Genuine Heteroleptic Complexes of Early Rare-Earth Metals: Synthesis, X-ray Structure, and Their Use for Stereospecific Isoprene Polymerization Catalysis

Fanny Bonnet,[b] Marc Visseaux,*[a] Denise Barbier-Baudry,[b] Estelle Vigier,[b] and Marek M. Kubicki[b]

Abstract: Genuine heteroleptic neodymium and samarium complexes of formula [Cp*′Ln{(*p*-tol)NN}(BH_4)] (Cp*′ = C_5Me_4(*n*Pr), (*p*-tol)NN = (*p*-tol)-NC(Me)CHC(Me)N(*p*-tol), Ln = Sm: **1a**, Ln = Nd: **1b**) have been synthesized for the first time. These unprecedented homologues of early lanthanocenes are prepared by a metathetic reaction between their monocyclopentadienylbisborohydrido precursors with the corresponding potassium diketiminate. Both complexes were obtained in good yields and were characterized by ^{1}H NMR spectroscopy and elemental analysis. Complex **1a** has an non-solvated dimeric structure, as indicated by its crystallographic data. The chloroneodymium analogue [Cp*′Nd{(*p*-tol)NN}(Cl)] (**2b**) was only obtained as a part of a mixture. Analysis of crystals of **2b** by X-ray diffraction revealed a molecular structure very similar to that of **1a**. Preliminary isoprene polymerization experiments were carried out with **1b** in the presence of an alkylmagnesium coactivator. The resulting bimetallic Nd/Mg system behaves as an efficient and highly stereospecific catalyst with the synthesis of *trans*-1,4-polyisoprene with more than 98% regularity. The control of the polymer structure is related to the steric hindrance around the lanthanide atom.

Keywords: borohydrides • catalysis • neodymium • polymerization • samarium

Introduction

Lanthanide catalysts are nowadays widely employed in the field of coordination polymerization because they can produce high added-value polymers or copolymers.[1–5] They can also work without conventional aluminum additives to afford materials that do not contain traces of toxic metals.[6,7]

We recently described an ansa-samarocene catalyst capable of carrying out, for the first time, the controlled copolymerization of isoprene with terminal olefins,[8] and/or with ε-caprolactone.[9] All the copolymers prepared were based on a 1,4-*trans* polydiene backbone, which was unambiguously related to the molecular structure of the samarium catalyst.[10] Also, there is no doubt that the possibility of copolymerization of a diene with olefins was associated with the formation of these sequences of *trans*-homopolymers.[10,11] Nevertheless, a small percentage of *cis*-polydiene moieties remained in our copolymers so that our subsequent research efforts were aimed at producing catalysts with a better *trans*-specificity.

To obtain *trans*-selectivity, a catalyst is required that affords only one or two vacant sites.[12,13] The larger early lanthanides, the best candidates for polymerization, must be surrounded by bulky ligands. However, such bulky ligands, which are also often good electron donors, do not facilitate the coordination of a monomer to the metal. For example, the metallocenes [$(C_5R_5)_2$LnR] are not efficient in diene polymerization,[14] whereas the above-mentioned ansa-samarocene exhibits good activity.

As an alternative to the classical metallocenes, we chose to elaborate "genuine heteroleptic" complexes. "Heteroleptic" complexes of lanthanides have been reviewed;[15] however, these reviews deal with complexes of the general formula [LnY_2Z], which are closer to being "non-homoleptic". Actually, structurally characterized lanthanide complexes of general formula [LnXYZ] bearing three different anionic li-

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[a] Prof. Dr. M. Visseaux
Laboratoire de Catalyse de Lille
CNRS UMR 8010, Université des Sciences et Technologies de Lille
Bat. C7, Cité Scientifique, BP 108
59652 Villeneuve d'Ascq Cedex (France)
E-mail: marc.visseau@ensc-lille.fr

[b] Dr. F. Bonnet, Dr. D. Barbier-Baudry, E. Vigier,
Prof. Dr. M. M. Kubicki
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques
Crystallography Group, CNRS UMR 5188, Université de Dijon
9 Avenue A. Savary, BP 47870, 21078 Dijon cedex (France)
Fax: (+33) 380-396084

[+] LSEO crystallography group.

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gands are very scarce,[16] they are mainly limited to the late lanthanides[17] or to divalent Sm compounds.[18] Our heteroleptic complexes contain one substituted Cp ligand, commercially available tetramethylpropylcyclopentadienyl C_5Me_4nPr (abbreviated here as Cp*′), and a diketiminate ligand, (*p*-tol)NC(Me)CHC(Me)N(*p*-tol) (abbreviated to (*p*-tol)NN) which is supposed to have a lower propensity for electron donation.[19] These anions have been widely used to synthesise a large number of metal complexes,[20–23] including lanthanides,[24–27] some of which are efficient catalysts.[28–31]

Herein, we present the syntheses and characterization of a series of new genuine heteroleptic complexes. We include X-ray data and some preliminary results on their potential utilization as stereospecific polymerization catalysts.

