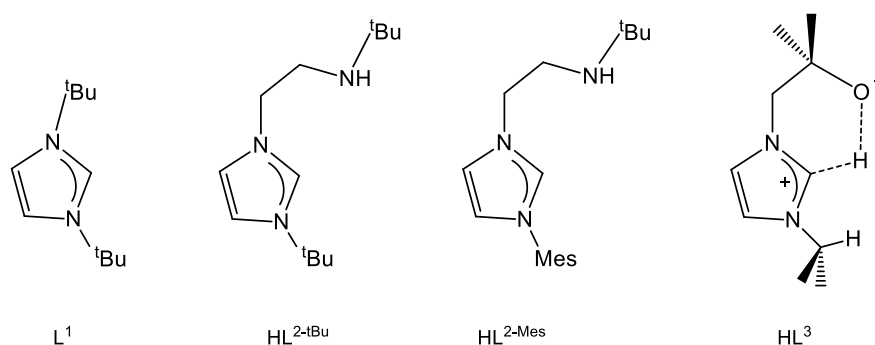

Scheme 3. NHC-ligands assessed as additional ligands in isoprene polymerisation

Polymerisation experiments were conducted as described in the previous section, *ie* by combining the precatalyst with borate/Al($^iBu)_3$ cocatalyst, but in the presence of the carbene ligand (scheme 4). When the latter was bearing a tethered protio -NHR function, the necessary amount of BEM (^nBuEtMg, or DBM = Mg^nBu_2) for deprotonation was added, similarly as conducted in the case of the "*in situ* B/A route" (run 1.4, table 1), since it was clear from ^1H NMR spectroscopic analysis that **2b** did not react with HL^{2-tBu} *via* protonolysis to form a putative $(L^{2-tBu})Nd(BH_4)_2(THF)_2$ (see experimental section). From the results gathered in table 2, one can observe that HL^{2-R} ligands behave differently depending on the R group, and on the metal considered. While **2b** affords 100 % yield of polymer in 30 min at room temperature (run 1.21, table 1), the addition of a NHC ligand has a strong impact in terms of activity: the conversion needs 24 h to be completed in the presence of 1 equiv L^1, and 20 h with L^{2-tBu} (runs 2.1 and 2.2, respectively). This result is in line with a previous observation made by some of us: the carbene adduct of a samarium allyl initiator

$(C_5H_4{}^tBu)_2Sm(C_3H_5)[C(N^iPr)_2(CMe)_2]$ was poorly active for isoprene polymerisation.[40] Interestingly however, the selectivity is switched with $L^{2\text{-tBu}}$ from 90/4 to 52/46 % *cis/trans* (run 2.2). When $L^{2\text{-Mes}}$ is used, the reaction is even slower, but the *cis*-selectivity is preserved (run 2.3). The impact of a carbene ligand was less negative when added to pre-catalyst **2a**. Whereas the system is not selective with **2a**/TB/Al($^iBu)_3$,[16] the *cis*-selectivity was more pronounced with 2 equiv trityl borate (run 1.23), and this was maintained in the presence of L^1 carbene, though with lower activity (run 2.4). Higher *cis*-rate (79 %) was received with 2.6 equiv borate activator (run 2.5). With 1 equiv $L^{2\text{-tBu}}$, no effect of the NHC was observed; both activity and selectivity being similar to the reference experiment (run 2.6, but 2 TB). On the other hand, spectacular result was obtained when 1 equiv $HL^{2\text{-Mes}}$ was added in the catalytic mixture: the selectivity switched to *trans*-selective, along with significant slowdown of the reaction rate (run 2.7), which strongly differs with what takes place in the case of neodymium (run 2.3). This trend was confirmed with run 2.8: 2 equiv $L^{2\text{-tBu}}$ were added to **2a**/TB/Al($^iBu)_3$, which lead to the formation of highly *trans*-polyisoprene, accompanied with total conversion. This *trans*-stereoregularity is tentatively ascribed to the steric hindrance around the scandium atom, due to the likely coordination of the bulky functionalized NHC ligands. An increase of the *trans*-1,4 content in butadiene polymerisation with Nd catalysts in the presence of an excess of DIBAH was similarly ascribed to impediment of η^4-coordination of the monomer with benefit to η^2-coordination.[41] To our knowledge, the result of run 2.8 is a rare example of *trans*-polyisoprene obtained with a scandium cationic based catalyst, since steric congestion is generally known to favour η^2 coordination of the monomer, and thus *3,4*-polymerisation.[42] Regarding the half-sandwiches, a polymerisation test was conducted with **1b** in the presence of L^1 carbene (1 equiv) at monomer/precatalyst ratio of 500, which resulted in the production of polymer, with very high *cis*-regularity (run 2.9). This result is in contrast with the one in absence L^1 which gave no polymer (run 1.8). One can advance here that the effect of L^1 ligand is parallel to an increase of monomer/precatalyst ratio (run 1.10).[43] Furthermore, one can also propose that the carbene moiety would help to dissociate the cluster structure – possibly of **1b'**type– of **1b** after storage, since dry batches of precatalyst **1b** are used. The addition of one equivalent of $HL^{2\text{-Mes}}$ to **1b** switches the selectivity from highly 1,4-*cis* in the presence of L^1 to 1,4-*trans* at 69% (run 2.10). This can be attributed to the bulk of the $HL^{2\text{-Mes}}$ ligand compared to L^1 resulting in η^2 coordination mode of the monomer to the scandium atom. With neodymium compound **1a**, the behavior is different: in the presence of L^1 (1 equiv) we observed, along with high activity (100 % conversion in 3 min, run 2.11), a switch

in selectivity, this time oriented towards *3,4*-polymerisation of isoprene. A stereoselective polymerisation of isoprene with NHC-tethered fluorenyl and indenyl supported catalysts was already reported to yield *3,4*-polyisoprene, but the stereo-inductive effect of the NHC moiety was not established.[44,45] Adding an additional equiv L[1] led to lower activity but similar *3,4*-preference (run 2.12). When half-sandwich **1a** is associated to HL[2-Mes] the activity is even lower but the selectivity remains unchanged (run 2.13).

$$ \text{1a,b-2a,b / L}^1 \text{ or HL}^2 \text{/ MgR}_2 $$
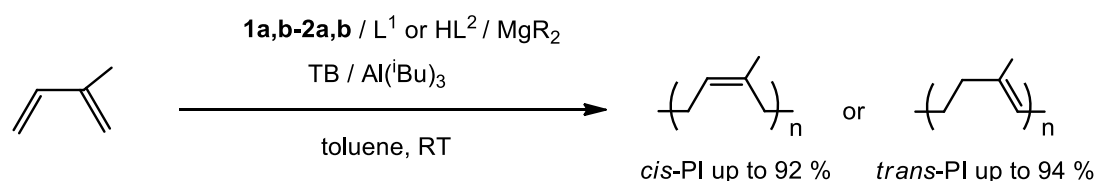
Scheme 4. Isoprene polymerisation with **1a,b-2a,b** / L[1] or HL[2] (MgR$_2$) / borate / Al(iBu)$_3$ systems (table 2)

Table 2. Isoprene polymerisation with borohydride precatalysts combined with borate/alkylaluminum compounds in the presence of NHC ligands.

