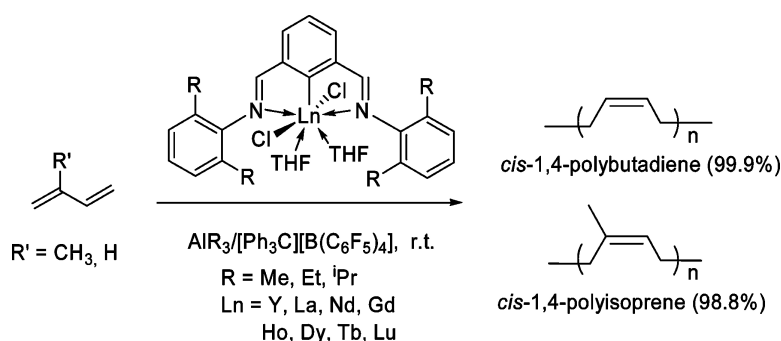# Highly *cis*-1,4 Selective Polymerization of Dienes with Homogeneous Ziegler−Natta Catalysts Based on NCN-Pincer Rare Earth Metal Dichloride Precursors

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Highly *cis*-1,4 Selective Polymerization of Dienes with Homogeneous Ziegler−Natta Catalysts Based on NCN-Pincer Rare Earth Metal Dichloride Precursors

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Abstract: The first aryldiimine NCN-pincer ligated rare earth metal dichlorides (2,6-(2,6-C$_6$H$_3$R$_2$N=CH)$_2$-C$_6$H$_3$)LnCl$_2$(THF)$_2$ (Ln = Y, R = Me (**1**), Et (**2**), ^{i}Pr (**3**); R = Et, Ln = La (**4**), Nd (**5**), Gd (**6**), Sm (**7**), Eu (**8**), Tb (**9**), Dy (**10**), Ho (**11**), Yb (**12**), Lu (**13**)) were successfully synthesized via transmetalation between 2,6-(2,6-C$_6$H$_3$-R$_2$N=CH)$_2$-C$_6$H$_3$Li and LnCl$_3$(THF)$_{1\sim3.5}$. These complexes are isostructural monomers with two coordinating THF molecules, where the pincer ligand coordinates to the central metal ion in a κC:κN:κN' tridentate mode, adopting a meridional geometry. Complexes **1**−**6**, **9**−**11**, and **13** combined with aluminum tris(alkyl)s and [Ph$_3$C][B(C$_6$F$_5$)$_4$] established a homogeneous Ziegler−Natta catalyst system, which exhibited high activities and excellent *cis*-1,4 selectivities for the polymerizations of butadiene (T_p = 25 °C, 99.9%; 0 °C, 100%) and isoprene (T_p = 25 °C, 98.8%). Remarkably, such high *cis*-1,4 selectivity almost remained at elevated polymerization temperatures up to 80 °C and did not vary with the type of the central lanthanide element, however, which was influenced obviously by the ortho substituent of the *N*-aryl ring of the ligands and the bulkiness of the aluminum alkyls. The Ln-Al bimetallic cations were considered as the active species. These results shed new light on improving the catalytic performance of the conventional Ziegler−Natta catalysts for the specific selective polymerization of dienes.

Introduction

cis-1,4 selective polymerization of dienes is a very important process in the chemical industry to afford products that are among the most significant and widely used rubbers.[1] It is believed that a slight increase in the *cis*-1,4 regularity of the product leads to a great improvement in the elastic properties.[2] Thus, the investigation of new catalyst systems that are homogeneous, well-defined, straightforward and high yielding in synthesis, thermostable, and providing over 98% *cis*-1,4 selectivity has been one of the most fascinating and challenging subjects in both academic and industrial fields. The transition metal η^3-allyl derivatives,[3] the homogeneous Ziegler−Natta catalyst systems composed of lanthanide (Ln) carboxylates (including phosphates)[4] or alkoxides[5] and co-activators aluminum alkyls or aluminum alkyl chlorides, have been investigated extensively and industrially applied.[6] Among these catalysts, the Ln-based mixtures are superior with respect to the activity and the *cis*-1,4 selectivity (>97%) to provide polymers with

outstanding characteristics such as excellent abrasion and cracking resistance, raw polymer strength, and high tensile strength of the vulcanizates. For these industrial recipes, little is known about the structures of the precatalysts; however, it is commonly accepted that the active rare earth metal center involves the formation of an active Ln-alkyl or Ln-H species and cationation via Al-to-Ln chloride transfer.[7] Therefore, well-defined Ln−C bond containing complexes, for instance, lanthanide-based metallocene alkyl complexes,[8] lanthanocene

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‡ Jilin University.
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Scheme 1. Synthesis of Aryldiimino NCN-Pincer Rare Earth Metal Dichlorides via Transmetalation
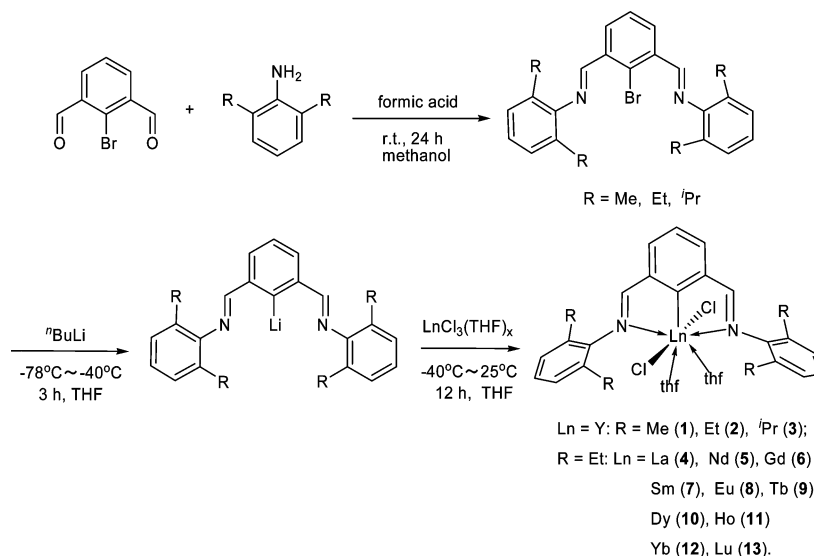
aluminates,[9] and alkyl bridged lanthanide carboxylates,[10] were developed. With these systems, more controllable or even living polymerization of butadiene can be achieved with a *cis*-1,4 selectivity within 97−99% or as high as 99.9% if performing the polymerization at low temperatures. These systems are strongly metal-dependent, showing intrinsic Nd[7b,10] or Sm and Gd[8,9] effects. Recently, yttrium alkyl dications have been reported to be highly active and showed a 97% *cis*-1,4 selectivity for the polymerization of isoprene.[11] Meanwhile, another cationic system based on lanthanide alkyls bearing the PNP-type auxiliary ligand[12] has received an upsurge in research interest, providing the living polymerization of dienes and an over 99% *cis*-1,4 selectivity, whereas the central metals are restricted to the late lanthanide elements.