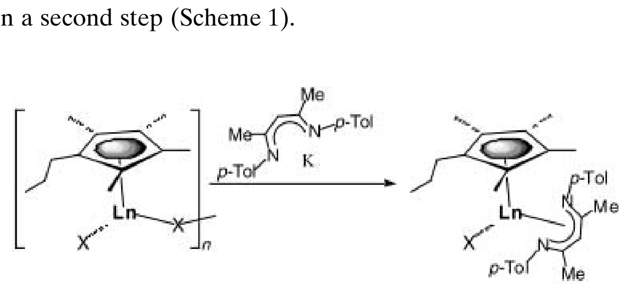
Results

Organometallic complexes

Preliminary studies: Our initial approach was to use a one-pot synthesis: the three components LnX_3 (Ln = Nd, Sm; X = Cl, BH_4), (*p*-tol)NNK, and Cp*′K were mixed with the appropriate stoichiometry. We realized that this was not a good strategy because the formation of homoleptic $[\{(p\text{-tol})NN\}_3Ln]$ complexes occurred immediately, as established by NMR experiments (see the chloride complexes in the Experimental Section). Moreover, signals identical to those observed after mixing $[LnCl_3(thf)_3]$ with only Cp*′K were detected. However, these signals decreased significantly after a few hours, which indicated some ligand-exchange reactions. Hence, the comproportionation leading to the expected compound did occur [Eq. (1)], but not completely, even

$$2/3\,[\{(p\text{-tol})NN\}_3Ln] + [Cp^{*\prime}_2LnX]' \rightleftharpoons 2\,[Cp^{*\prime}Ln\{(p\text{-tol})NN\}X] \qquad (1)$$

after a few days. This can probably be attributed to the high stability of the sterically hindered $[\{(p\text{-tol})NN\}_3Ln]$ and $[Cp^{*\prime}_2LnX]$ complexes. Comparable behavior that led to ligand-redistributed products was recently observed during the tentative syntheses of cyclopentadienyldiketiminato complexes of ytterbium.[32]We had previously obtained monocyclopentadienyl derivatives of Nd and Sm by a simple metathetic reaction of the inorganic precursors $[LnX_3(thf)_3]$ (X = Cl or BH_4) with the bulky $Cp^{*\prime -}$ ion.[33] These derivatives could be convenient starting materials to afford the expected heteroleptic cyclopentadienyldiketiminato complexes in a second step (Scheme 1).



Scheme 1. Schematic pathway of synthesis of the heteroleptic complexes.

We conducted preliminary syntheses from the soluble borohydrides on the NMR scale with deuterated benzene (THF is necessary, at least in the first step, if chlorides are chosen as the starting material). It was rapidly established that $[Cp^{*\prime}Sm\{(p\text{-tol})NN\}(BH_4)]$ formed readily, and that the bulk syntheses were then carried out.

Synthesis of the heteroleptic borohydride complexes: Two complexes $[Cp^{*\prime}Ln\{(p\text{-tol})NN\}(BH_4)]$ (Ln = Sm, **1a**; Ln = Nd, **1b**) were synthesized from the direct metathetic reaction of their monocyclopentadienyl precursors, $[Cp^{*\prime}Sm(BH_4)_2(thf)]$ and $[Cp^{*\prime}Nd(BH_4)_2(thf)_2]$,[33] with anionic $\{(p\text{-tol})NN\}K$ [Eq. (2)]. We had already used this strategy to prepare the complexes $[(Cp^{4i})_2Ln(BH_4)]$ ($Cp^{4i} = C_5HiPr_4$),[34] and the same synthetic pathway was employed for the synthesis of $[Cp^*Nd(BH_4)_2(thf)_2]$.[35] Conversely, Schumann et al. obtained $[(C_5Me_4iPr)_2Sm(BH_4)(thf)]$ from $[SmCl_3(thf)_3]$ by successive substitutions of the chloride ligands with $(C_5Me_4iPr)Na$, then with $NaBH_4$.[36]

$$\begin{aligned}&[Cp^{*\prime}Ln(BH_4)_2(thf)_n] + K\{(p\text{-tol})NN\}\\ &\rightarrow [Cp^{*\prime}Ln\{(p\text{-tol})NN\}(BH_4)] + KBH_4 + n\,THF \qquad (2)\\ &Ln = Sm: \mathbf{1a};\ Nd: \mathbf{1b}\end{aligned}$$

Although **1a** (Ln = Sm) was prepared in toluene, whereas THF was used for the synthesis of **1b** (Ln = Nd), both complexes were isolated nonsolvated, as indicated by ^1H NMR spectroscopy and elemental analyses.