Run [a]	Precatalyst/NHC	t (min)	yield (%)	Mn_{exp} (g/mol) [b]	PDI [b]	Mn_{th} (g/mol) [c]	*cis/trans/3,4*(%) [d]
1.21	**2b/-**	30	100	24,700	2.5	34,000	90.0/4.3/5.7
2.1	**2b/L**[1]	1440	100	14,400 [e]	1.4 [e]	34,000	83.2/13.0/3.8
2.2	**2b**/0.5DBM/HL[2-tBu]	1200	100	35,600 [f]	2.7 [f]	34,000	52.1/46.0/1.9
2.3	**2b**/0.5DBM/HL[2-Mes]	960	15	-	-	5,100	92.0/6.0/2.0
ref[16g]	**2a**	10	97.0	15,500	1.9	27,700	55.2/40.8/4.0
1.23 [h]	**2a**	1	100	42,500	3.0	28,600	69.7/27.9/2.4
2.4	**2a** /L[1]	5	100	21,500	2.9	34,000	66.7/29.9/4.1
2.5 [i]	**2a** /L[1]	5	100	24,300	4.0	34,000	79.7/16.2/3.4
2.6	**2a** /0.5DBM/ HL[2-tBu]	10	87.5	ins	ins	29,700	56.8/38.7/4.5
2.7	**2a** /0.5DBM/ HL[2-Mes]	960	48.3	16,200 [f]	2.0 [f]	16,400	9.4/88.6/2.0
2.8	**2a** /1DBM/ 2 HL[2-tBu]	1440	100	6,800	2.2	34,000	4.2/94.1/1.7
2.9	**1b** /L[1]	1440	41	6,800	1.6	13,900	92.5/3.5/4.0
2.10	**1b** /0.5BEM/ HL[2-Mes]	3900	100	17,100	1.9	34,000	29.3/68.9/1.8
2.11	**1a** /L[1]	3	100	13,900	5.1	34,000	41.1/3.1/55.8
2.12	**1a** /2L[1]	1440	100	15,400	5.3	34,000	39.7/3.3/57.0
2.13	**1a** /0.5BEM/ HL[2-Mes]	3900	100	multimodal	–	34,000	48(1,4)/52(3,4)

[a] [I]/[Ln] = 500; [TB]/[Ln] = 2 ; [Al]/[Ln] = 10, room temperature, V(toluene) = 0.5 mL; ins: insoluble; nd: not determined. [b] Determined by SEC against polystyrene standards. [c] Mn_{th} = [I]/[Ln] x yield x 68. [d] From ^{1}H and ^{13}C NMR. [e] bimodal: a minor contribution is observed at high Mn values. [f] Partly soluble. [g] [I]/[Ln] = 420; [TB]/[Ln] = 1. [h] [I]/[Ln] = 420; [TB]/[Ln] = 2. [i] [TB]/[Ln] = 2.6.

Polymerisation experiments were further conducted with pre-catalysts **1b**, Cp*Sm(BH$_4$)$_2$(THF)$_2$ (**1c**), **2b** and Sm(BH$_4$)$_3$(THF)$_3$ (**2c**), in the presence of NHC ligands, and in combination with BEM as co-catalyst (scheme 5). Selected results are given in Table 3. As before, with amino-tethered N-heterocyclic carbenes HL$^{2\text{-R}}$, an additional equimolar amount of alkyl reagent was added to ensure the deprotonation of the ligand (see experimental). This was not however necessary when the carbene ligand was bearing a tethered protio –OH group (HL^3), due to higher acidity of the latter.

1b,c-2b,c / L^1, HL^2 or HL^3 / MgR$_2$

toluene, 50°C

trans-PI up to 98 %
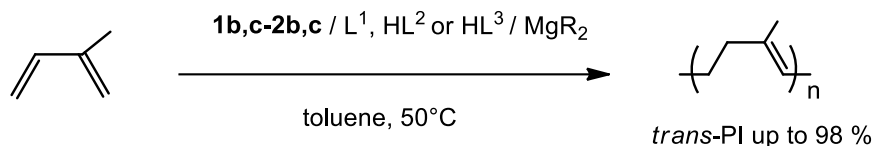
Scheme 5. Isoprene polymerisation with **1b,c-2b,c** / L^1, HL^2 or HL^3 / MgR$_2$ systems (table 3)

At the addition of NHC ligands, one can observe that the *trans*- character of the reference catalysts Ln(BH$_4$)$_3$(THF)$_3$/BEM (95.5%)[46] is preserved, and in general little improved. On the other hand, the activity is severely lowered (runs 3.1, 3.2, 3.3). It was established by a series of NMR experiments that the functionalized NHC ligands act as chelates, the carbene moiety being coordinated to the Nd atom in solution (see experimental). The result of the reaction of HL^3 with **2b** affords a set of paramagnetic resonances in the NMR spectra that can be assigned to an L^3-supported Nd compound (scheme 6, top). Despite our efforts, it was not possible to isolate this compound in bulk conditions. The reaction of **2b** with the protio imidazolium precursor (H$_2$L^3)$^+$,I$^-$ gave (with intense bubbling) a compound which ^{1}H NMR paramagnetic spectrum was very similar, thus confirming the previous reaction. Run 3.4, which was carried out with the protio ligand, gives as expected highly *trans*-regular polymer, though in little quantity. The same tendency was noticed in the presence of 2 equiv HL^3, *ie* *trans*-selectivity and lesser activity (run 3.5). One can note however that in the case of samarium, the addition of 1 equiv HL^3 yields some polymer, with fair *trans*-selectivity (run 3.6), whereas **2c**/BEM was inactive in the absence of carbene ligand.[46] With amino-tethered N-heterocyclic carbenes HL$^{2\text{-R}}$, whatever the substituent *ter*-butyl or mesityl, the activity is low, and the selectivity remains 1,4-*trans* (runs 3.7-3.9). The reaction of HL$^{2\text{-R}}$ with **2b** after deprotonation with DBM and the coordination of the carbene moiety to the Nd atom are clearly established by ^{1}H NMR (scheme 6, bottom, and experimental part). The scale up synthesis of the reaction of HL$^{2\text{-tBu}}$ with **2b** in the presence of BEM led to the isolation of the