Ziegler−Natta catalysts based on Ti, Co, Ni, and Nd metal chlorides, first innovated to initiate the polymerization of butadiene in the early 1960s, are highly active to give polymers with 98% *cis*-1,4 selectivity but are heterogeneous, leading to gel formation.[13,14] The addition of an electron donor to lanthanide trichlorides improves the catalytic activity and selectivity

slightly, whereas the system is still heterogeneous.[4a,15] Modifying the lanthanide chloride species with cylopentadienyl or silylene-bridged cyclopentadienyl fluorenyl moieties generates an inert system for the polymerization of butadiene, which is active for copolymerization with ethylene, affording *trans*-1,4-butenyl units.[8,16]

We have been interested in pincer ligated complexes[17] in a general formula of [(ECE)M] (E = PR$_2$, SR, NR$_2$) because the symmetrically coordinating geometry and the electron donating nature of such a ligand are anticipated to induce specific selectivity to the metal center. Pincer complexes based on the Ru, Os,[18] Ni,[19] Pd,[20] Pt,[21] and Rh[22] etc. transition metals have attracted widespread interest in catalysis on Heck coupling and C−C bond formation reactions and material science,[23] whereas the rare earth metal counterparts have been exploited less. The only reported rare earth metal complexes are stabilized by an aryldiamino NCN-pincer ligand that is not suitable for preparing the corresponding analogues based on lanthanide elements with a large ionic radius,[24] and their chemistry is unknown.
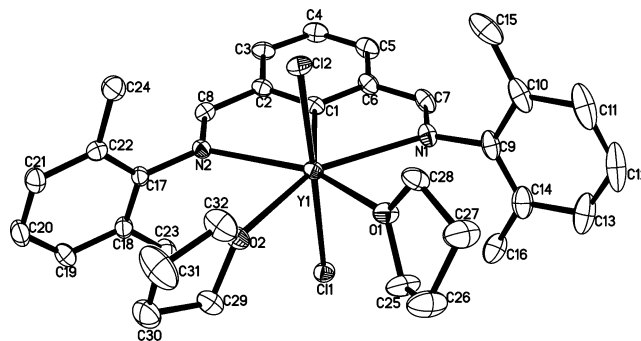
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Herein, we report the first successful synthesis of aryldiimino NCN-pincer stabilized rare earth metal dichlorides via trans-metalation methodology. These complexes in combination with aluminum alkyls and organoborate generated a new type of homogeneous Ziegler−Natta catalyst system that displayed high activities and distinguished *cis*-1,4 selectivities for the polymerizations of butadiene and isoprene. These excellent catalytic performances did not show an obvious metal-type dependence except for the inert Yb, Sm, and Eu counterparts but were influenced significantly by the spacial sterics of the auxiliary ligand and the aluminum alkyl. Remarkably, the high *cis*-1,4 selectivity remained at elevated polymerization temperatures up to 80 °C. These results are in striking contrast to the conventional Ziegler−Natta systems in the specific selective polymerization of dienes. The living species and the probable mechanism are also presented.

Results and Discussion

Synthesis and Characterization of Aryldiimino NCN-Pincer Rare Earth Metal Dichlorides. The straightforward synthetic route for preparing pincer complexes is metal introduction, including direct cyclometalation, oxidative addition, transmetalation, as well as transcyclometalation,[23a] which is suitable for small metal ions and aryldiamino NCN-pincer ligands,[25] whereas most aryldiimino pincer compounds are unstable under metalation conditions, leading to C=N double bond addition[26] or metalation at the undesired 3,5-positions.[27] Thus, complexes bearing an aryldiimino pincer ligand have been limited to Pd complexes prepared via ligand introduction,[20a] Pt complexes via direct platination,[26] and Ir and Rh halides via oxidative addition.[22] The title rare earth metal complexes bearing aryldiimino pincer ligands were successfully prepared via sequential lithiation and transmetalation. Keeping in mind that the lithiation of such aryldiimino pincer compounds swiftly induced the imino C=N bond addition, we performed the reaction of (2,6-dialkyl)isophthalaldimine-2-bromide[28] with *n*-BuLi at a very low temperature (−78 °C) for 1 h and then at −40 °C for another 2 h. The lithium salt 2,6-(2,6-C_6H_3-R_2N=CH)$_2$-C_6H_3Li was isolated selectively without visible C=N bond addition. The transmetalation took place immediately upon the addition of rare earth metal trichlorides, $LnCl_3(THF)_{1\sim3.5}$, to the THF solution of the lithium salt at −40 °C and was stirred for another 12 h at room temperature. This reaction did not show restriction to the size of the metal ion; thus, complexes based on varied lanthanide elements, [2,6-(2,6-$C_6H_3R_2$N=CH)$_2$-C_6H_3]-$LnCl_2(THF)_2$ (Ln = Y, R = Me (**1**), Et (**2**), ^{i}Pr (**3**); R = Et, Ln = La (**4**), Nd (**5**), Gd (**6**), Sm (**7**), Eu (**8**), Tb (**9**), Dy (**10**), Ho (**11**), Yb (**12**), Lu (**13**)), were isolated in 50−80% yield (Scheme 1). No metalation at the 3,5-positions was observed. This represented the first example of preparing aryldiimino NCN-pincer metal compounds via transmetalation methodology.