The borohydride signal in **1a** was recorded at $\delta = -9.3$ ppm in C_6D_6. This value lies between that recorded for the non-solvated monomer $[(Cp^{4i})_2Sm(BH_4)]$ ($\delta = -7.5$ ppm)[34] and the THF adducts $[(C_5Me_4iPr)_2Sm(BH_4)(thf)]$ ($\delta = -16.4$ ppm)[36] and $[(Cp^{*\prime})_2Sm(BH_4)(thf)]$ ($\delta = -17.3$ ppm)[36] in the same solvent. The more paramagnetic neodymium (complex **1b**) exhibits a broad borohydride resonance only at 50 °C ($\delta = +59$ ppm); however, this value is in good agreement with that expected for a borohydridoneodymocene compound ($[(C_5H_4CH_2CH_2OCH_3)_2Nd(BH_4)]$ $\delta = 74$ ppm,[37] $[(Cp^{4i})_2Ln(BH_4)]$: $\delta = +74.4$ ppm,[34] $[(C_8H_8)Nd(BH_4)(thf)_2]$: $\delta = +44$ ppm[38]).

Crystallization of **1a** in pentane led to the isolation of bright orange crystals of which were suitable for an X-ray crystallographic study (see Experimental Section). Light blue crystals of the neodymium homologue were obtained under similar conditions. Unfortunately, a rapid alteration of these crystals was observed in the glove box. Decomposition was ruled out because the resulting green compound exhibited a clean ^1H NMR spectrum, corresponding to the formula of **1b** but with the presence of pentane. Moreover, decomposition of these compounds generally produces yellow-to-white insoluble material. A desolvation was then supposed, which is very likely since **1a** exhibited a nonsolvated dimeric structure. Indeed, it has often been observed that a pure samarium complex can be isolated, whereas the corresponding neodymium complex, which has the same framework but is a larger atom, additionally bears one coordinated or included molecule.[39] The stability of a non-solvated samarium complex implies ready desolvation of the neodymium analogues. One could suggest that the blue crystals correspond to the monomeric complex [Cp*′Nd{(*p*-tol)NN}(BH_4)(thf)], rather than the solvated dimeric complex [{Cp*′Nd[(*p*-tol)NN](BH_4)}$_2$](solvent)$_n$. However, the high rate and ease of decomposition tends to suggest a second hypothesis, namely, the incorporation of a solvent (pentane or THF) in the unit cell, and that both **1a** and **1b** were formed as dimers. The ^1H NMR spectrum of the green crystals of **1b** did indeed indicate the presence of pentane, which was subsequently removed under vacuum. Finally, elemental analysis of the latter sample established unambiguously the nonsolvated molecular structure of [Cp*′Nd{(*p*-tol)NN}(BH_4)].

X-ray structure analysis of [Cp*′Sm{(p-tol)NN}(BH_4)]$_2$ (1a): X-ray structure analysis revealed a dimeric samarium complex (Figure 1) with a disordered solvent molecule of pentane included in the asymmetric unit in a 0.25:1 ratio relative to Sm. Complex **1a** exhibits a nonsolvated dimeric structure, in accordance with the previously recorded NMR data and elemental analyses. It can be best described as a distorted tetrahedral arrangement around the Sm atom, consisting of one cyclopentadienyl, one diketiminate, and two tetrahydroborato ligands bridging through H atoms to the lanthanide. Selected bond lengths and angles are given Table 1, crystallographic data are reported in Table 2.

The Sm–CP distance (2.430 Å, where CP is the centroid of the cyclopentadienyl ligand) is typical of a large lanthanide tetrahydroboratobiscyclopentadienyl complex, as in [Cp*′Sm(BH_4)$_2$(thf)] (2.456 Å),[33] or [{(C_5H_3tBu$_2$)$_2$Sm(BH_4)}$_2$] (2.46 Å).[40] It is noteworthy that the Sm–B distances in **1a** are comparable to those observed for the abovementioned dimer: [{(C_5H_3tBu$_2$)$_2$Sm(BH_4)}$_2$], 2.83 and 2.86 Å, as well as for the solvated [(C_8H_8)Nd(BH_4)(thf)$_2$], 2.875 and 2.941 Å.[38] In the case of monomeric compounds, the BH_4 ligand is terminal and tridentate, with short Ln–B distances (≈2.6 Å).[36] A slight dissymmetry can be observed for the μ-(BH_4) bridges in **1a** (Sm–B = 2.929(3), Sm–B′ 3.006(3) Å) which reveals a possible weakness. As a consequence, this complex could be potentially reactive to the opening of the bridge between the two Ln^{III} units.