bis THF adduct $(L^{2\text{-tBu}})Nd(BH_4)_2(THF)_2$ **3** as a crude product (43% yield). After work-up and prolonged drying, a non-solvated compound $(L^{2\text{-tBu}})Nd(BH_4)_2$ **3'**, according to elemental analysis, was finally obtained as a blue-red solid (see experimental section). Unfortunately no suitable crystals were obtained for X-Ray analysis. This compound which initially bears two THF molecules per neodymium when freshly prepared, has a tendency to desolvate as the unsolvated form is obtained when the complex is further dried.[30]
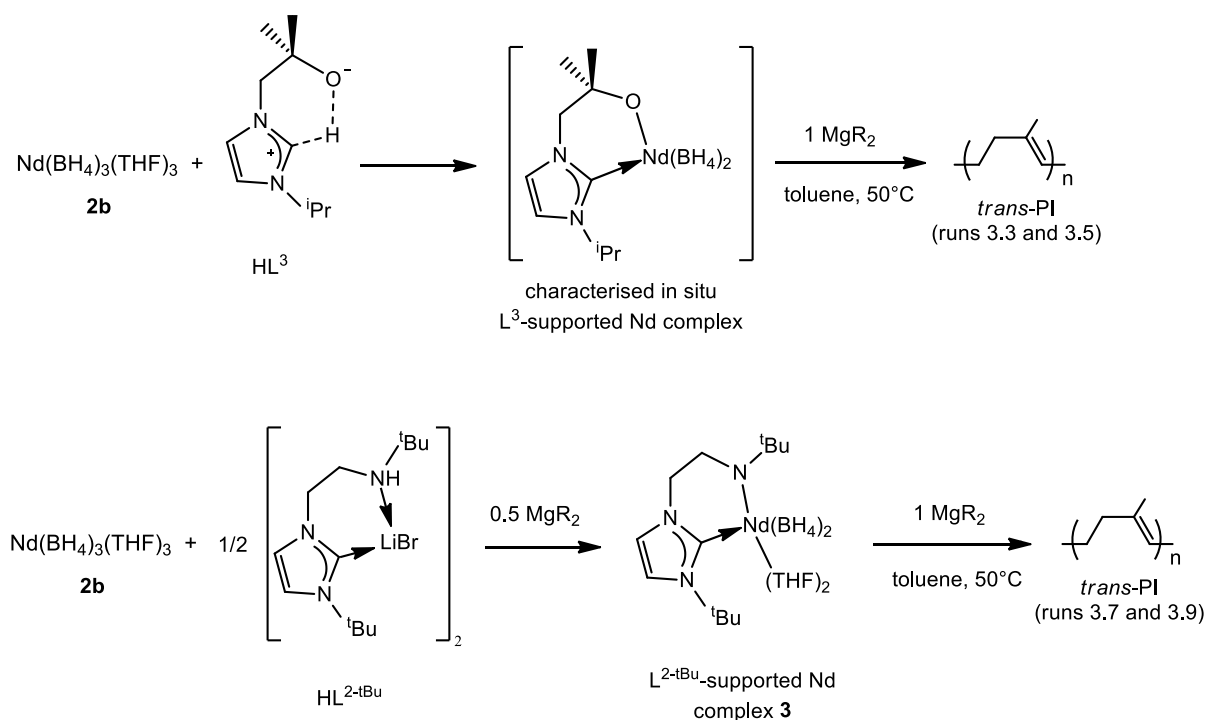
Scheme 6. Reaction of **2b** with HL^3 (top) and with $HL^{2\text{-tBu}}$ in the presence of dialkylmagnesium (bottom).

Table 3. Isoprene polymerisation with borohydride precatalysts combined with BEM in the presence of NHC ligands.

Run [a]	Pre-catalyst/NHC	[Mg]/[Nd]	t (h)	yield (%)	Mn_{exp} (g/mol) [d]	PDI [d]	Mn_{th} (g/mol) [e]	cis/trans/3,4 (%) [f]
Ref [42]	**2b/-**	1	2	87.0	52,100	1.3	58,100	-/95.5/-
3.1	**2b**/1 L^1	1	2	30.9	27,000	1.2	21,000	1.5/96.5/2.0
3.2	**2b**/1 HL^3	1	2	26.5	34,600	1.3	18,000	1.6/96.1/2.3
3.3	**2b**/1 HL^3	1	18	80.2	39,800	1.2	54,500	1.0/96.6/2.4
3.4	**2b**/1 $(H_2L^3)^{+}$ [b]	1	16	25.0	6,200	1.7	8,500	2.0/94.0/3.0
3.5	**2b**/2 HL^3 [b]	1	16	50.2	9,800	1.6	17,100	1.9/96.1/2.0
3.6	**2c**/1 HL^3	1	96	18.6	3,700	1.8	12,600	6.4/70.2/23.4
3.7	**2b**/1 $HL^{2\text{-tBu}}$ [b]	1.5	16	56.4	4,800	1.6	19,200	2.0/95.6/2.4

15

3.8	**2b**/1 HL$^{2\text{-Mes}}$ ^{b}	1.5	16	13.5	2,200	1.5	4,600	3.2/94.4/2.4
3.9	**2b**/2 HL$^{2\text{-tBu}}$ ^{b}	2	16	18.5	2,500	1.4	6,300	2.9/94.8/2.3
3.10	**1b**/1 L^1	1	2	63.0	27,000	1.1	42,800	0.1/97.7/2.3
3.11	**1b**/1 HL^3	1	2	63.2	43,300	1.1	43,000	0.1/98.3/2.3
3.12	**1c**/1 L^1	1	2	40.8	27,300/10,100	1.1/1.2	27,700	0.2/98.0/2.0
3.13	**1c**	1	2	51.6	50,100/17,100	1.1/1.2	35,100	0.4/97.3/2.3

^{a} T = 50 °C; V(toluene) = V(isoprene); [I]/[Nd] = 1000; ^{b} [I]/[Nd] = 500; ^{c} activity (kg/mol/h); ^{d} determined by SEC against polystyrene standards and corrected by a factor of 0.5 in case of *trans*-PI;[43] ^{e} Mn$_{th}$ = [I]/[Nd] x yield x 68; ^{f} from ^{1}H and ^{13}C NMR.