Complexes **1**−**4** and **13** were characterized by ^{1}H NMR spectra that displayed a similar topology, giving singlets within
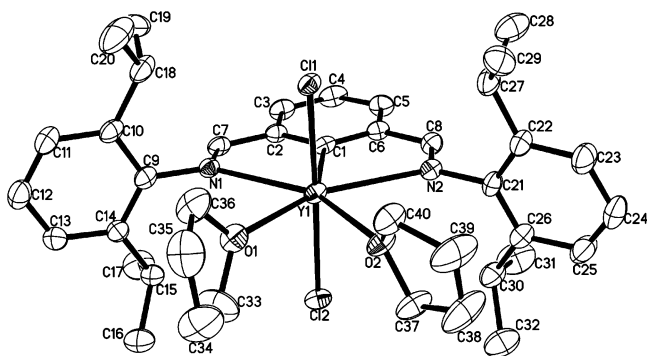
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Figure 1. Perspective view of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−C1 2.393(3), Y1−N1 2.640(3), Y1−N2 2.649-(3), Y1−Cl1 2.6152(9), Y1−Cl2 2.6105(10), Y1−O1 2.392(2), Y1−O2 2.436(2), Cl1−Y1−Cl2 174.98(3), Cl1−Y1−O1 92.07(6), Cl2−Y1−O1 84.54(6), Cl1−Y1−O2 83.92(6), Cl2−Y1−O2 91.69(6), Cl1−Y1−N1 90.23(7), Cl1−Y1−N2 90.82(6), Cl2−Y1−N1 92.52(7), Cl2−Y1−N2 90.47(7), O1−Y1−O2 76.64(8), and N1−Y1−N2 131.77(9).
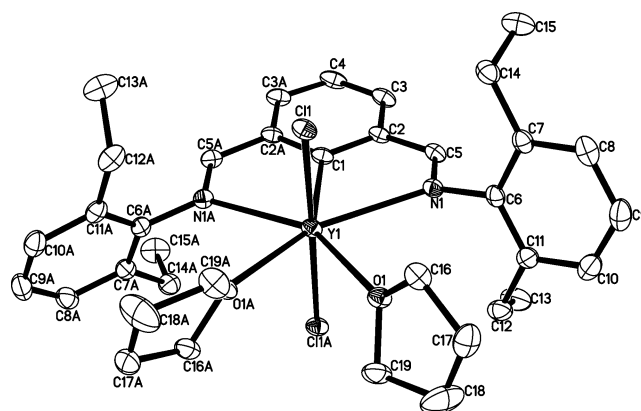
Figure 2. Perspective view of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−C1 2.411(4), Y1−N1 2.671(2), Y1−Cl1 2.6072-(7), Y1−O1 2.457(2), Cl1−Y1−Cl1(A) 173.47(3), Cl1−Y1−O1 85.97-(5), Cl1−Y1−N1 95.88(5) O1−Y1−O1(A) 75.08(9), and N1−Y1−N1(A) 130.24(10).

δ 8.35−8.45 ppm assigned to the CH=N proton. The ^{13}C NMR spectra confirmed further the formation of the Ln-σ-C bond, which showed typical downfield shifts around δ 194.15 −200.13 ppm.[29] Complexes **1**−**3**, **5**−**7**, **9**, **10**, **12**, and **13** were characterized by X-ray diffraction analysis as isostructural monomers with two coordinating THF molecules (Figures 1−4 for **1**−**3** and **6**). The monoanionic NCN-pincer ligand coordinates to the central metal ion in a κC:κN:κN′ tridentate mode to form a meridional conformation. The two N-aryl rings dispose the vertical positions against the NCN plane, which are parallel to the two *cis*-located THF rings, respectively. The chloride groups arrange in *trans*-positions to form a large Cl−Ln−Cl angle (av. 176.25(4)° in **1**−**3**) bisected by the NCN plane. The Ln^{3+} ion is essentially coplanar with the NCN plane except in the cases of **1** and **3** with deviations of 0.0927(2) and 0.0739(1) Å, respectively. The solid-state structures of these complexes have C_2 symmetry, adopting a pentagonal bipyramidal geometry around the central metal. In complexes **1**−**3** and **6**, the Ln−C bond lengths varying from 2.393(3) to 2.420(4) Å fall in a reasonable range for a linkage between a lanthanide ion and a

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Figure 3. Perspective view of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1−C1 2.398(3), Y1−N1 2.680(3), Y1−N2 2.680-(3), Y1−Cl1 2.6286(9), Y1−Cl2 2.5941(9), Y1−O1 2.427(3), Y1−O2 2.413(2), Cl1−Y1−Cl2 173.55(3), O1−Y1−O2 76.71(9), and N1−Y1−N2 131.49(9).
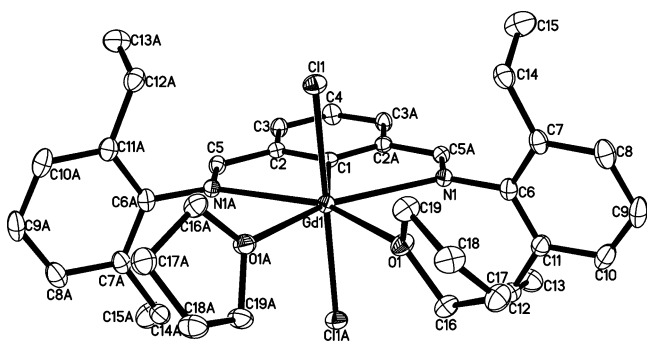
Figure 4. Perspective view of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Gd1−C1 2.421(4), Gd1−N1 2.682(2), Gd1−Cl1 2.6213(7), Gd1−O1 2.481(2), O1−Gd1−Cl1 91.06(5), N1−Gd1−N1A 130.80(10), Cl1−Gd1−Cl1A 176.25-(4), and O1−Gd1−O1A 75.63(10).

carbon atom;[30] the C−N$_{imine}$ bond lengths (av. 1.284(3) Å) are comparable to those in the analogous Rh and Pt complexes,[22] while the Ln−Cl$_{terminal}$ bond length with an average of 2.619 Å is close to 2.60 Å (av) for Y−Cl$_{terminal}$ given in the literature.[31] The N−Ln−N angle of 131.07° (av) is much smaller than 158° (av) in the related transition metal complexes owing to the crowded environment of the metal center arising from the bulky ligands, which may contribute greatly to the high selectivity of the complexes.

Catalytic Activity. The combination of complexes **1**−**13** with Al^{i}Bu$_3$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] established a Ziegler−Natta catalyst system that was homogeneous, providing varied catalytic activities toward the polymerization of butadiene. The selected polymerization data were summarized in Table 1. Complex **2** bearing the *o*-ethyl substituent of the N-aryl ring of the ligand was highly active to reach complete conversion within 1 h, while complex **1** with the *o*-methyl was less active comparatively than that under the same conditions: only 80% conversion could be attained. When the *o*-substituent was

replaced by the more bulky isopropyl in the case of complex **3**, a much more obvious decrease in the catalytic activity was observed (68% in 1 h) (Table 1, entries 1−3). These results indicated that the spacial sterics of the ancillary ligands greatly influenced the catalytic activity of the corresponding precursors. The catalytic activity was also strongly affected by the type of aluminum alkyls in the trend Al^{i}Bu$_3$ ≫ AlEt$_3$ > AlMe$_3$. When AlMe$_3$ or AlEt$_3$ was employed instead of Al^{i}Bu$_3$ to activate **2**, the polymerization became sluggish to reach a medium yield in 1 h (Table 1, entries 18 and 19).