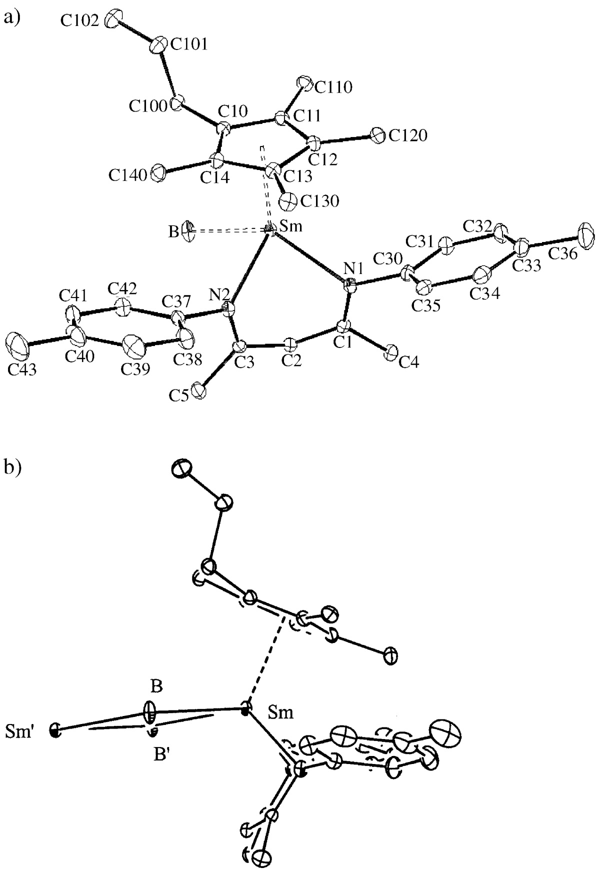


Figure 1. Structure of [{Cp*′Sm[(*p*-tol)NN](μ-BH_4)}$_2$] in **1a**·0.25 C_5H_{12} (ORTEP view; 30% probability level) showing the molecular unit (a) and the dimeric structure (b).

Table 1. Selected bond lengths [Å] and angles [°] in **1a**. CP is the centroid of C10-C11-C12-C13-C14, CP_N is the centroid of N1-N2-C1-C3.

Sm–N1	2.405(2)	Sm–CP	2.430
Sm–N2	2.385(2)	Sm–CP_N	2.176
Sm–C1	2.916(2)	N1-Sm-N2	76.54(7)
Sm–C2	2.895(2)	CP-Sm-N1	111.02
Sm–C3	2.895(2)	CP-Sm-N2	110.52
Sm–B	2.929(3)	CP-Sm-B	110.34
Sm–B′	3.006(3)	B-Sm-B′	78.85

Table 2. Crystallographic data and refinement parameters for **1a** and **2b**.

Compound	**1a**·0.25 C_5H_{12}	**2b**
color	orange	green
habit	prism	irregular
dimensions [mm^3]	0.37 × 0.20 × 0.10	0.25 × 0.10 × 0.05
chemical formula	$C_{32.25}H_{47}N_2BSm$	$C_{62}H_{80}N_4Cl_2Nd_2$
formula weight	623.88	1240.68
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
T[K]	120	120
a[Å]	11.1760(10)	13.3518(2)
b[Å]	12.4520(10)	14.0896(2)
c[Å]	13.3140(10)	16.2629(2)
α[°]	112.623(10)	87.917(1)
β[°]	104.955(10)	83.506(1)
γ[°]	93.824(10)	74.691(1)
V[$Å^3$]	1623.5(2)	2931.84(7)
Z	2	2
ρ[g cm^{-3}]	1.276	1.405
$\mu Mo_{K\alpha}$[Mm^{-1}]	1.829	1.883
$\lambda Mo_{K\alpha}$[Å]	0.71073	0.71073
F(000)	643	1268
Θ range [°]	–,–	1.018, 30.508
index ranges	$-15 \leq h \leq 14$ $-17 \leq k \leq 17$ $-18 \leq l \leq 18$	$-18 \leq h \leq 18$ $-19 \leq k \leq 19$ $-22 \leq l \leq 23$
collected reflections	14164	64763
unique reflections	7845	8611
observed reflections	6233	5668
R_{int}	0.0202	0.1081
parameters	326	465
restraints	0	0
goodness-of-fit on F^2	1.524	1.062
$R(F)$, $Rw(F^2)$[a] [$I > 2\sigma(I)$]	0.0346, 1.3427	0.0934, 0.2317
$R(F)$, $Rw(F^2)$[a] (all data)	0.0338, 0.0668	0.1453, 0.2683
w[b]/a, b	0.0346, 1.3427	0.1148, 53.2708
ρ_{max}, ρ_{min} [e Å^{-3}]	−1.308, 2.133	−3.992, 7.390