In contrast with homoleptic trisborohydrides, half-sandwich precatalysts remain quite active when NHC molecules are present (conversion > 60 % in 2 h, runs 3.10 and 3.11). Whatever L^1 or HL^3, the selectivity remains highly *trans*-, in the range observed with the reference **1b**/BEM catalyst.[14] The same is also noticed with samarium, although the process is less controlled, with bimodal SEC curves (runs 3.12, 3.13). These results are somewhat different from those reported by Anwander *et al.*: the presence of donor nitrogen functionality in quinolyl-substituted cyclopentadienyl yttrium and lanthanum catalysts was shown to slightly disfavor the *trans*-selectivity towards isoprene polymerisation.[9]

Finally, ^{1}H and ^{11}B NMR monitoring experiments were carried out with simple L^1 carbene in order to check just the coordination to Nd (**1b**) and to Sc (**2a**) (see figure 3 and experimental part). The signals of the initial compound in both cases disappear, in favour of new sets of signals. With paramagnetic Nd, one new Cp* and one new BH$_4$ (^{1}H and ^{11}B) signals can be observed, along with some diamagnetic THF, and one may clearly distinguish between paramagnetic and diamagnetic peaks for the L^1 ligand. Thus, some L^1 carbene is probably coordinated under a single new species. With scandium, the initial compound has reacted as well, but several ^{11}B resonances can be observed, and many peaks are assignable to coordinated L^1 ligand. This would possibly indicate a constrained molecular geometry which could be tentatively rationalized as in line with the surprising switch of selectivity from *cis*- to *trans*- with pre-catalyst **2a** (runs 2.6-2.8, 2.10, table 2). To summarize, the coordination of the L^1 carbene is established unambiguously, but the result may probably be interpreted in terms of dynamic exchange, which unfortunately does not allow to isolate well-defined adducts in this borohydride series.
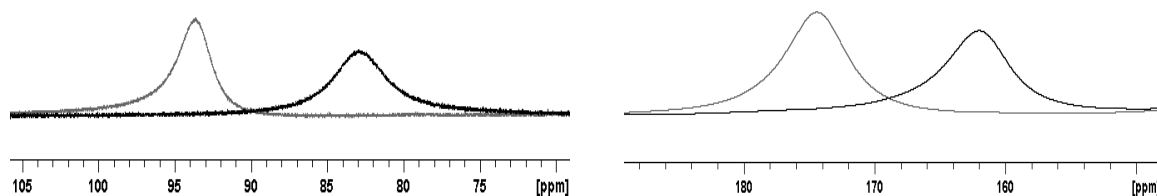
Figure 3. ^{1}H (left) and ^{11}B (right) NMR signals of borohydride groups (benzene-d_6). Grey curves: **1b** alone; black curves: **1b** + 1 equivalent of L^1 NHC ligand.

The situation is obviously more complicated in polymerisation experiments since several metallic species –the pre-catalyst and the co-catalyst– are present in the mixture. The carbene moiety may coordinate either to the Nd or the Mg atom (table 3), Nd or Al, Sc or Al (table 2), and even Nd/Sc, Mg or Al, when all three metals are present (table 2). This depends on the type of polymerisation, and thorough investigations which require the use of NHC ligands that are specific to a metal, are necessary to go further in the understanding of these phenomena. This will be the subject of our further studies in this area.

Conclusion.

We reported in a previous work the efficiency of the ternary scandium–based catalytic system Cp*Sc(BH$_4$)$_2$(THF)/[CPh$_3$][B(C$_6$F$_5$)$_4$]/Al(^{i}Bu)$_3$ towards the polymerisation of isoprene, leading to highly *cis*-polyisoprene along with a strong activity. These results were extended to neodymium which is less costly than scandium metal and more utilized as catalyst in the industry. The already reported complex Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** used in this study was characterized by X-Ray analysis, displaying a monomer structure including two tridentate borohydride ligands and two THF molecules. When activated in the same conditions as previously used with the scandium analog, *ie* with a borate activator and an aluminum alkyl, this neodymium compound also leads to highly active and *cis*-selective (up to 92 %) isoprene polymerization catalysts. The likely formation of the neodymium cationic species resulting from the reaction of Cp*Nd(BH$_4$)$_2$(THF)$_2$ with the borate activators was established by ^{1}H NMR experiments. In the second part of this work, scandium, neodymium and samarium half-metallocenes, as well as their precursors Ln(BH$_4$)$_3$(THF)$_x$, were associated *in situ* to different types of N-Heterocyclic Carbene ligands, with the aim to modify the polymerization active species and hence the polymerization catalysis. The amidocarbene (L^{2-tBu})Nd(BH$_4$)$_2$ **3'** could be synthesized and characterized. The most interesting result in terms of polymerization was obtained with the scandium complex Sc(BH$_4$)$_3$(THF)$_{1.5}$ **2a** which, associated to the HN^{t}BuCH$_2$CH$_2$[1-C{N(CHCH)N^{t}Bu}] (HL^{2-tBu}) carbene, leads to 94% *trans*-selectivity,

whereas it affords ca. 80% *cis*-selectivity when associated to 1-C{(NBu^tCH)}_2 (L[1]), and the process is not selective in the absence of NHC. This is the first example of highly *trans*-polyisoprene obtained with a scandium cationic based catalyst, whilst usually affording either mainly *cis*- or 3,4-polyisoprenes. Coordination of the carbene moiety to the rare earth centre is confirmed by NMR studies on paramagnetic neodymium precatalysts. This work shows the possibilities to tune the catalytic properties just by *in situ* addition of a "regulating" agent in the polymerisation medium.

Acknowledgements

Experimental section.

Materials and methods: All operations were performed under dry argon by using Schlenk techniques. The solvents were dried over sodium/benzophenone ketyl, deoxygenated by distillation, and stored on molecular sieves (3Å) in a glovebox. Isoprene (99% from Aldrich) were dried over calcium hydride, distilled twice, and stored over molecular sieves (3 A) in a glovebox. Dibutylmagnesium DBM (1.0 M solution in heptane), triisobutylaluminum $Al(^iBu)_3$, [CPh_3][B(C_6F_5)_4], [HNMe_2Ph][B(C_6F_5)_4] and [C{^tBuN(CHCH)NH^tBu}][BF_4] were purchased from Aldrich and used as received. *n*-Butylethylmagnesium BEM (20%, hexanes) was purchased from Texas Alkyl. N-heterocyclic carbenes HL^{2-R} (R = ^tBu, Mes) HL[3] and its potassium salt KL[3] were synthesized according to published procedures. [38,39] L[1] was prepared by the reaction of its imidazolium precursor with KH in boiling THF. The borohydride pre-catalysts $Sc(BH_4)_3(THF)_{1.5}$,[47] $Nd(BH_4)_3(THF)_3$,[33] $Sm(BH_4)_3(THF)_3$,[33] $Cp*Sc(BH_4)_2(THF)$[16] and $Cp*Nd(BH_4)_2(THF)_2$[33] were synthesized as previously reported. The bis-THF adduct $Cp*Sm(BH_4)_2(THF)_2$ was synthesized as previoulsy reported for the unsolvated complex $[Cp*Sm(BH_4)_2]_n$ (see experimental section further down).[48] Crystals of $Cp*Nd(BH_4)_2(THF)_2$ were grown in concentrated THF/pentane solution at room temperature. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 instrument at 293 K in C_6D_6, TDF

(organometallic complexes), or in $CDCl_3$ (polymers). ^{11}B NMR analyses were done with a Bruker Avance 400 instrument at 293 K, and calibrated against BF_3, Et_2O. The chemical shifts were calibrated by using the residual resonances of the solvent. Elemental analyses were carried out with a Fisons EA 1108 CHON by the Centre d'Analyses de l'Université de Dijon. Size exclusion chromatography of polymer samples was performed in THF as an eluent at 40 °C (1 mL min^{-1}) with a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards. A correction factor of 0.5 was applied for the determination of number-average molecular weight of poly(1,4-*trans* isoprene).[49]