To evaluate the role of the central metal type in this system, complexes based on various lanthanide elements bearing the *o*-ethyl substituent of the N-aryl ring of the pincer ligand were examined. The Nd (**5**), Gd (**6**), Tb (**9**), Dy (**10**), and Ho (**11**) precursors exhibited superior activity to reach complete conversion within 15 min at room temperature. Even the complexes attached by the early La (**4**) or the late Lu (**13**) lanthanide elements showed notable catalytic activities, albeit slightly lower than their Y analogue **2** (Table 1, entries 4−6, 9−11, and 13). To date, only a few examples of diene polymerization catalysts based on La have been reported. In contrast, all precursors attached by lanthanide elements Sm (**7**), Yb (**8**), as well as Eu (**12**) were demonstrated to be inert, owing to their reducible nature[9e] (Table 1, entries 7, 8, and 12).

When **2** was chosen as the precursor to initiate the polymerization of butadiene under various monomer-to-initiator ratios varying from 500 to 5000, the molecular weight of the resultant PB was found to increase almost linearly when the ratio was below 4000, which reached up to 133.0 × 10^4 (M_n) at a ratio of 5000; meanwhile, the molecular weight distribution did not change obviously or became even narrower (M_w/M_n = 2.40− 1.79) (Table 1, entries 2 and 14−17). Thus, this system was probably a single site to induce controllable polymerization. It should be noted that all these molecular weights of the measured values were essentially 3 times higher than the calculated ones (Table 1, entries 14−16), leading to about 30% catalytic efficiency (M_{calcd}/M_{nmeasd}), consistent with the previously reported homogeneous single-site catalyst systems or even the living systems,[10b,12a] which had been attributed to fast propagation as compared to the initiation, the aggregation of the active species, or the heterogeneous nature of some catalyst systems.

***cis*-1,4 Selectivity.** Remarkably, this new type of Ziegler− Natta catalytic system provided extremely high *cis*-1,4 selectivity at room temperature, varying within a narrow range of 99.3− 99.9% despite the central metal type (Table 1, entries 2, 4−6, 9−11, and 13). These results were in contrast to the conventional Ziegler−Natta systems such as LnCl$_3$/EtOH/AlEt$_3$, Ln(O-COCl$_3$)$_3$/Al^{i}Bu$_3$/AlEt$_2$Cl, and the modified Ziegler−Natta system [Me$_2$Al(O$_2$CC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_2$]$_2$Ln[(μ-Me)$_2$AlMe$_2$]/R$_2$AlCl, where Nd-based mixtures were the mostly active and selective (intrinsic Nd effect).[3−5,10,32] These results were also quite different from the system composed of Cp*$_2$Ln[(μ-Me)$_2$AlMe$_2$(μ-Me)]$_2$LnCp*$_2$ and AlEt$_2$Cl, where the *cis*-1,4 selectivity showed a strong dependence on the central metal type, changing from 38.8% for Ce to 97.3% for Gd.[9c,e]

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Table 1. Polymerization of Butadiene under Various Conditions[a]

entry	complex	[BD]/[Ln]	T_p (°C)	time (min)	yield (%)	$M_n{}^c$ (×10⁴)	M_w/M_n	micros tructure (%)[b]		
								cis-1,4	trans-1,4	1,2-
1	Y^Me(**1**)	500	25	60	80	3.96	1.47	98.5	1.3	0.2
2	Y^Et(**2**)	500	25	60	100	8.60	2.23	99.7	0.3	
3	Y^iPr(**3**)	500	25	60	68	2.63	1.31	95.3	4.2	0.5
4	La^Et(**4**)	500	25	60	87	7.01	1.59	99.3	0.5	0.2
5	Nd^Et(**5**)	500	25	15	100	18.00	2.08	99.5	0.4	0.1
6	Gd^Et(**6**)	500	25	10	100	32.21	2.18	99.7	0.3	
7	Sm^Et(**7**)	500	25	120	0					
8	Eu^Et(**8**)	500	25	120	0					
9	Tb^Et(**9**)	500	25	10	100	21.00	2.43	99.7	0.3	
10	Dy^Et(**10**)	500	25	10	100	26.00	2.24	99.4	0.6	
11	Ho^Et(**11**)	500	25	15	100	14.22	2.44	99.4	0.6	
12	Yb^Et(**12**)	500	25	120	0					
13	Lu^Et(**13**)	500	25	60	90	9.75	2.48	99.3	0.6	0.1
14	Y^Et(**2**)	1000	25	60	100	18.63	2.31	99.3	0.7	
15[d]	Y^Et(**2**)	2000	25	60	93	39.50	2.40	99.4	0.6	
16[e]	Y^Et(**2**)	4000	25	180	90	79.20	2.13	99.7	0.3	
17[f]	Y^Et(**2**)	5000	25	180	85	133.00	1.79	99.9	0.1	
18[g]	Y^Et(**2**)	500	25	60	43	31.88	2.11	66.5	31.7	1.8
19[h]	Y^Et(**2**)	500	25	60	65	17.40	1.68	51.5	47.5	1.0
20	Gd^Et(**6**)	500	0	30	85	33.10	1.89	100		
21	Gd^Et(**6**)	500	40	5	100	21.35	2.03	99.3	0.7	
22	Gd^Et(**6**)	500	60	5	100	11.70	1.87	97.6	2.1	0.3
23	Gd^Et(**6**)	500	80	5	80	10.23	1.95	96.9	2.6	0.5

[a] C_6H_5Cl (5 mL), complex (20 μmol), $[Ln]_0/[Al^iBu_3]_0/[B]_0$ = 1:20:1 (B = $[Ph_3C][B(C_6F_5)_4]$. [b] Determined by ^{13}C NMR spectrum of polybutadiene. [c] Determined by GPC with respect to a polystyrene standard. [d] C_6H_5Cl (15 mL). [e] C_6H_5Cl (20 mL). [f] C_6H_5Cl (30 mL). [g] $[Y]_0/[AlMe_3]_0/[B]_0$ = 1:20:1. [h] $[Y]_0/[AlEt_3]_0/[B]_0$ = 1:20:1.

The *cis*-selectivity of this system was found to be influenced by the ortho substituent of the *N*-aryl ring of the ligands, reaching as high as 99.7% for **2** bearing *o*-ethyl, which dropped slightly for **1** bearing *o*-methyl (98.5%) and even more in the case of **3** with the bulky *o*-isopropyl (95.3%) (Table 1, entries 1−3). This might be ascribed to the different steric environment of the center metal that was pinched by the two ortho-substituted *N*-aryl rings. The dihedral angle formed by the aryl rings was 118.56(13)° in **1**, 109.9° in **2**, and 133.28(15)° in **3**, respectively. The smaller the dihedral angle is, the bulkier the metal center is, leading to the higher *cis*-1,4 selectivity. Meanwhile, the *cis*-selectivity also showed that it was sensitive to the steric demands of the aluminum alkyl. When applying AlMe₃ as the activator, the catalyst system based on precursor **2** exhibited only medium *cis*-selectivity (66.5%) to afford PB with an as high as 31.7% *trans*-1,4 regularity. Switching to AlEt₃, the system showed almost an equal *cis*-1,4 (51.5%) and *trans*-1,4 (47.5%) selectivity (Table 1, entries 18 and 19). Both the sterics of the ligand and the aluminum alkyls influenced the catalytic performances, suggesting that the active living species of this new system should contain an Ln-Al bimetallic unit that was not cleaved during the polymerization process (vide infra).