[a] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $Rw(F^2) = [\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

The diketiminate ligand exhibits a typical bonding mode for a lanthanide complex: the six-membered MNCCCN ring adopts a boat conformation, with a short Sm−C2 bond length.[19] The central carbon atom C(2) is slightly out of the N1-N2-C1-C3 plane with a deviation of 0.2546(33) Å. The Sm−CP_N (2.176 Å) distance and the Sm−N bond lengths are in the expected range for diketiminate lanthanide complexes (Figure 2).[41]

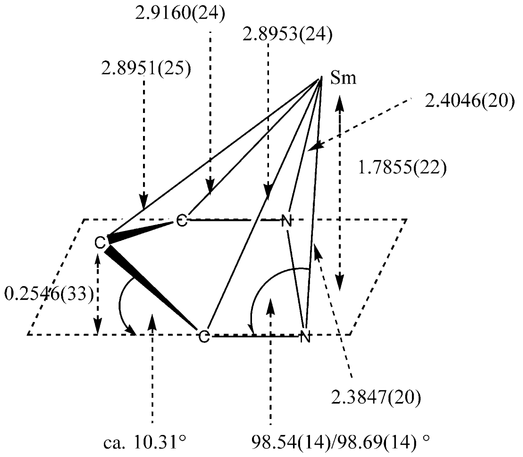


Figure 2. Bonding mode of the dikiketiminate ligand in **1a**.

Chloride complexes: The syntheses of the corresponding chloride derivatives were not as straightforward as those of the borohydrides. They were conducted in the same manner, starting from $[LnCl_3(thf)_3]$ (Ln = Sm, Nd), and compounds of general formula [Cp*′Ln{(*p*-tol)NN}(Cl)(solvent)] were expected. Unfortunately, in both cases, a sticky paste was obtained as the product of the reaction, and the elemental analyses were not satisfactory.

^{1}H NMR analyses of the crude Sm material indicated the formation of a mixture of paramagnetic compounds. Some signals were consistent with the presence of [Cp*′Sm{(*p*-tol)NN}Cl]; signals from $[\{(p\text{-tol})NN\}_3Sm]$ were also present.[42] Diamagnetic diketimine signals were also detected. It should be noted that decomposition of scandium complexes into imines has been reported.[43] Data were not interpretable in the case of Nd; however, a crop of low quality crystals of **2b** were collected. They were analyzed by X-ray diffraction. After application of an absorption correction (SORTAV[44]), the largest residual peak of 7.39 $e\text{Å}^{-3}$ was close (0.9 Å) to the Nd atom. Moreover, the high *R* value (0.0934) shows that this structure can not be considered as being be well-solved. Nevertheless, it establishes the expected molecular structure for **2b** with a neodymium atom surrounded by a Cp*′, a diketiminate, and a bridging chloro ligand: $[\{Cp^{*\prime}Nd\{(p\text{-tol})NN\}Cl\}_2]$. An idea of the structure of **2b** was gained, despite the poor quality of the crystal (Figure 3). The structure is dimeric, analogous to that of the samarium borohydride **1a**.

The crystals of the heteroleptic chloride **2b** were collected from a bulk mixture containing several products that result from ligand-redistribution reactions. We thus decided to continue our studies with the borohydride complexes.

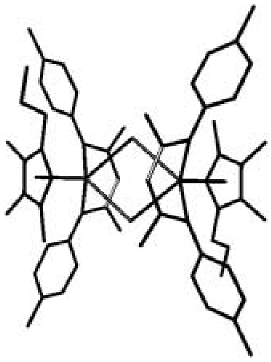


Figure 3. Schematic view of $[\{Cp^{*\prime}Nd[(p\text{-tol})NN]Cl\}_2]$ in **2b** showing its dimeric $(\mu^2\text{-}Cl)_2Nd_2$ structure.

Polymerization experiments: It was shown very recently that the trivalent pseudo-halide complex $[Nd(BH_4)_3(thf)_3]$ is an efficient initiator for the ring-opening polymerization of ε-caprolactone. The monomer first inserts into the Nd−$H(BH_3)$ bond, then propagation occurs via the resulting alkoxy moiety.[45] We have discovered that to become active towards dienes, neodymium trisborohydride must be activated with an alkylating reagent, such as $Al(Et)_3$ or Mg*n*Bu_2. The Nd/Mg system produces quantitatively *trans*-1,4-polyisoprene with more than 96 % regularity.[46]

We carried out preliminary isoprene polymerization experiments using a catalytic system made of $[\{Cp^{*\prime}Nd\{(p\text{-tol})NN\}(BH_4)\}_2]$ (**1b**) and one equivalent of Mg*n*Bu_2. The results are given in Table 3.