X Ray structure determination of Cp*Nd(BH₄)₂(THF)₂ (1b): Bright blue X-Ray quality crystals were grown from THF/pentane of freshly prepared **1b** according to the literature.[33] X-ray analysis of the crystals displayed compound Cp*Nd(BH₄)₂(THF)₂. X-Ray data: compound **1b** ($C_{18}H_{39}B_2NdO_2$, Mw = 453.35) crystallizes in the monoclinic space group P2₁/n with a = 8.6110(10), b = 17.3480(3), c = 14.9131(3) Å, β = 105.060(1), V = 2151.3(3) Å^3, and ρ = 1.400 gcm^{-3} for Z = 4. Data were collected at 100(1) K on a Bruker Smart Apex CCD 4K system. The structure was solved by charge flipping methods using Superflip software,[50] and least-square refined with Olex2 software.[51] The model based on 9533 reflections ($I > 2.0σ(I)$, Rint = 0.026), total number of reflections = 59452, converged to a final *R1* = 2.5 % (*wR*1 = 5.6 %). CCDC 892290.

X Ray structure determination of [Cp*Nd(BH₄)₂]₆ (1b'): Bright blue X-Ray quality crystals were grown from saturated benzene solution of freshly prepared **1b** according to the literature.[34] X-ray analysis of the crystals displayed the unsolvated hexamer [Cp*Nd(BH₄)₂]₆. X-Ray data: compound **1b'** ($C_{60}H_{90}B_{12}Nd_6 \cdot 2(C_6H_6)$), Mw = 1962.8 g/mol) crystallizes in the triclinic space group P-1 with a = 15.979(4), b = 16.981(4), c = 21.702(6) Å, α = 90.181(5)°, β = 109.502(5)°, γ = 119.054(5)°, V = 4586(2) Å^3, and ρ = 1.421 gcm^{-3} for Z = 2. Data were collected at 100(1) K on a Bruker Smart CCD 1K system. All tested crystals were systematically twinned (180° around real 1 0 0 axis); thus the study was undertook using such a sample where twin ratio refined afterward to 49.6%. The structure was solved by charge flipping methods using Superflip software,[50] and least-square refined with Jana2000 software[52] including Rigid Body approach. The model based on 9735 reflections ($I > 3.0σ(I)$, Rint = 0.065), total number of reflections = 20508, converged to a final *R1* = 5.4 % (*wR*1 = 5.6 %). CCDC 892289.

Cp*Nd(BH$_4$)$_2$(THF)$_2$ 1b from [Cp*Nd(BH$_4$)$_2$]$_6$: Complex [Cp*Nd(BH$_4$)$_2$]$_6$ was stirred overnight in THF. The blue solution was evaporated to dryness without any further drying under vacuum. ^{1}H NMR in C$_6$D$_6$ of the compound after treatment was consistent with Cp*(BH$_4$)$_2$(THF)$_2$ showing that the clustering is reversible. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 93.65 (br, 8H, BH$_4$); 8.66 (br, 15H, Me-Cp*), -1.95 (br, 8H, THF); -5.32 (br, 8H, THF). ^{11}B NMR (C$_6$D$_6$, 298 K, calibrated against BF$_3$.Et$_2$O, δ in ppm): 174.3 (br, BH$_4$).

^{1}H NMR experiments:

Nd(BH$_4$)$_3$(THF)$_3$ 2b with one equivalent of HL^3: At the addition of 1 equiv HL^3 to **2b** (6.7 mg, 16.4 μmol) in C$_6$D$_6$ in an NMR tube equipped with a teflon valve (Young ™) an immediate bubbling was observed along with formation of a partially soluble compound. ^{1}H NMR analysis recorded immediately showed resonances of a paramagnetic compound fully compatible with the formula (BH$_4$)$_2$NdOCMe$_2$CH$_2$[1-C{N(CHCH)N^{i}Pr}]. ^{1}H NMR (C$_6$D$_6$, 298K, δ in ppm): 41.3 (br, 2H, CH_2), 39.1 (br, 6H, CMe_2), ca 35 ppm (elapsed in the baseline, 4H, BH$_4$), 17.4 (s, 1H, C-H), 8.6 (br, 1H, C-H), -8.4 (s, 6H, ^{i}Pr), -10.4 (br, 1H, ^{i}Pr). A tentative synthesis carried out at bulk scale in THF failed to obtain the desired product.

Nd(BH$_4$)$_3$(THF)$_3$ 2b with one equivalent of [H$_2$L^3]$^+$,[I]$^-$: The reaction of **2b** (8.1 mg, 20 μmol) with 1 equiv [H$_2$L^3]$^+$,[I]$^-$ (6.2 mg) in C$_6$D$_6$/THF mixture in an NMR Young tube was as same very bubbly, giving a major set of signals similar as above. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 43 (br, 2H, CH_2), 39 (br, 6H, CMe_2), 21.5 (s, 1H, C-H), 9.2 (br, 1H, C-H), -5.1 (s, 6H, ^{i}Pr), -8.1 (br, 1H, ^{i}Pr). This was fully compatible with the formula (BH$_4$)INdOCMe$_2$CH$_2$[1-C{N(CHCH)N^{i}Pr}].

Nd(BH$_4$)$_3$(THF)$_3$ 2b with one equivalent of HL$^{2\text{-tBu}}$/0.5DBM: No gas evolution was observed at the addition of 1 equiv HL$^{2\text{-tBu}}$ (LiBr adduct, 4.8 mg) to **2b** (5 mg, 12.3 μmol) in C$_6$D$_6$, the poorly soluble HL$^{2\text{-tBu}}$ remaining unchanged at the bottom the tube. Addition of 0.5 equiv DBM afforded a clean spectrum with paramagnetic resonances. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 60 (vbr, 8H, BH$_4$), 29.8 (vbr, 2H, CH_2), 14.6 (s, 9H, ^{t}Bu), 11.1 (s, 2H, CH_2), 6.7 (s, 1H, C-H), 3.6 (s, 9H, ^{t}Bu), 2.8 (br, THF), 1.48 (br, THF) which could be compatible with the formula (L$^{2\text{-tBu}}$)Nd(BH$_4$)$_2$(THF)$_n$. The chemical shifts of both ^{t}Bu signals at paramagnetic values unambiguously establish the coordination of the carbenic moiety to the Nd atom in solution. After removal of the volatiles and addition of a new batch C$_6$D$_6$, the spectrum corresponds to the bis THF adduct (L$^{2\text{-tBu}}$)Nd(BH$_4$)$_2$(THF)$_2$. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 68 (vbr, 8H, BH$_4$), 30.2 (vbr, 2H, CH_2), 14.6 (s, 9H, ^{t}Bu), 12.0 (s, 2H, CH_2), 6.26 (s, 1H, C-

H), 4.03 (s, 9H, ^{t}Bu), 2.59 (br, 8H, THF), 1.71 (br, 8H, THF). The scale up syntheses of (L^{2-tBu})Nd(BH$_4$)$_2$(THF)$_2$ **3** and (L^{2-tBu})Nd(BH$_4$)$_2$ **3'** are described further down in the experimental part.