More strikingly, this system exhibited a distinguished tolerance toward the polymerization temperature. With the Gd-based precursor **6**, when the polymerization was performed at 40 °C, a *cis*-1,4 selectivity of 99.3% could be obtained that was comparable to 99.7% at 25 °C, which decreased slightly to 96.9% when the temperature was increased up to 80 °C, suggesting that the active species did not decompose under these conditions (Table 1, entries 6 and 21−23). Lowering the polymerization temperature to 0 °C, a perfect *cis*-1,4 selectivity (100%) could be achieved with an amazing activity (a 85% conversion in 30 min) (Table 1, entry 20). No 1,2- and *trans*-1,4 regularities were detectable from the ^{13}C NMR spectrum of the resultant PB (Figures S11 and S12.). These results demonstrated for the first time, as far as we are aware, that an

excellent *cis*-1,4 selectivity for the polymerization of butadiene could be maintained at elevated temperatures, in contrast to many previous systems where the selectivity varied drastically with the polymerization temperature. Moreover, this present system displayed a similar catalytic behavior for the polymerization of isoprene to that for butadiene, which need not be discussed further.[33]

Active Species. The active center of the conventional Ziegler−Natta catalyst system was generated in a two-step activation sequence involving the formation of a reactive Ln-alkyl or Ln-hydride bond and the Al-to-Ln chlorotransfer (cationization).[34] Anwander et al.[36] proved that preformed Ln/Al heterobimetallic complexes such as $[LnAl_3Me_8(O_2CC_6H_2-^iPr_3-2,4,6)_4]$, $[Ln(OR)_3(AlMe_3)_n]$ (R = 2,6-R*₂C₆H₃, R* = ^tBu, ^iPr), and $[Ln(AlMe_4)_3]$ are the alkylated intermediates that upon further activation with Et₂AlCl give highly efficient initiators for isoprene polymerization. $[Me_2LnCl]_n$ and $[MeLnCl_2]_n$ are considered as the actual initiating species,[10] while the mechanistic scenarios elucidated by Taube et al., Okuda et al., Hou et al., and Anwander et al. involve cationic initiators [Nd-$(C_3H_5)(C_4H_6)_n]^{2+}$,[35] $[YMe(sol)_6]^{2+}$,[11] $[(PNP)Y(CH_2SiMe_3)-(thf)_x]^+$,[12a] or $[\{[(C_5Me_5)La\{(\mu-Me)_2AlMe(C_6F_5)\}][Me_2Al-(C_6F_5)_2]\}_2]$.[36] To obtain information about the active species of this system, the pincer yttrium dichlorides (**2**) were first treated with aluminum alkyls in C_6D_5Cl. The alkylation, we noted, did not take place at room temperature within 12 h, suggesting that

(33) The high *cis*-1,4 regulated (98.8%) polyisoprene ($M_n = 7.78 \times 10^4$, $M_w/M_n = 1.76$) was obtained by using a system composed of **2**, Al^iBu_3, and $[Ph_3C][B(C_6F_5)_4]$ at room temperature for 2 h, yielding 100%. The selected polymerization data are listed in Table S1 of the Supporting Information.
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(36) For the active species $[\{[(C_5Me_5)La\{(\mu-Me)_2AlMe(C_6F_5)\}][Me_2Al(C_6F_5)_2]\}_2]$ for *trans*-1,4 polymerization of isoprene, see: Zimmermann, M.; Törnroos, K.; Anwander, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 775.

Scheme 2. Probable Active Species
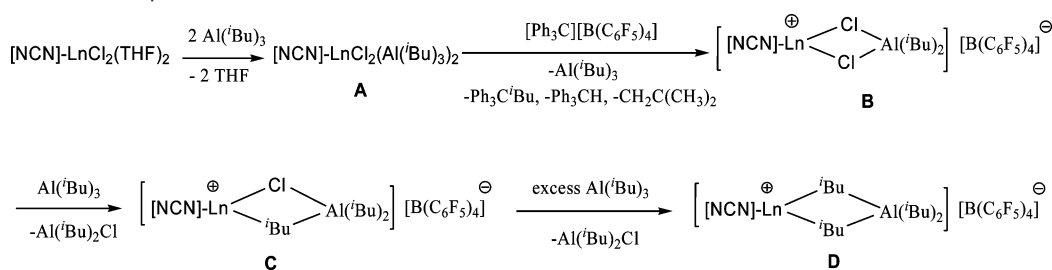
the Ln–Cl bond in **2** was strengthened by the chelating NCN-pincer donor as compared to LnCl$_3$. Instead, an intermediate **A** ([NCN]LnCl$_2$·(Al(^{i}Bu)$_3$)$_2$) of the coordination adduct of Al^{i}Bu$_3$ to **2** was generated (Scheme 2).[10a] The methine proton of the CH=N group of the NCN moiety shifted to δ 8.17 in **A** as compared to δ 8.38 in **2**, while the methylene protons of the group C*H$_2$*CH(CH$_3$)$_2$ gave a doublet around δ 0.06 shifting upfield as compared to δ 0.35 in free Al(C*H$_2$*CH(CH$_3$)$_2$)$_3$ (C$_6$D$_5$-Cl).[37] It is reasonable that **A** could not induce the polymerization of butadiene at room temperature. The addition of aluminum alkyl chloride Et$_2$AlCl as the weak cationizing cocatalyst to **A** did not improve its catalytic activity. When activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$], **A** was swiftly transferred into the ion pair **B**, [NCN]Ln[(μ-Cl)$_2$(Al(^{i}Bu)$_2$)]$^+$[B(C$_6$F$_5$)$_4$]$^-$,[38] with releasing Ph$_3$C*H* (δ 5.52), CH$_2$C(CH$_3$)$_2$ (δ 4.48, 1.70), and minor Ph$_3$C^i-Bu[39] via [Ph$_3$C][B(C$_6$F$_5$)$_4$] electrophilic attack of the ^{i}Bu group of **A**. Correspondingly, the methylene protons of the *o*-ethyl group gave one multiple resonance at the upfield region (δ 2.20) different from the two discrete multiplets (δ 2.91 and 3.19) in **A**. **B** was still inert to the polymerization. When adding one more equivalent Al(^{i}Bu)$_3$ to **B**, a heteroleptic alkyl/chloride bridged bimetallic intermediate **C**, [NCN]Ln[(μ-Cl)(μ-^{i}Bu)(Al-(^{i}Bu)$_2$)]$^+$[B(C$_6$F$_5$)$_4$]$^-$, was generated.[40] The signals for the bridged isobutyl group shifted to a much higher region (δ −0.04), while the terminal isobutyl groups did not change. No visible polymerization was found with **C**. Under the presence of excess Al(^{i}Bu)$_3$, **C** initiated the polymerization of butadiene (isoprene) immediately. Thus, we suggest that the homoleptic alkyl bridged **D** might be formed and that it acted as the actual active species.[41]

The mode of the diene monomer enchainment via 1,4 insertion (i.e., the formation of *cis*-1,4 or *trans*-1,4 monomeric units in the polymer) is determined by the structure, *anti* or *syn*, of the last inserted monomeric unit in the growing chain. The *anti* form of the η^3-butyl group gives rise to the formation of a *cis*-1,4 monomeric unit, whereas the *syn* form leads to a *trans*-1,4 unit. Thus, the exclusive *cis*-1,4 selectivity of this present Ziegler–Natta system suggested that the *anti* form was favored, which could be ascribed to the concert influences of the pincer-like geometry of the ancillary ligand and the steric demands of aluminum alkyl (Scheme S1). Increasing the polymerization temperature gave a rise in *trans*-1,4 content as the isomerization to the thermally stable *syn* π-allylic form became faster.[42]

Conclusion

The first aryldiimine NCN-pincer stabilized rare earth metal dichlorides were successfully synthesized via transmetalation methodology and were well-defined, which in combination with aluminum alkyls and borate established a new type of Ziegler–Natta catalyst system. This system provided extremely high activity and perfect *cis*-1,4 selectivity for the polymerization of butadiene (*cis*-1,4 99.9%) and isoprene (*cis*-1,4 98.8%). The spacial sterics of the ortho substituent of the *N*-aryl ring of the NCN-pincer ligand and the bulkiness of aluminum alkyls played significant roles in controlling the catalytic activity and selectivity. In contrast, the central metal type had almost no effect on the specific selectivity but slightly influenced the catalytic activity. Remarkably, such distinguished catalytic performances remained under broad ranges of monomer-to-initiator ratios (500−5000) and polymerization temperatures (25−80 °C). The alkyl bridged Ln-Al bimetallic cations were proven to be the actual active species. These results were in striking contrast to the conventional Ziegler–Natta catalysts and the other previously reported systems, which might shed light on to a new and more applicable procedure for highly *cis*-1,4 selective catalysts.

Experimental Procedures

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. All solvents were purified from an MBraun SPS system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC experiments when necessary. The molecular weight and molecular weight distribution of the polymers were measured by

(37) ^{1}H NMR spectrum of **A**: ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ 0.06 (d, J_{H-H} = 8 Hz, 12H, Al-C*H$_2$*CH(CH$_3$)$_2$), 1.09 (d, J_{H-H} = 4 Hz, 36H, Al-CH$_2$CH(C*H$_3$*)$_2$), 1.14 (t, J_{H-H} = 8 Hz, 12H, CH$_2$C*H$_3$*), 1.42 (b, 16H, THF), 1.97 (m, 6H, Al-CH$_2$C*H*(CH$_3$)$_2$), 2.91 (m, 4H, C*H$_2$*CH$_3$), 3.19 (m, 4H, C*H$_2$*-CH$_3$), 3.70 (b, 16H, THF), 6.97−7.11 (m, 6H, N-C$_6$H$_3$, 1H, *p*-Y-C$_6$H$_3$) 7.27 (d, J_{H-H} = 8 Hz, 2H, *m*-Y-C$_6$H$_3$), 8.17 (s, 2H, C*H*=N).

(38) ^{1}H NMR spectrum of **B**: ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ 0.06 (d, J_{H-H} = 4 Hz, 4H, Al-C*H$_2$*CH(CH$_3$)$_2$), 0.95 (t, J_{H-H} = 8 Hz, 12H, CH$_2$C*H$_3$*), 1.09 (d, 12H, Al-CH$_2$CH(C*H$_3$*)$_2$), 1.54 (b, 16H, THF), 1.61 (s, 6H, CH$_2$=C(C*H$_3$*)$_2$), 1.98 (m, 2H, Al-CH$_2$C*H*(CH$_3$)$_2$), 2.20 (m, 8H, C*H$_2$*-CH$_3$), 3.62 (b, 16H, THF), 4.78 (s, 2H, C*H$_2$*=C(CH$_3$)$_2$), 5.43 (s, 1H, Ph$_3$C*H*), 6.97−7.20 (m, 6H, N-C$_6$H$_3$, 1H, *p*-Y-C$_6$H$_3$, 15H, Ph$_3$C), 7.31 (d, J_{H-H} = 8 Hz, 2H, *m*-Y-C$_6$H$_3$), 8.06 (s, 2H, C*H*=N).

(39) Dealkylation of the *iBu* group of aluminum alkyls of **A** by [Ph$_3$C][B(C$_6$F$_5$)$_4$] took place swiftly to give Ph$_3$C-*iBu* as the normal product; meanwhile, Ph$_3$C$^+$ could also abstract a proton from the *iBu* group to afford Ph$_3$CH and CH$_2$CH*iBu$_2$* as the main products according to the resonances. In the case of AlMe$_3$ as the coactivator, the NMR monitoring result showed that Ph$_3$CMe was given exclusively, showing a singlet resonance at δ 2.03 (CH$_3$).

(40) ^{1}H NMR spectrum of **C**: ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ −0.04 (b, 2H, Y-C*H$_2$*CH(CH$_3$)$_2$), 0.05 (d, J_{H-H} = 4 Hz, 4H, Al-C*H$_2$*CH(CH$_3$)$_2$), 0.95 (t, J_{H-H} = 8 Hz, 12H, CH$_2$C*H$_3$*), 1.09 (m, 6H, Y-CH$_2$CH(C*H$_3$*)$_2$, 12H, Al-CH$_2$CH(C*H$_3$*)$_2$), 1.54 (b, 16H, THF), 1.61 (m, 6H, CH$_2$=C(C*H$_3$*)$_2$), 1.98 (m, 2H, Al-CH$_2$C*H*(CH$_3$)$_2$), 2.20 (m, 8H, C*H$_2$*CH$_3$), 2.44 (m, 1H, Y-CH$_2$C*H*(CH$_3$)$_2$), 3.62 (b, 16H, THF), 4.78 (s, 2H, C*H$_2$*=C(CH$_3$)$_2$), 5.43 (s, 1H, Ph$_3$C*H*), 6.97−7.20 (m, 6H, N-C$_6$H$_3$, 1H, *p*-Y-C$_6$H$_3$, 15H, Ph$_3$C), 7.31 (d, J_{H-H} = 8 Hz, 2H, *m*-Y-C$_6$H$_3$), 8.06 (s, 2H, C*H*=N).

(41) ^{1}H NMR spectrum of the species **D**/(excess Al^{i}Bu$_3$) was not informative owing to the strong signals from the free Al^{i}Bu$_3$, whereas washing off the free Al^{i}Bu$_3$ with hexane gave an unknown inert species, most likely due to the decomposition of **D** at the absence of Al^{i}Bu$_3$.

(42) Tobisch, S. *Acc. Chem. Res.* **2002**, *34*, 96.

TOSOH HLC 8220 GPC at 40 °C using THF as an eluent against polystyrene standards. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). 2,6-Dimethylaniline, 2,6-diethylaniline, and 2,6-diisopropylaniline was obtained from Aldrich and purified by distillation before use.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the following preparations. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. For crystallographic data and refinement of complexes **1**−**3**, **5**−**7**, **9**, **10**, **12**, and **13**, see the Supporting Information.

[Bis(*N*-2,6-dimethylphenyl)isophthalaldimine-2-yl]YCl$_2$(THF)$_2$ (1). Under a nitrogen atmosphere, ^{n}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) was added dropwise to a THF solution (25 mL) of 2,6-(2,6-Me$_2$−C$_6$H$_3$N═CH)$_2$−C$_6$H$_3$−1-Br (0.42 g, 1.00 mmol) at −78 °C and was stirred for 1 h. The reaction solution was warmed to −40 °C to react for another 2 h and then was added to a THF suspension (15 mL) of YCl$_3$(THF)$_{3.5}$ (0.67 g, 1.5 mmol). The reaction mixture was allowed to warm to room temperature gradually and was stirred for 12 h. Removal of volatiles under reduced pressure, extracting the residue with toluene, and evaporating the toluene to dryness afforded **1** as yellowish powder (0.53 g, 82.6%). Single crystals for X-ray analysis grew from the mixture of THF and hexane at −30 °C within several days and were yellow blocks. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.44 (b, 8H, THF), 2.47 (s, 12H, CH$_3$), 3.73 (m, 8H, THF), 7.00 (t, J_{H-H} = 7.2 Hz, 2H, *p*-N-C$_6$H$_3$), 7.06 (d, J_{H-H} = 7.2 Hz, 4H, *m*-N-C$_6$H$_3$), 7.23 (t, J_{H-H} = 7.2 Hz, 1H, *p*-Y-C$_6$H$_3$), 7.45 (d, J_{H-H} = 7.2 Hz, 2H, *m*-Y-C$_6$H$_3$), 8.35 (d, J_{H-H} = 2 Hz, 2H, C*H*═N). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 19.16 (s, 4C, CH$_3$), 24.84 (s, 4C, THF), 70.83 (b, 4C, THF), 124.95 (s, 2C, *p*-N-C$_6$H$_3$), 126.32 (s, 1C, *p*-Y-C$_6$H$_3$), 127.73 (s, 4C, *m*-N-C$_6$H$_3$), 130.24 (s, 2C, C═N−*C*), 132.04 (s, 2C, *m*-Y-C$_6$H$_3$), 143.61 (s, 2C, *o*-Y-C$_6$H$_3$), 151.39 (s, 4C, *o*-N-C$_6$H$_3$), 178.12 (s, 2C, *C*═N−C), 194.15 (d, J_{C-Y} = 43 Hz, 1C, *C*-Y) ppm. Anal. calcd for C$_{32}$H$_{37}$Cl$_2$N$_2$O$_2$Y (%): C, 59.92; H, 5.81; N, 4.37. Found: C, 59.83; H, 5.74; N, 4.31.

[Bis(*N*-2,6-diethylphenyl)isophthalaldimin-2-yl]YCl$_2$(THF)$_2$ (2). Following the same procedure described for the formation of **1**, the treatment of 2,6-(2,6-Et$_2$-C$_6$H$_3$N═CH)$_2$-C$_6$H$_3$-1-Br (0.48 g, 1.00 mmol in 25 mL of THF) with ^{n}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then in situ adding YCl$_3$(THF)$_{3.5}$ (0.67 g, 1.5 mmol) gave **2** in an 85.9% yield (0.60 g). Yellow crystals for X-ray analysis grew from the mixture of THF and hexane at − 30 °C within several days. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.17 (t, J_{H-H} = 8 Hz, 12H, CH$_2$C*H$_3$*), 1.36 (b, 8H, THF), 2.84 (m, 4H, C*H$_2$*CH$_3$), 3.07 (m, 4H, C*H$_2$*CH$_3$), 3.69 (b, 8H, THF), 7.13 (m, 6H, N-C$_6$H$_3$), 7.23 (t, J_{H-H} = 8 Hz, 1H, *p*-Y-C$_6$H$_3$), 7.46 (d, J_{H-H} = 8 Hz, 2H, *m*-Y-C$_6$H$_3$) 8.38 (s, 2H, C*H*═N). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 15.08 (s, 4C, CH$_2$*C*H$_3$), 24.62 (s, 4C, *C*H$_2$CH$_3$), 24.77 (s, 4C, THF), 71.34 (s, 4C, THF), 125.39 (s, 2C, *p*-N-C$_6$H$_3$), 125.88 (s, 4C, *m*-N-C$_6$H$_3$), 126.39 (s, 1C, *p*-Y-C$_6$H$_3$), 132.11 (s, 2C, *m*-Y-C$_6$H$_3$), 136.18 (s, 4C, *o*-N-C$_6$H$_3$), 143.49 (s, 2C, *o*-Y-C$_6$H$_3$), 150.34 (s, 2C, C═N−*C*), 177.77 (s, 2C, CH═N−*C*), 194.20 (d, J_{C-Y} = 43 Hz, 1C, *C*-Y) ppm. Anal. calcd for C$_{36}$H$_{45}$Cl$_2$N$_2$O$_2$Y: C, 61.98; H, 6.50; N, 4.02. Found: C, 61.92; H, 6.47; N, 4.09.

[Bis(*N*-2,6-diisopropylphenyl)isophthalaldimin-2-yl]YCl$_2$-(THF)$_2$ (3). Following the same procedure described for the formation of **1**, treatment of 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N═CH)$_2$-C$_6$H$_3$-1-Br (0.53 g, 1.00 mmol) with ^{n}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then in

situ adding YCl$_3$(THF)$_{3.5}$ (0.67 g, 1.5 mmol) yielded **3** (0.41 g, 55%). Yellow crystals for X-ray analysis grew from the mixture of THF and hexane at −30 °C within several days. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.08 (d, 6H, J_{H-H} = 6.8 Hz, CH(C*H$_3$*)$_2$), 1.30 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H$_3$*)$_2$), 1.75 (b, 8H, THF), 3.76 (m, 4H, C*H*(CH$_3$)$_2$), 3.92 (b, 8H, THF), 7.11 (m, 6H, Ph), 7.24 (m, 1H, Ph), 7.46 (d, J_{H-H} = 6 Hz, 2H, Ph), 8.40 (s, 2H; C*H*═N). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 22.14 (s, 4C, THF), 25.19 (s, 8C, CH(*C*H$_3$)$_2$) 27.46 (s, 4C, *C*H(CH$_3$)$_2$), 70.58 (s, 4C, THF), 123.23 (s, 2C, *p*-N-C$_6$H$_3$), 125.76 (s, 4C, *m*-N-C$_6$H$_3$), 126.41 (s, 1C, *p*-Y-C$_6$H$_3$), 132.19 (s, 2C, *m*-Y-C$_6$H$_3$), 140.93 (s, 4C, *o*-N-C$_6$H$_3$), 143.30 (s, 2C, *o*-Y-C$_6$H$_3$), 149.27 (s, 2C, C═N−*C*), 177.57 (s, 2C, *C*═N−C), 194.25 (d, J_{C-Y} = 41 Hz, 1C, *C*-Y). Anal. calcd for C$_{40}$H$_{53}$Cl$_2$N$_2$O$_2$Y: C, 63.74; H, 7.09; N, 3.72. Found: C, 63.64; H, 6.98; N, 3.63.

Synthesis of 4−13. Following the procedure described previously, **4**−**13**, [bis(*N*-2,6-diethylphenyl)isophthalaldimin-2-yl]LnCl$_2$(THF)$_2$ (Ln = La, Sm, Eu, Nd, Ho, Dy, Gd, Tb, Yb, Lu), were synthesized from LnCl$_3$(THF)$_x$: Sm, yellow microcrystals, yield 62.1%; Eu, purple microcrystals, yield 35.2%; Nd, yellow microcrystals, yield 65.8%; Ho, yellow microcrystals, yield 54.3%; Dy, yellow microcrystals, yield 64.2%; Tb, yellow microcrystals, yield 67.7%; Yb, yellow microcrystals, yield 54.6%. The NMR spectra of these complexes were not available due to paramagnetism. La, yellow microcrystals, yield 54.2%. NMR data: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.14 (t, J_{H-H} = 7.5 Hz, 12H, CH$_2$C*H$_3$*), 1.53 (b, 8H, THF), 2.73 (q, J_{H-H} = 7.5 Hz, 4H, C*H$_2$*CH$_3$), 2.92 (q, J_{H-H} = 7.5 Hz, 4H, C*H$_2$*CH$_3$), 3.56 (b, 8H, THF), 6.92 (m, 6H, N-C$_6$H$_3$), 7.30 (t, J_{H-H} = 7.5 Hz, 1H, *p*-La-C$_6$H$_3$), 7.40 (d, J_{H-H} = 7.5 Hz, 2H, *m*-La-C$_6$H$_3$) 8.36 (s, 2H, C*H*═N); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 15.26 (s, 4C, CH$_2$*C*H$_3$), 25.08 (s, 4C, H$_2$CH$_3$), 25.62 (s, 4C, THF), 70.25 (s, 4C, THF), 125.68 (s, 2C, *p*-N-C$_6$H$_3$), 125.96 (s, 4C, *m*-N-C$_6$H$_3$), 126.30 (s, 1C, *p*-La-C$_6$H$_3$), 132.30 (s, 2C, *m*-La-C$_6$H$_3$), 136.24 (s, 4C, *o*-N-C$_6$H$_3$), 144.86 (s, 2C, *o*-Lu-C$_6$H$_3$), 150.54 (s, 2C, C═N−*C*), 179.49 (s, 2C, *C*═N−C), 206.89 (s, 1C, La-*C*) ppm; Lu, pale yellow microcrystals, yield 59.4%, NMR data: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.16 (t, J_{H-H} = 8 Hz, 12H, CH$_2$C*H$_3$*), 1.56 (b, 8H, THF), 2.84 (q, J_{H-H} = 8 Hz, 4H, C*H$_2$*-CH$_3$), 3.10 (q, J_{H-H} = 8 Hz, 4H, C*H$_2$*CH$_3$), 3.72 (b, 8H, THF), 7.12 (m, 6H, N-C$_6$H$_3$), 7.24 (t, J_{H-H} = 8 Hz, 1H, *p*-Lu-C$_6$H$_3$), 7.50 (d, J_{H-H} = 8 Hz, 2H, *m*-Lu-C$_6$H$_3$) 8.44 (s, 2H, C*H*═N). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ 15.10 (s, 4C, CH$_2$*C*H$_3$), 24.57 (s, 4C, *C*H$_2$CH$_3$), 25.06 (s, 4C, THF), 69.91 (s, 4C, THF), 125.39 (s, 2C, *p*-N-C$_6$H$_3$), 125.91 (s, 4C, *m*-N-C$_6$H$_3$), 126.24 (s, 1C, *p*-Lu-C$_6$H$_3$), 132.30 (s, 2C, *m*-Lu-C$_6$H$_3$), 136.27 (s, 4C, *o*-N-C$_6$H$_3$), 143.51 (s, 2C, *o*-Lu-C$_6$H$_3$), 150.66 (s, 2C, C═N−*C*), 175.27 (s, 2C, *C*═N−C), 200.13 (s, 1C, Lu-*C*) ppm.

Polymerization of Butadiene. A typical procedure for the polymerization was as follows (Table 1, entry 2): in a glovebox, a chlorobenzene solution of butadiene (2 mL, 10 mmol), 5 mL of chlorobenzene, and 400 μmol of AlR$_3$ were added into a 25 mL flask. Then, 20 μmol of **2** and equimolar borate ([Ph$_3$C][B(C$_6$F$_5$)$_4$]) were added to initiate the polymerization. After a designated time, methanol was injected into the system to quench the polymerization. The mixture was poured into a large quantity of methanol to precipitate the white solids. Filtered and dried under vacuum at 40 °C for 24 h, polybutadiene resulted at a constant weight (0.54 g, 100%).

Supporting Information Available: ^{1}H, ^{13}C, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HMQC NMR spectra of **1**; ^{1}H and ^{13}C NMR spectra of **2**; ^{1}H NMR spectra of **3** and **13**; ^{1}H NMR spectra of intermediates **A**−**C**; ^{1}H−^{1}H COSY of **A**; selected data for the

high *cis*-1,4 polymerization of isoprene; ^{1}H and ^{13}C NMR spectra of selected polybutadiene and polyisoprene samples; ORTEP drawings for molecular structures of **5**, **7**, **9**, **10**, **12**, and **13**; scheme for the probable mechanism; and X-ray crystallographic data and refinement for **1**−**3**, **5**−**7**, **9**, **10**, **12**, and **13** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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