Good activity was observed, and highly regular (up to 98.4 %) *trans*-1,4-polyisoprene was formed. According to ^{1}H NMR spectroscopy, there is no evidence of the presence of *cis*-polyisoprene. The *trans*-stereospecificity is much better controlled than with $[Nd(BH_4)_3(thf)_3]$/Mg*n*Bu_2, and also than with the single component catalyst $[(C_5H_4CMe_2)_2Sm(allyl)ClMgCl_2Li(ether)_2]_n$.[7]

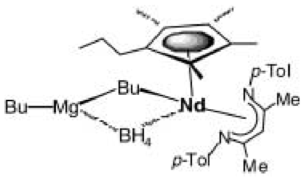
Table 3. Isoprene polymerization with **1b**/Mg*n*Bu_2.

Run[a]	$[I]_0$/[Nd]	[Mg]/[Nd]	time [h]	yield [%]	Structure[b] *trans*-1,4 [%]	*cis*-1,4 [%]	3,4 [%]
1	135	1	22	100	97.3	–	2.7
2	600	1	22	60	98.4	–	1.6

[a] Polymerization conditions: isoprene = 1 mL, toluene = 0.5 mL, *T* = 50 °C; $[I]_0$: initial isoprene concentration. [b] Determined on the basis of ^{1}H NMR integration in $CDCl_3$.

The formation of *trans*-polydienes is generally explained by the η^4 coordination of the monomer, followed by the *syn–anti* isomerization.[47] Another possibility is η^2 coordination.[7,12] In both cases, the steric hindrance around the metal center seems to be a key factor in the production of *trans*-regular polydienes.

It is well known that the reaction of a halide derivative of a lanthanide with a bisalkymagnesium affords a bimetallic bridged compound.[47,48] It is therefore reasonable to assume that the active species obtained in our case is also a bimetallic compound, and a postulated molecular structure is represented in Scheme 2.



Scheme 2. A possible molecular structure of the active bimetallic species.

The improved *trans*-stereospecificity observed with this catalyst could be attributed to the presence of both voluminous Cp*′ and diketiminate ligands, which cause a higher steric hindrance than the BH_4 in $[Nd(BH_4)_3]/MgnBu_2$. However, one can argue that the approach of the monomer to the metal center would be more difficult with **1b** rather than with $[Nd(BH_4)_3]$. But the methyne deviation observed within the diketiminate ligand (see Figures 1 and 2) could be regarded as a labile contribution which aids the coordination of a conjugated diene. This is a major difference with regard to classical metallocenes that bear six-electron donating cyclopentadienyl moieties and which are known to be inactive towards isoprene polymerization under similar conditions.

The best activity was obtained with a monomer/catalyst molar ratio of 135:1 (run 1) that gave quantitative conversion of the monomer. Molecular weights were measured by size-exclusion chromatography (SEC): $M_n = 7000$ (run 1) and 16000 (run 2). They are within the expected range of molecular weights, taking the yield of polymer into account (see Experimental Section): 9100 and 24000, respectively. More detailed studies concerning these catalytic Nd/Mg combinations are in progress.

Conclusion

We have synthesized "genuine heteroleptic" early lanthanide complexes of the general formula [Cp*′Ln{(*p*-tol)NN}X] that bear three different kinds of ionic ligands. Two of them have been structurally characterized; they exhibit a nonsolvated dimeric structure.

The synthesis of these new complexes was possible because the synthesis of their monocyclopentadienyl precursors had been mastered. An analogous Yb complex has been reported very recently. It was synthesized differently, starting from a bischloromonodiketiminate complex, which is attainable only for the smallest late lanthanides.[49]

Preliminary polymerization experiments were conducted with the borohydridoneodymium compound mixed with a magnesium activator. Good activity was observed in isoprene polymerization, allowing the formation of highly regular (98.4%) *trans*-1,4-polyisoprene. To our knowledge, this **1b**/Mg*n*Bu$_2$ catalytic system is the most *trans*-stereospecific described for homogeneous coordination polymerization of isoprene.

Finally, one may consider these heteroleptic complexes as equivalents of hindered metallocenes, but less electron-rich than the persubstituted $[Cp^{*}_2LnX]$ complexes, thus allowing the polymerization of conjugated dienes. The behavior of the "genuine heteroleptic" complexes described in this work provides support to our strategy of elaborating a new kind of lanthanide polymerization catalyst.