Cp*Nd(BH$_4$)$_2$(THF)$_2$ 1b **with one equivalent of L^1:** 10 mg of Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** (2.2×10^{-5} mol) were mixed with 4 mg of L^1 (2.2×10^{-5} mol) in C$_6$D$_6$ in an NMR tube equipped with a young valve. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 82.93 (br, 8H, BH$_4$); 8.41 (br, 15H, Me-Cp*), 6.80 (br, 2H, free H-L^1); 1.51 (br, 18H, free tBu-L^1), -0.67 (br, 4H, THF); -1.74 (br, 4H, THF); additional peacks (attributable to coordinated-L^1): 13.02, 11.02, 9.99, 7.97, 4.69, 0.85, -1.41, -4.85. Some free THF is present in the spectrum. ^{11}B NMR (C$_6$D$_6$, calibrated against BF$_3$, Et$_2$O): 162(br, BH$_4$).

Sc(BH$_4$)$_3$(THF)$_{1.5}$ 2a **with one equivalent of L^1:** 10 mg of Sc(BH$_4$)$_{1.5}$(THF)$_{1.5}$ **2a** (5×10^{-5} mol) were mixed with 9 mg of L^1 (5×10^{-5} mol) in C$_6$D$_6$ in an NMR tube equipped with a young valve. ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 6.80 (s, 2H, free H-L^1); 6.45 (s, 2H, coordinated H-L^1); 3.64 (m, 4H, THF); 1.59 (s, 18H, coordinated ^{t}Bu-L^1), 1.51 (s, 18H, free ^{t}Bu-L^1), 1.41 (m, 4H, THF); 2.7-0.5 (br, 8H, BH$_4$); peaks which could be attributed to coordinated-L^1 ligand: 13.02, 11.02, 9.99, 7.97, 4.69, 0.85, -1.41, -4.85. ^{11}B NMR (C$_6$D$_6$, calibrated against BF$_3$.Et$_2$O, 293K, δ in ppm): -21.35 and -31.89 (br, BH$_4$). Non-attributed peaks (all minor except the last one): 8.09, 7.47, 7.35, 1.22, 0.90. Initial data for **2a** (2 THF). ^{1}H NMR (C$_6$D$_6$, 293K, δ in ppm): 3.89 (m, 8H, THF); 1.14 (m, 8H, THF); 2-0.25 (br, 12H, BH$_4$); ^{11}B NMR (C$_6$D$_6$, calibrated against BF$_3$, Et$_2$O, 293K, δ in ppm): -18.79 (br, BH$_4$).

NMR scale synthesis of [Cp*Nd(BH$_4$)(THF)$_x$][B(C$_6$F$_5$)$_4$]: in an NMR tube equipped with a teflon valve 3 mg of Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** (6.61×10^{-6} mol) and 6.1 mg of [CPh$_3$][B(C$_6$F$_5$)$_4$] (6.61×10^{-6} mol) were mixed in THF-*d*$_8$. The solution instantly turns from pale blue to pale yellow. Formation of a single product with δ BH$_4$ = 100.3 ppm (δ BH$_4$ in Cp*Nd(BH$_4$)$_2$(THF)$_2$ initially at 67.9 ppm) and δ Cp* = 8.96 ppm (δ Cp* in Cp*Nd(BH$_4$)$_2$(THF)$_2$ initially at 7.46 ppm) corresponding to [Cp*Nd(BH$_4$)(THF)$_x$][B(C$_6$F$_5$)$_4$]. Deuteriated THF was polymerized after standing one week at room temperature. When the reaction was conducted with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] instead of [CPh$_3$][B(C$_6$F$_5$)$_4$], slightly different chemical shifts was observed (δ BH$_4$ = 100.4 ppm and δ Cp* = 9.21 ppm) along with the formation of free amine PhNMe$_2$ (δ = 7.83; 7.44; 7.32; 3.12 ppm).

Synthesis of (L^{2-tBu})Nd(BH$_4$)$_2$(THF)$_2$ (3) : Nd(BH$_4$)$_3$(THF)$_3$ (442 mg, 1.09×10^{-3} mol) and HL^{2-tBu} (LiBr adduct, 338 mg, 1.09×10^{-3} mol) were weighted in a double-neck flask in a glove

box. The vessel was connected to the vacuum line and 20 mL of toluene were distilled into the flask. BEM (0.5 equiv, 300 mg of a 20 % hexane solution) diluted in toluene (10 mL) was added dropwise at room temperature to the mixture of **2b** and HL^{2-tBu}. Immediately a deep blue-green solution was formed, along with a white precipitate. The mixture was allowed to stir one night at room temperature and was filtered and concentrated to ca 10 mL. No crystals were obtained after 24 h at room temperature. Pentane (10 mL) was added by distillation, leading to the precipitation of a light blue powder which expanded when drying, after isolation of this blue powder from the mother liquor. 0.248 g (43 % yield) of $(L^{2-tBu})Nd(BH_4)_2(THF)_2$ **3** was finally obtained as a blue-red dichroic solid. ^1H NMR (C_6D_6, 293 K, δ in ppm): 28.8 (vbr, 2H, CH_2), 15.2 (s, 9H, ^tBu), 11.96 (s, 2H, CH_2), 6.1 (s, 1H, C-H), 3.87 (s, 9H, ^tBu), 2.73 (br, 8H, THF), 1.44 (br, 8H, THF), one CH signal from the NHC carbene and BH_4 signals could not be observed. After prolonged drying, unsolvated complex $(L^{2-tBu})Nd(BH_4)_2$ **3'** is obtained : elemental analysis calculated (%) ($NdC_{13}H_{32}B_2N_3$; 396.28 g/mol): C 39.40, H 8.14, N 10.60; found: C 39.29, H 8.19, N 10.55. Recrystallization attempts in THF/pentane at various temperatures (room temperature, freezer) failed to afford suitable crystals for X-Ray studies.