Experimental Section

Reagents and standards: All operations were performed under argon using standard vacuum line techniques or in an argon-filled Jacomex glove box ($O_2 < 2$ ppm). Solvents were stored over sodium/benzophenone ketyl and transferred by distillation to reaction vessels. $[LnCl_3(thf)_3]$ was prepared by THF extraction of the commercial $LnCl_3$ (STREM). $[Ln(BH_4)_3(thf)_3]$ and (*p*-tol)NNH were obtained following the published methods.[21,50] (*p*-tol)NNK was prepared by treatment of the corresponding diketimine with KH in THF. The syntheses of the monocyclopentadienyllanthanide precursors $[Cp^{*\prime}LnX_2(thf)_n]$ (Ln = Nd, Sm; X = BH_4, Cl; $n = 0, 1$),[33] as well as the ansa-samarocene catalysts[10] have been described elsewhere. Mg*n*Bu$_2$ (heptane solution, 1 M) was purchased from Aldrich.

Measurements: ^1H and ^{13}C NMR spectra were recorded on Bruker AC300 or DRX500 spectrometers (300 K, C_6D_6 solutions or if necessary, 370 K, deuterated toluene). X-ray analyses were carried out on a Nonius Kappa CCD diffractometer at 120.0(2) K with $Mo_{K\alpha}$ radiation (graphite monochromator, $\lambda = 0.71073$ Å). The measured intensities were reduced with the DENZO program.[51] The heavy atoms were located by using the Dirdif-99.2 package.[52]All models were further refined with full-matrix least-squares methods (SHELXL97) based on $|F^2|$.[53] All non-hydrogen atoms of **1a** were refined with anisotropic thermal parameters, except those constituting the solvent molecule. In **2b**, only the Nd atoms as well as the N and C atoms constituting the ring of the diketiminate ligand were refined with anisotropic thermal parameters. All the hydrogen atoms were included in calculated positions and refined with a riding model. Crystallographic data and refinement parameters are gathered in Table 2. CCDC-209562 (**1a**) and CCDC-209563 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336033; or deposit@ccdc.cam.uk). Size-exclusion chromatography (SEC) analyses were carried out on a Gynkotek P580A apparatus equipped with two Jordi Gel DVB mixed B columns and an IOTA2 refractive index detector. Polystyrene standards were used for column calibration, and Mark–Houwink corrections were performed to determine the absolute values of the molecular weights. Theoretical values of molecular weights were calculated according to the formula: yield × ($[I]_0$/[Nd]). Polymers samples were dissolved in THF (10 mg mL^{-1}) and elution was performed with THF at 20 °C at a flow rate of 1 mL min^{-1}.

Polymerizations: Isoprene was dried over calcium hydride, stored under argon on molecular sieves and then distilled twice before use. The polymerizations were performed under argon in a Jacomex glove box with standard vacuum line techniques. Typical experiment: inside the glove box, the organometallic catalyst (5–10 mg) was weighed into a flask, toluene (1 mL), the corresponding amount of Mg*n*Bu$_2$ (1 M heptane solution) and the diene (1 mL) were added with a syringe. The flask was placed in a thermostated bath at 50 °C for a given time, or until the formation of a highly viscous material that impeded the magnetic stirring. The flask was opened, toluene (5 mL) was added to dissolve the mixture, and the solution was poured into ethanol (100 mL), with vigorous stirring.

Synthesis of [Cp*′Sm{(*p*-tol)NN}(BH$_4$)] (1a): $[Cp^{*\prime}Sm(BH_4)_2(thf)]$ (685 mg, 1.65 mmol) and (*p*-tol)NNK (527 mg, 1.66 mmol) were weighed into a vessel in the glove box. The vessel was connected to the vacuum line and toluene (30 mL) was distilled into it. After the mixture had been stirred overnight at room temperature, a brown-yellow solution was obtained, no significant amounts of precipitated inorganic salts were observed. The mixture was pumped dry, pentane was added, and the clear orange-red solution was separated from the colorless salts. After concentration, some microcrystals formed. The flask was left without stirring for 12 h. Crystals suitable for a structure determination were obtained. After 24 h at room temperature, a second crop of **1a** was obtained (total yield: 650 mg, 65 %). ^{1}H NMR (300 MHz, C$_6$D$_6$, 323 K, TMS): δ = 3.28 (s, 6H; CH$_3$, (*p*-tol)NN), 1.09 (s, 6H; CH$_3$, Cp*′), 0.30 (s, 6H; CH$_3$, Cp*′), 0.23 (s, 6H; CH$_3$, (*p*-tol)NN), 2.53 (br, 2H; CH$_2$), 1.26 (br, 2H; CH$_2$), 1.22 (t, 3H; CH$_3$), 3.7 (br, 4H; (*p*-tol)NN), −0.27 (br, 4H; (*p*-tol)NN), 10.16 (s, 1H; (*p*-tol)NN), −9.3 ppm (br, 4H; BH$_4$); elemental analysis calcd (%) for C$_{31}$H$_{44}$BN$_2$Sm (605.9): C 61.45, H 7.32, N 4.62; found: C 61.51, H 7.24, N 4.60.

Synthesis of [Cp*′Nd{(*p*-tol)NN}(BH$_4$)] (1b): [Cp*′Nd(BH$_4$)(thf)$_2$] (367 mg, 0.77 mmol) and (*p*-tol)NNK (286 mg, 0.9 mmol) were dissolved in THF (40 mL). After the mixture had been stirred overnight at room temperature, a greenish orange solution with a pale precipitate was obtained. After decantation and filtration, the remaining salts were washed with solvent (5 mL). The organic layers were combined and evaporated, leading to an oily material. A second precipitation of salts was observed after the addition of pentane (10 mL). The clear pentane solution was separated, and then slowly concentrated until some microcrystals formed. After the mixture had been left overnight at −30 °C and one day at room temperature, well-formed blue crystals were obtained. They were isolated, and selected crystals were mounted in the glove box for the crystal structure determination. The crystals immediately turned into an opaque green material, corresponding to the molecular formula of **1b**. A second crop of unsuitable crystals was obtained and collected (total yield: 275 mg, 60 %). The remaining pentane solution was evaporated to give a viscous, greenish orange oil. ^{1}H NMR (300 MHz, C$_6$D$_6$, 300 K, TMS): δ = 9.50 (s, 6H; CH$_3$, Cp*′), 8.71 (s, 6H; CH$_3$, Cp*′), 4.82 (s, 6H; CH$_3$, (*p*-tol)NN), −1.80 (s, 6H; CH$_3$, (*p*-tol)NN), 2.91 (br, 2H; CH$_2$), 2.41 (br, 5H; CH$_2$CH$_3$), 24 (s, 1H; (*p*-tol)NN), 59 ppm (only visible at 323 K, br, 4H; BH$_4$); Ar (4 H + 4H; (*p*-tol)NN): signals not located; elemental analysis calcd (%) for C$_{31}$H$_{44}$BN$_2$Nd (599.8): C 62.08, H 7.32, N 4.67; found: C 62.36, H 7.36, N 4.76.

Synthesis of chloro complexes: The procedure used was identical to that described for the synthesis of **1a**, starting from [Cp*′SmCl$_2$)(thf)] (500 mg, 1.10 mmol), and (*p*-tol)NNK (346 mg, 1.10 mmol). Slow evaporation of the pentane filtrate led to a yellow-orange oil. A sticky solid was finally obtained after prolonged evacuation, and satisfactory elemental analyses could not be achieved. ^{1}H NMR spectroscopy (300 MHz; [D$_8$]THF, 300 K, TMS) showed the formation of a mixture: in addition to four new signals, indicating the presence of [Cp*′Sm{(*p*-tol)NN}Cl], δ = 3.06, 1.78, 1.06, 1.05 ppm (MeCp, Me(*p*-tol)), a set of known signals, those of [{(*p*-tol)NN}$_3$Sm], and of (*p*-tol)NNH were present. The heteroleptic [Cp*′Sm{(*p*-tol)NN}Cl] could not be isolated.

[Cp*′Nd{(*p*-tol)NN}Cl]$_2$ (2b): [Cp*′NdCl$_2$(thf)] (crude solvated material, 400 mg, 0.88 mmol), and (*p*-tol)NNK (280 mg, 0.88 mmol) were dissolved in THF (40 mL). After the mixture had been stirred overnight at room temperature, a greenish orange solution with a very small quantity of pale precipitate was obtained. After decantation and filtration, the solvent was evaporated to give a greenish orange oil. After addition of pentane (15 mL), only a part of this material dissolved. On addition of THF (15 mL), the entire colored organometallic compound dissolved and additional colorless salts deposited. As the salts were being separated by filtration, small green crystals began to grow. After one day, they were bigger and were suitable for X-ray analysis (35 mg, 6 %). The remaining solution was evaporated to dryness to afford a green sticky paste which did not give satisfactory elemental analysis data. The crystals were found to be insoluble in C$_6$D$_6$, and the NMR spectrum obtained in deuterated THF was not interpretable. However, X-ray analysis did reveal a dimeric structure: [{Cp*′Nd{(*p*-tol)NN}Cl}$_2$](**2b**).

NMR synthesis: A reaction was monitored in an NMR tube charged with [NdCl$_3$(thf)$_3$], (*p*-tol)NNK, and Cp*′K into which deuterated THF was condensed. After a few minutes, a very complicated spectrum was recorded in which several sets of signals were superimposed. One of these sets of signals was also observed in the spectrum of a 3:1 stoichiometric mixture of (*p*-tol)NNK and [NdCl$_3$(thf)$_3$]. These signals were attributed to the homoleptic [{(*p*-tol)NN}$_3$Nd] compound. After a few hours the spectrum changed and became less complex; however, the tube obviously still contained a mixture of compounds.

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