Synthesis of Cp*Sm(BH₄)₂(THF)₂ (1c) : $[Cp*Sm(BH_4)_2]_n$ was already described as an unsolvated compound.[48] $Sm(BH_4)_3(THF)_3$ (1.3 g, 3.16×10^{-3} mol) and KCp* (0.54 g, 3.10×10^{-3} mol) were weighted in a vessel in a glove box. The vessel was connected to the vacuum line and 75 mL of THF were distilled into the flask. After one night stirring at room temperature, an orange solution was obtained with white salts. The solution was filtered and THF was removed under vacuum. The red solid was then washed with 30 mL of pentane and dried under dynamic vacuum at room temperature for 2 hours. 1.314 g (92 % yield) of Cp*Sm(BH₄)₂(THF)₂ (according to ^1H NMR) were obtained as a red solid. ^1H NMR (C_6D_6, 293 K, δ in ppm): □-12.1 (broad, 8H, BH_4); 0.61 (broad, 8H, THF); 0.83 (s, 15H, Cp*); 2.02 (broad, 8H, THF). Elemental analysis calculated (%) for Cp*Sm(BH₄)₂(THF)₁.₅ ($SmC_{16}H_{35}B_2O_{1.5}$; 415.43 g/mol) : C 45.38, H 8.3; found: C 45.67, H 8.04.

Typical isoprene polymerisation experiment with 1b/[CPh₃B][(C₆F₅)₄]/Al(ⁱBu)₃ **(run 1.12, table 1):** In a glove box under argon (H_2O and O_2 < 2 ppm), 2.4 mg of complex Cp*Nd(BH₄)₂(THF)₂ **1b** (5.3×10^{-6} mol) are dissolved in 0.5 mL of dry and degassed toluene. Two equivalents of [CPh₃B][(C₆F₅)₄] (9.5 mg, 1.06×10^{-5} mol) were then added under stirring

and after several minutes an orange solution was obtained. 10 equivalents of Al(^{i}Bu)$_3$ (d = 0.786, 14 μL, 5.5×10^{-5} mol) were then added with a microsyringe and after several minutes the solution turns to pale yellow. 3.2 mL of isoprene (0.032 mol) were then added, and the reaction was carried out at 20 °C for 3 h. At the end of the reaction the medium is viscous. The reaction was quenched by addition of some methanol drops. The polymer was dissolved in toluene, poured in a large amount of methanol, filtered and dried under vacuum. The yield reaches 40%, the average molecular weight of the obtained polymer is M_n = 104500 g/mol, and the polydispersity index of 2.0. ^{1}H and ^{13}C NMR analyses in CDCl$_3$ showed that the polyisoprene obtained was up to 91.7 % *cis*-1,4 stereoregular.

Typical isoprene polymerisation experiment with 1a/L^1/[CPh$_3$B][(C$_6$F$_5$)$_4$]/Al(^{i}Bu)$_3$ (run 2.11, table 2): In a glove box under argon (H$_2$O and O$_2$ < 2 ppm), 2.8 mg of complex Cp*Sc(BH$_4$)$_2$(THF) **1a** (1×10^{-5} mol) are dissolved in 0.5 mL of dry and degassed toluene. 1 equivalent of L^1 ligand (1.8 mg, 1×10^{-5} mol) was added under stirring. After several minutes, 2 equivalents of [CPh$_3$B][(C$_6$F$_5$)$_4$] (18 mg, 2×10^{-5}mol) were then added also under stirring and an orange solution was obtained. 10 equivalents of Al(^{i}Bu)$_3$ (d = 0.786, 28 μL, 1×10^{-4} mol) were then added with a microsyringe and after several minutes the solution turns to pale orange. 0.5 mL of isoprene (5×10^{-3} mol) was then added, and the reaction was carried out at 20°C. After 3 min the reaction medium is completely solid. The reaction was quenched by adding a THF solution containing some methanol drops. The polymer was poured in a large amount of methanol, filtered and dried under vacuum. The yield reaches 100%, the average molecular weight of the obtained polymer is M_n = 13900 g/mol, and the polydispersity index of 5.1. ^{1}H and ^{13}C NMR analyses in CDCl$_3$ showed that the polyisoprene obtained was 55.8 % *3,4*-stereoregular.

Typical isoprene polymerisation experiment with 1b/HL^{2Mes}/ ^{n}BuEtMg/[CPh$_3$B][(C$_6$F$_5$)$_4$]/Al(^{i}Bu)$_3$ (run 2.10, table 2): In a glove box under argon (H$_2$O and O$_2$ < 2 ppm), 4.5 mg of complex Cp*Nd(BH$_4$)$_2$(THF)$_2$ **1b** (1×10^{-5} mol) are dissolved in 0.5 mL of dry and degassed toluene. 1 equivalent of HL^{2-Mes} ligand (3.6 mg, 1×10^{-5} mol) was added under stirring, followed by 0.5 equivalent of ^{n}BuEtMg (BEM, 20 wt% in hexanes, 4μL, 5×10^{-6} mol). After several minutes, two equivalents of [CPh$_3$B][(C$_6$F$_5$)$_4$] (18 mg, 2×10^{-5}mol) were then added also under stirring and a green-brown solution was obtained. 10 equivalents of Al(^{i}Bu)$_3$ (d = 0.786, 28 μL, 1×10^{-4} mol) were then added with a microsyringe. 0.5 mL of isoprene (5×10^{-3} mol) was then added, and the reaction was carried out at 20 °C for 65 h. At

the end of the reaction the medium was viscous. The reaction was quenched by adding some methanol drops, and then dissolved in THF. The polymer was poured in a large amount of methanol, filtered and dried under vacuum. The yield reaches 100%, the average molecular weight of the obtained polymer is M_n = 17100 g/mol, and the polydispersity index of 1.9. ^{1}H and ^{13}C NMR analyses in CDCl$_3$ showed that the polyisoprene obtained was 68.9 % *trans*-stereospecific.

† Foot note: ^{1}H NMR signals of Cp*Nd(BH$_4$)$_2$(THF)$_x$: when freshly synthesized, Cp*Nd(BH$_4$)$_2$(THF)$_2$ is a monomer bearing two THF molecules (^{1}H NMR, THF-d_8, δCp*= 7.4 ppm, δBH$_4$ = 69 ppm, ref. 33). With time, this complex tends to clustering as a desolvated hexamer leading to the appearance of a new BH$_4$ signal at 96 ppm either in THF-d_8 or benzene-d_6. This cannot be attributed to Nd(BH$_4$)$_3$(THF)$_3$ which gives a BH$_4$ signal at 92 ppm in THF-d_8. The X-Ray structure of the hexamer **1b'** [Cp*Nd(BH$_4$)$_2$]$_6$ is available in the ESI (CCDC 892289). A similar hexamer [Cp$^{(Me4nPr)}$Nd(BH$_4$)$_2$]$_6$ was already reported.[30]

‡ Electronic supplementary information (ESI) available: crystallographic data of compounds **1b** CCDC 892290 and **1b'** CCDC892289. For crystallographic data in CIF see DOI: XX

References.

[1] *Science and Technology of Rubber*, 3rd edition, ed. J. E. Mark, B. Erman and F. R. Eirich, Elsevier, 2005.

[2] L. Friebe, O. Nuyken and W. Obrecht, *Adv. Polym. Sci*., 2006, **204**, 1.

[3] Z. Zhang, D. Cui, B. Wang, B. Liu and Y. Yang, *Struct. Bond*, 2010, **137**, 49.

[4] Z. Jian and D. Cui, *Dalton Trans.*, 2012, **41**, 2367.

[5] S. Loughmari, A. Hafid, A. Bouazza, A. El Bouadili, P. Zinck and M. Visseaux, *J. Polym. Sci. (A): Polym Chem.*, 2012, **50**, 2898.

[6] G. Du, Y. Wei, L. Ai, Y. Chen, Q. Xu, X. Liu, S. Zhang, Z. Hou and X. Li, *Organometallics*, 2011, **30**, 160.

[7] Y. Luo, S. Fan, J. Yang, J. Fang and P. Xu, *Dalton Trans.*, 2011, **40**, 3053.

[8] Z. Jian, S. Tang and D. Cui, *Chem. Eur. J.*, 2010, **16**, 14007.

[9] R. Litlabø, M. Enders, K. W. Tornroos and R. Anwander, *Organometallics*, 2010, **29**, 2588.

[10] A. Valente, P. Zinck, M. J. Vitorino, A. Mortreux and M. Visseaux, *J. Polym. Sci. (A): Polym. Chem.*, 2010, **48**, 4640.

[11] D. Robert, E. Abinet, T. P. Spaniol and J. Okuda, *Chem. Eur. J.*, 2009, **15**, 11937.

[12] M. Visseaux and F. Bonnet, *Coord. Chem. Rev.*, 2011, **255**, 374.

[13] Z. Hou, Y. Luo and X. Li, *J. Organomet. Chem.*, 2006, **691**, 3114.

[14] F. Bonnet, M. Visseaux, A. Pereira and D. Barbier-Baudry, *Macromolecules,* 2005, **38***, 3162.

[15] J. Cheng and Z. Hou, *Sci China Chem*, 2011, **54**, 2032.

[16] F. Bonnet, C. Da Costa Violante, P. Roussel, A. Mortreux and M. Visseaux, *Chem. Commun.*, 2009, 3380.

[17] L. Zhang, M. Nishiura, M. Yuki, Y. Luo and Z. Hou, *Angew. Chem. Int. Ed.,* 2008, **47**, 2642.

[18] N. Ajellal, L. Furlan, C. M. Thomas, O. L. Casagrande, Jr. and J. F. Carpentier, *Macromol. Rapid Commun.*, 2006, **27**, 338.

[19] C. S. Tredget, F. Bonnet, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2005, **26**, 3301.

[20] L. Lukesova, B. D. Ward, S. Bellemin-Laponnaz, H. Wadepohl, and L. H. Gade, *Organometallics,* 2007**, 26***, 4652.

[21] P. L. Arnold and I. J. Casely, *Chem. Rev*., 2009, **109**, 3599.

[22] W. Fegler, T. P. Spaniol and Jun Okuda**, *Dalton Trans.*, 2010, **39**, 6774.

[23] S. Arndt and J. Okuda, *Chem. Rev*., 2002, **102**, 1953.

[24] H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev*., 1995, **95**, 865.

[25] R. Qi, B. Liu, X. Xu, Z. Yang, Y. Yao, Y. Zhang and Q. Shen, *Dalton Trans*., 2008, 5016.

[26] H. J. Heeres, A. Meetsma and J. H. Teuben, *Organometallics*, 1989, **8**, 2637.

[27] H. van der Heljden, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1989, **8**, 255.

[28] H. M. Dietrich, C. Zapilko, E. Herdtweck, and R. Anwander, *Organometallics*, 2005, **24**, 5767.

[29] R. Anwander, *Angew. Chem., Int. Ed.*, 1998, **37**, 599.

[30] F. Bonnet, M. Visseaux, D. Barbier-Baudry, A. Hafid, E. Vigier and M.M. Kubicki, *Inorg. Chem.*, 2004, **43**, 3682.

[31] D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann and M. Visseaux, *Eur. J. Inorg. Chem.*, 2000, 2333.

[32] M. Visseaux, P. Zinck, M. Terrier, A. Mortreux and P. Roussel, *J. Alloys Compd.*, 2008, **451**, 352.

[33] S.M. Cendrowski-Guillaume, G. Le Gland, M. Nierlich and M. Ephritikhine, *Organometallics*, 2000, **19**, 5654.

[34] L. Wang, D. Liu, D. Cui., *Organometallics*, 2012, **31**, 6014

[35] 75.2 % *cis*-polybutadiene was obtained at 65 °C with a bisiminomethylpyrrolyl supported neodymium borohydride in comparable catalytic combinations, see: J. Jenter, N. Meyer, P.W. Roesky, S. K. H. Thiele, G. Eickerling and W. Scherer, *Chem. Eur. J.*, 2010, **16**, 5472.

[36] M. Visseaux, M. Mainil, M. Terrier, A. Mortreux, P. Roussel, T. Mathivet and M. Destarac, *Dalton Trans.*, 2008, 4558.

[37] Y. Luo, J. Baldamus, and Z. Hou, *J. Am. Chem. Soc.* 2004, **126**, 13910.

[38] P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.,* 2003, **42**, 5981.

[39] P. L. Arnold, M. Rodden and C. Wilson, *Chem. Commun.*, 2005, 1743.

[40] D. Baudry-Barbier, N. Andre, A. Dormond, C. Pardes, P. Richard, M. Visseaux and C. J. Zhu, *Eur. J. Inorg. Chem.*, 1998, 1721.

[41] L. Friebe, O. Nuyken, H. Windisch, W. Obrecht, *Macromol. Chem. Phys.*, 2002, **203**, 1055.

[42] S. Li, D. Cui, D. Li and Z. Hou, *Organometallics*, 2009, **28**, 4814.

[43] H. Iovu, G. Hubca, E. Simionescu, E.G. Badea, M. Dimonie, *Angew. Makromol. Chem.*, 1997, **249**, 59.

[44] B. L. Wang, D. Wang, D. M. Cui, W. Gao, T. Tang, X. S. Chen and X. B. Jing, *Organometallics*, 2007, **26**, 3167.

[45] B. Wang, D. Cui and K. Lv, *Macromolecules,* 2008, **41**, 1983.

[46] M. Terrier, M. Visseaux, T. Chenal and A. Mortreux, *J. Pol. Sci. Pol. Chem. A*, 2007, **45**, 2400.

[47] L. Mirsaidov, I. B. Shaimuradov, M. Khikmatov, *Russian Journal of Inorganic Chemistry,* 1986, **31(5)**, 753.

[48] J. Richter and F. T. Edelmann, *Eur. J. Solid State Inorg. Chem.* 1996, **33**, 1063.

[49] P. Zinck, M. Terrier, A. Mortreux and M. Visseaux A. *Polym Test*, 2009, **28**, 106.

[50] L. Palatinus, and G. Chapuis, *J. Appl. Cryst.* 2007, **40**, 786.

[51] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

[52] V. Petricek, M. Dusek, and L. Palatinus, 2000. Jana2000. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic.