ORGANOMETALLICS

Rare-Earth-Metal Complexes Bearing Phosphazene Ancillary Ligands: Structures and Catalysis toward Highly Trans-1,4-Selective (Co)Polymerizations of Conjugated Dienes

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Supporting Information

ABSTRACT: The bis-arylated phosphazene compounds $[HN(PPh_2NAr)_2]$ (Ar = phenyl (HL^1) , 2,6-dimethylphenyl (HL^2) , 2,6-diisopropylphenyl (HL^3)) and the imidodiphosphinate compound HN(PPh₂O)₂ (HL⁴) have been prepared via the Staudinger reaction. Treatment of the neutral compounds HL^1 , HL^2 , and HL^3 with $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y, Lu) generated the solvent-free bis(alkyl) complexes $L^{1}Ln(CH_{2}SiMe_{3})_{2}$ (Ln = Sc (1a), Y (1b), Lu



(1c), $L^2Sc(CH_2SiMe_3)_2$ (2a), $L^3Y(CH_2SiMe_3)_2$ (3b), and $L^3Lu(CH_2SiMe_3)_2$ (3c), respectively. The reaction between HL⁴ and $Y(CH_2SiMe_3)_3(THF)_2$ gave the rare zwitterionic complex 4b. Lithiation of the ligand HL¹ by *n*BuLi followed by a metathesis reaction with Nd(BH₄)₃(THF)₃ afforded the corresponding complex $L^1Nd(BH_4)_2(THF)_2$ (5). Complexes 1 upon incorporation of $[Ph_3C][B(C_6F_5)_4]$ and AliBu₃ led to ternary systems that initiated isoprene polymerization with high activities, among which complex 1a was the first example of a scandium catalytic precursor providing trans-1,4-selectivity (90.0%), while the lutetium analogue 1c had medium trans-1,4-selectivity (54.3%) and the yttrium complex 1b exhibited high cis-1,4-selectivity (76.3%). The ternary system based on the zwitterion 4b displayed the highest activity for the isoprene polymerization among these complexes and gave cis-1,4-regularity-enriched polyisoprene (70.6%). Highly stereospecific homopolymerizations of isoprene (trans-1,4content: 97.0%) and butadiene (trans-1,4-content: 94.0%) were achieved by using the borohydrido complex 5 upon the activation of dibutylmagnesium. The copolymerization of isoprene and butadiene with $1a/[Ph_3C][B(C_6F_5)_4/AliBu_3]$ gave randomly arranged trans-1,4-regulated polybutadiene and polyisoprene sequences. The kinetics study displayed competitive polymerization rates of $r_{\rm BD}$ = 2.89 and $r_{\rm IP}$ = 0.41. The thermal behaviors of the (co)polymers were investigated.

INTRODUCTION

The stereospecific polymerization of conjugated dienes has developed extensively since the 1950s, carried along by the scientific and technical challenges of the synthetic elastomer industry. In particular, great achievements have been made about cis-1,4-selective polymerization of dienes, because the resulting polymers are the most important rubbers used for tires and other elastic materials.¹⁻⁷ Lanthanide-based catalyst systems represent a prominent class of such high-performance catalysts:⁷ for instance, the notable Ziegler-Natta catalysts employed as the industry recipe for producing cis-1,4polybutadiene and the academically valuable single-sited and cationic catalysts based on the lanthanide alkyl,⁸ carboxylate (versatate),⁹ halide,^{7a,c,10} or alkoxide precursors.^{11,12} Compara-tively, trans-1,4-polymerization has received rather limited attention.¹³ One reason might be the lack of efficient catalysts for this type of polymerization, and the few known systems usually feature low activity, unpromising monomer conversion, and less control in molecular weight, even under the conditions

of elevated temperatures or prolonged polymerization time.¹⁴ Another is that trans-1,4-polyisoprene, although having a microstructure similar to that of natural gutta percha, has been found few applications. Recently, long-life "green" tires with low rolling resistance and slip resistance have become a concept for sustainable development of the rubber and automobile industries because of their source and the energy crisis. Plastic trans-1,4-polyisoprene mixed in less than 15 wt % percent with its cis-1,4-isomer or natural rubber constructs high-performance rubbers for preparation of the resulting green tires, which are anticipated to have properties superior to those of conventional butadiene-styrene copolymers. In addition, trans-1,4-polyisoprene has been employed as a material for medical purposes (orthopedics, reconstructive surgery).¹⁵

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Therefore, the exploration of highly efficient catalyst systems for trans-1,4-selective diene polymerizations has attracted increasing research interest. The lanthanide borohydrides $Ln(BH_4)_3(THF)_n$ and $Cp*Ln(BH_4)_2(THF)_n/Mg(nBu)_2^{14a,b}$ reported by Visseaux and the lanthanide allyl complexes rac- $[{Me_2C(Ind)_2}Y(1,3-(SiMe_3)_2C_3H_3)] (Ln(allyl)_2Cl(MgCl_2)_2/$ AlR₃)^{14c,d} reported by Carpentier are efficient catalysts for trans-1,4-isoprene polymerization. The yttrium mono(allyl) complex^{14d} is the first example of a single-component catalyst for the preparation of trans-1,4-polyisoprene. The lanthanide aluminate $(C_5Me_5)Ln(AlMe_4)_2/organoborate^{14e,f}$ discovered by Anwander remains the most highly trans-1,4-selective (>99%) system to date. Well-defined neodymium alkoxides/ aryloxides in combination with dialkylmagnesiums polymerize butadiene with a high trans-1,4-stereospecificity (95%).^{14g} Other than these achievements, utilization of non-cyclopentadienyl (non-Cp)-ligated rare-earth-metal precursors for trans-1,4-polymerizations of conjugated dienes is still scarce.

On the other hand, rare-earth-metal bis(alkyl)s supported by monoanionic non-Cp ancillary ligands have been demonstrated as highly active single-component catalysts or excellent precursors for the polymerizations of conjugated dienes and olefins under the activation of borates or/and aluminum alkvls.7b,8 Our group has designed a series of non-Cp-ligated rare-earth-metal bis(alkyl)s^{16,17} and found that the ligands containing N, O, and P heteroatoms play distinctive roles in governing the catalytic performance of the attached central metal ions. For instance, the cationic NCN-tridentate pincer type bis(aryliminomethylene)-2,6-phenyl-1-yl and bis(N-cyclocarbenemethylene)-2,6-phenyl-1-yl, bis(phospheno)carbazolyl rare-earth-metal complexes show high cis-1,4-selectivity for diene monomers,^{7a,8a,10a} rare-earth-metal bis(alkyl) complexes bearing an iminophosphonamido ligand (NPN type) have been employed as catalyst precursors to provide extremely high activity for 3,4-selectivity polymerization of isoprene,¹⁷ and the thiophene-NPN ligands and quinolinyl anilido ligands supported rare-earth-metal complexes, under the activation of organoborates and aluminum alkyls, exhibited distinguished catalytic activity and trans-1,4-selectivity for both butadiene and isoprene homo- and copolymerizations.^{17a,b} Meanwhile, the bis(silylated phosphazene) $[HN(PPh_2NSiMe_3)_2]$ originately explored by Oakley and Roesky as early as the 1990s¹⁸ has been developed into versatile NPNPN-type ligands consisting of a five-atom scaffold, and their supported complexes based on various metals such as Na, K, Ca,¹⁹ Al, Ga, In,²⁰ V,²¹ Zn, Cd, Hg,²² Ti,²³ Zr,²⁴ As, and U²⁵ have been synthesized and their

chemistry has been investigated. Comparatively, the rare-earthmetal complexes supported by such NPNPN-type ligands still have been untapped to date, although their bis-(phosphinimino)methanide ligand (PNCPN) supported analogues have been reported.²⁶ Recently rare-earth-metal borohydrides have attracted research interest again, as their easy accessibility, high temperature resistance, and wide utilization in the polymerizations of ethylene,²⁷ styrene,^{28,29} butadiene,³⁰ isoprene,^{28,31,32} and some polar monomers such as ε -caprolactone,^{33,34} methyl methacrylate,³⁵ and trimethylene carbonate.^{26,36}

HL³: R = ^{*i*}Pr, 88%

Herein we report the synthesis and structural characterization of a series of bis-arylated phosphazene [HN-(PPh₂NAr)₂] and imidodiphosphinate [HN(PPh₂O)₂] stabilized rare-earth-metal dialkyl and borohydrido complexes that show unique structures and versatile catalytic performances. Under the activation of some cocatalysts, the bis-phenylated phosphazene scandium bis(alkyl) complex and bis-phenylated phosphazene neodymium borohydrido complex displayed high activity and trans-1,4-selectivity toward both isoprene and butadiene polymerizations.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes 1a-c, 2a, and 3b,c. The bis-arylated phosphazene compounds $[HN(PPh_2NAr)_2]$ (Ar = benzene (HL¹), *m*-xylene (HL²), 1,3diisopropylbenzene (HL³)) were prepared via the Staudinger reaction in two steps according to a modified literature procedure (Scheme 1).²⁵ The reaction of chlorodiphenylphosphine with hexamethyldisilazene in a 2:1 molar ratio in toluene gave $HN(PPh_2)_2$. Treatment of $HN(PPh_2)_2$ with the corresponding azides resulted in the formation of HL¹, HL², and HL³, respectively. The ¹H NMR spectra of these three ligands display different chemical shifts for NH protons. The amino proton NH of the ligand HL¹ is found as a very broad singlet around δ 3–5 ppm, which appears as a singlet at 4.06 ppm for the ligand HL^2 , but the NH proton in HL^3 is not observed in C_6D_6 or $CDCl_3$. The ³¹P NMR spectra of all these ligands reveal a singlet at δ 6.51 ppm (HL¹), 1.85 ppm (HL²), or 6.26 ppm (HL³), respectively, indicating the equivalence of the two phosphine atoms in each molecule.

Treatment of these ligands with rare-earth metal tris(alkyl)s, Ln(CH₂SiMe₃)₃(THF)₂, afforded the bis(alkyl) complexes $[L^{1-3}Ln(CH_2SiMe_3)_2]$ (L¹, Ln = Sc (1a), Y (1b), Lu (1c); L², Ln = Sc (2a); L³, Ln = Y (3b), Lu (3c)) in 55–72% yields (Scheme 2). All of these complexes are soluble in THF and Scheme 2. Synthesis of the NPNPN-Type Complexes 1a-c, 2a, and 3b,c



toluene but insoluble in *n*-hexane. The methylene protons of $Y-CH_2SiMe_3$ in **1b** and **3b** give doublet resonances at δ 0.29 (**1b**) and 0.10 (**3b**), respectively, due to coupling with the yttrium ion ($J_{Y-H} = 2.8$ Hz for both), while the methylene protons of Sc- CH_2SiMe_3 and Lu- CH_2SiMe_3 in the scandium and lutetium complexes **1a**, **2a**, **1c**, and **2c** exhibit singlet resonances, respectively, suggesting that the metal alkyl species in these complexes are fluxional in the solution state. No THF molecule coordination is observed. The solid-state structures of complexes **1a**, **c**, **2a**, and **3c** were established by single-crystal X-ray diffraction, as shown in Figure 1 and Figures S27–S29



Figure 1. X-ray structure of **1a** (thermal ellipsoids at the 35% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1-N1 = 2.237(2), Sc1-N2 = 2.233(2), Sc1-N3 = 2.294(2), Sc1-C37 = 2.214(3), Sc1-C41 = 2.205(3), N1-P1 = 1.616(2), N2-P2 = 1.613(2), N3-P1 = 1.593(2), N3-P2 = 1.596(2); N1-Sc1-N2 = 129.95(8), C37-Sc1-C41 = 110.79(11), P1-N3-P2 = 158.42(15).

(Supporting Information) along with selected bond lengths and bond angles. These complexes are structural analogues. There are two alkyl species σ -bound to each central metal ion. Meanwhile, the pincer-type ligands adopt a κ^3 coordination mode via the three nitrogen atoms, which bisects the C-Ln-C bond angle formed by the alkyl groups and the central metal ion, generating a heavily distorted trigonal bipyramidal geometry around the central metal. It is worth noting that the NPNPN skeleton consists of two planar fused fourmembered rings with the covalent bond Ln-N as the sharing edge. The dihedral angle of the fused four-membered rings is 170.83° for 1a, very close to 170.39° for 1c, suggesting that the overall NPNPN skeleton has a slightly distorted planar geometry. In contrast, the dihedral angles in complexes 2a and 3c are much smaller (144.88° vs 139.88°), suggesting the NPNPN skeleton is far from a plane, which might be attributed to the Me and *i*Pr substituents of phenyl rings increasing the steric hindrance around the metal center. It is particularly noteworthy that the average phosphinimine P==N double-bond lengths (1a, 1.615 Å; 1c, 1.614 Å; 2a, 1.608 Å; 3c, 1.614 Å) are comparable to the average P–N bonds in the corresponding complexes (1a, 1.595 Å; 1c, 1.595 Å; 2a, 1.598 Å; 3c, 1.605 Å).³⁷ This indicates delocalization of the electrons over the fused four-membered rings.¹⁹ The distances between the lanthanide atoms and the central nitrogen atoms Ln–N (2.294(2) Å (1a), 2.406(3) Å (1c), 2.472(2) Å (2a), 2.494(3) (3c) fall in the normal region reported previously.³⁸

Synthesis and Characterization of Zwitterionic OPNPO-Type Yttrium Bis(alkyl) Complex 4b. The imidodiphosphinate ligand, $HN(PPh_2O)_2$ (HL⁴), was prepared by treatment of chlorodiphenylphosphine with hexamethyldi-

Scheme 3. Synthesis of the OPNPO-Type Ligand HL⁴ and Corresponding Complex 4b



silazane followed by oxidation with H_2O_2 (Scheme 3).³⁹ The ¹H NMR spectrum of HL⁴ in CDCl₃ shows three resonances within the regions of δ 7.78–7.83, 7.39–7.42, and 7.27–7.32 in a 2:1:2 ratio, which are assignable to the phenyl protons. The N*H* proton resonance is broad and weak. The ³¹P NMR spectrum in CDCl₃ shows a single resonance at δ 20.27 ppm, corresponding to two equivalent phosphorus atoms as observed in the literature.³⁹ Treatment of HL⁴ with 1 equiv of Y(CH₂SiMe₃)₃(THF)₂ at room temperature afforded the

bis(alkyl) complex L⁴Y(CH₂SiMe₃)₂(THF)₂ (**4b**) in 65% yield. The ¹H NMR spectrum of **4b** exhibits two doublets at δ –0.30 and –0.69 ppm assigned to the methylene protons Y– CH₂SiMe₃, which is in good correlation with the two doublets at δ 33.91, 33.56 ppm ($J_{\rm YC}$ = 35.3 Hz) and 29.93, 29.54 ppm ($J_{\rm YC}$ = 39.5 Hz) in its ¹³C NMR spectrum, suggesting that the methylene protons are diastereotopic and the two alkyl moieties might be located in different chemical environments.⁴⁰ In addition, there are two coordinated THF molecules in **4b**, evidenced by signals at 1.31 and 3.80 ppm in the ¹H NMR spectrum. Interestingly, complex **4b** is a zwitterion, as revealed by X-ray diffraction analysis (Figure 2). The anionic OPNPO



Figure 2. X-ray structure of **4b** (thermal ellipsoids at the 35% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1-O1 = 2.229(2), Y1-O2 = 2.303(2), Y1-O3 = 2.365(2), Y1-O4 = 2.465(2), Y1-C25 = 2.421(4), Y1-C29 = 2.438(4), N1-P1 = 1.578(3), N1-P2 = 1.587(3), P1-O1 = 1.521(2), P2-O2 = 1.510(2); O1-Y1-O2 = 84.20(8), C25-Y1-C29 = 102.56(13), Y1-O1-P1 = 135.18(14), Y1-O2-P2 = 131.93(13), P1-N1-P2 = 129.41(19).

chelates to the yttrium ion in a bidentate κ^2 coordination mode via the two neutral oxygen atoms,^{41a} while the nitrogen anion has no bond to the yttrium ion with a long Y...N distance of 3.856 Å. The bond distances between the coordinated oxygen atoms and the yttrium ion are approximately equal (Y1-O1 =2.229(2) Å, Y1–O2 = 2.303(2) Å) and are slightly shorter than that of oxygen atom from THF and the yttrium ion (Y1-O3 =2.365(2) Å, Y1-O4 = 2.465(2) Å), suggesting that the coordination of THF molecules is fluxional. Meanwhile, the bond lengths between the yttrium ion and the alkyl carbons (Y1-C25 = 2.421(4) Å, Y1-C29 = 2.438(4) Å) fall within the normal range for yttrium trimethylsilylmethyl complexes. The average P-N bond length (1.583 Å) is much shorter than the corresponding values found in structurally characterized organometallic complexes containing P-N single bonds such as $[NiCl_2(PN-iPr)]$ (1.6839 Å)^{41b} but are very close to the P= N double-bond lengths of the neutral bis(phosphinimine)pyrrole-based ligand (1.562 Å, 1.572 Å).^{37a} This can be ascribed to the strong electron-donating ability of oxygen and the highly electropositive nature of the metal center. Although the zwitterionic metal complexes have been reported to possess special properties and unique catalysis,^{41c,d} those based on rareearth metals are scarce and their reactivity has remained less explored.41a

Synthesis and Characterization of NPNPN-Type Neodymium Bis(borohydrido) Complex 5. The synthesis of the neodymium analogue is impossible by following the same procedure as for the preparation of complexes 1a, as the neodymium tris(alkyl) precursor Nd(CH₂SiMe₃)₃(THF)₂ has not been isolated as a stable product to date. Therefore, we modified the above synthetic method by lithiating the ligand HL¹ (HN(PPh₂NPh)₂) with *n*BuLi and then adding NdCl₃(THF)₃ and LiCH₂SiMe₃ in situ to the system sequentially. Unfortunately, this attempt also failed, which might be due to the larger Nd³⁺ radius and its higher coordination number. Thus, the bulky precursor Nd-(BH₄)₃(THF)₃ was employed instead of NdCl₃(THF)₃. Delightfully, the neodymium bis(borohydrido) complex L¹Nd-(BH₄)₂(THF)₂ (**5**) was successfully isolated under the optimized conditions (Scheme 4). As Nd³⁺ is paramagnetic,





the NMR spectrum analysis of **5** is uninformative, and its structure was resolved by X-ray diffraction analysis to be a monomer with two THF solvate molecules. The metal center is seven-coordinate, adopting a pentagonal-bipyamidal geometry with the two η^3 -tetrahydridoborate moieties in the axial positions (B–Nd–B = $169.83(13)^\circ$), and the two THF molecules and tridentate [N(PPh₂NPh)₂]⁻ ligand occupying the equatorial sites (Figure 3). The Nd···B contacts (Nd···B1 = 2.729(5) Å, Nd···B2 = 2.703(4) Å) are comparable to the reported data.^{31,42} The dihedral angle formed by the planes Nd1–N1–P1–N2 and Nd1–N1–P2–N3 (151.29°) is between those found in complexes **1c**, **2a**, and **3c**. This means the combination of the steric bulkiness of ligand L¹ with the higher coordination number of borohydride in complex **5** contributes to the stability of this Nd-based complex.

Polymerization of Isoprene. We explored the isoprene polymerization catalyzed by these precursors in toluene under different conditions. The representative polymerization data are summarized in Table 1. It was noted that complexes 1-4 alone showed no activity, and the binary catalytic systems generated by combining aluminum alkyls (AlR_3) also did not induce visible polymerization. Delightfully, as soon as an organoborate was added, the formed ternary systems initiated polymerization immediately. Overall, both the ligands and the types of the central metals exerted significant influences on the catalytic performances. Complexes 1a-c with the sterically less bulky ligand L^1 (N(PPh₂NAr)₂, Ar = phenyl) showed similar high activity upon activation with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ and 10 equiv of AliBu₃, achieving complete conversion within 5 h at room temperature (Table 1, entries 1, 6, and 7), which were comparable to those of the lanthanide allyl complexes rac- $[{Me_2C(Ind)_2}Y(1,3-(SiMe_3)_2C_3H_3)]/CTA^{14d}$ and the lanthanide aluminate $[(C_5Me_5)Ln(AlMe_4)_2]/organoborate,^{14e}$ while complexes 2a and 3b,c bearingthe larger ligands $N(PPh_2NAr)_2$ (Ar = 2,6-dimethylphenyl, 2,6-diisopropylphenyl) were totally inert under the same conditions, suggesting that more crowded



Figure 3. X-ray structure of **5** (thermal ellipsoids at the 35% probability level): (A) hydrogen atoms omitted for clarity, except for the freely refined B–H atoms; (B) all the hydrogen and carbon atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd1–N1 = 2.464(3), Nd1–N2 = 2.617(3), Nd1–N3 = 2.483(3), Nd1–B1 = 2.729(5), Nd1–B2 = 2.703(4), Nd1–H1A = 2.4869, Nd1–H1B = 2.7784, Nd1–H1C = 2.4673, Nd1–H2A = 2.4719, Nd1–H2B = 2.5766, Nd1–H2C = 2.6237, N1–P1 = 1.600(3), N2–P1 = 1.597(3), N2–P2 = 1.598(3), N3–P2 = 1.603(3); B2–Nd1–B1 = 169.83(13), N1–Nd1–N3 = 112.13(10), N1–Nd1–O1 = 91.73(9), O2–Nd1–O1 = 76.63(9), N1–Nd1–N2 = 58.74(10), N3–Nd1–N2 = 58.77(9), P1–N2–P2 = 146.0(2).

Table	1.	Pol	vmerization	of	Iso	prene	under	Va	arious	Conditions
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entry ^a	cat.	amt of AlR ₃ (equiv) [R or Mg compd]	$(^{\circ}C)^{T_{p}}$	time (h)	yield (%) ^b	cis-1,4/trans-1,4/3,4 microstructure (%) ^c	$M_{n}^{d} \times 10^{-4}$	${M_{ m w}}/{M_{ m n}}^d$	$T_{\rm g}/T_{\rm m}~(^{\circ}{\rm C})^e$
1	1a + A	10 [<i>i</i> Bu]	25	5	100	1.3/90.0/8.7	1.27	1.47	-63.2/23.5
2	1a + A	10 [Et]	25	5	82	11.3/78.6/10.1	1.24	2.05	-64.1/25.9
3	1a + A	10 [Me]	25	5	75	67.3/23.2/9.5	2.48	2.13	-60.0/-
4	1a + B	10 [<i>i</i> Bu]	25	5	100	1.8/88.8/9.4	1.70	1.49	-63.7/25.0
5	1a + C	10 [<i>i</i> Bu]	25	5	0				
6	1b + A	10 [<i>i</i> Bu]	25	5	100	76.3/11.5/12.2	2.37	1.54	-58.6/-
7	1c + A	10 [<i>i</i> Bu]	25	5	100	34.1/54.3/11.6	1.94	1.66	-61.3/-
8	4b + A	10 [<i>i</i> Bu]	25	0.5	100	70.6/9.2/20.2	5.64	1.59	-53.9/-
9	5 + A	$1 \left[Mg(nBu)_2 \right]$	25	5	93	6.0/92.7/1.3	4.38	1.38	-69.1/32.5
10	5	$1 \left[Mg(nBu)_2 \right]$	25	12	62	1.2/97.0/1.8	2.37	1.18	-61.5/37.3
11^{f}	5	$1 \left[Mg(nBu)_2 \right]$	50	12	60	2.6/94.0/3.4 ^g	2.15	1.34	48.3/90.6 ^h

^{*a*}General conditions: 10^{-5} mol of Ln complex; toluene 5 mL; $[IP]_0:[Ln]_0 = 1000:1$; $[activator]_0:[Ln]_0 = 1:1$ (activator = $[Ph_3C][B(C_6F_5)_4]$ (A), $[PhNHMe_2][B(C_6F_5)_4]$ (B), $B(C_6F_5)_3$ (C)). ^{*b*}Isolated yield of polymer. ^{*c*}Determined by ¹³C NMR and ¹H NMR. ^{*d*}Determined by GPC in THF at 40 °C against a polystyrene standard. ^{*e*}Determined from the second heating cycle of DSC measurements run at 10 °C min⁻¹. ^{*f*}Monomer: butadiene, $[BD]_0:[Ln]_0 = 1000.$ ^{*g*}1,2-vinyl polybutadiene. ^{*h*} T_t/T_m .

metal center hinders the orientation and insertion of the incoming monomer after incorporation of one isoprene molecule.^{17a} Among these complexes the zwitterion complex 4b exhibited the highest catalytic activity, finishing the polymerization in 30 min, which might be attributed to the smaller steric hindrance of the ligand L^4 (N(PPh₂O)₂) as well as the larger Y metal ion (Table 1, entry 8). Although zwitterionic complexes have been known to catalyze organic synthesis, there is only one case reported previously by us that a heteroscopionate yttrium zwitterion complex could initiate heteroselective polymerization of rac-lactide. Therefore, complex 4b is the first zwitterionic complex to show catalysis toward isoprene polymerization. The borohydrido complex 5, although it could not be activated by aluminum alkyls and zinc alkyls, in combination with 1 equiv of $Mg(nBu)_2$ exhibited activity similar to those of complexes 1 toward the polymerization of isoprene at room temperature (for butadiene, a higher polymerization temperature was needed). Addition of organoborate to the $5/Mg(nBu)_2$ system dramatically accelerated the polymerization rate; both the conversion and the molecular weight almost doubled (Table 1, entries 9 and 10).

The selectivity of the polymerization showed strong dependence on the central metal ions. Bearing the same L^1 ligand, scandium complex 1a provided high trans-1,4-selectivity (90.0%), while the lutetium complex 1c had medium trans-1,4selectivity (54.3%). In contrast, both yttrium complexes 1b and 4b displayed enriched cis-1,4-selectivity (76.3 and 70.6%) (Table 1, entries 1 and 6-8). These results were consistent with those found in the catalytic system composed of the scandium dialkyl complex bearing a thiophene-NPN ligand, which initiated the highly trans-1,4-selective polymerization of butadiene activated by [NHMe₂Ph][B(C₆F₅)₄] and AliBu₃.^{17a} The stereoselectivity can be explained on the basis of the wellestablished mechanism for polymerization of conjugated dienes.^{43a} The polymerization was initiated by the coordination of the monomer to the metal center followed by its insertion into a metal- σ -alkyl (allyl) active species for propagation. The monomer η^2 -trans coordinates to the metal center to form mainly the syn Ln-allyl transition state species, which is inserted by the monomer at the C1-Ln bond to give trans-1,4regulated polyisoprene. When the attached ligand was electronwithdrawing, the addition of isoprene monomer to the Ln-C3 carbon was favored to arouse the advantage of 3,4-regularity. In

Table 2	. Copol	ymerization	of Butadiene	(BD)	and	Isoprene	(IP)) using	Comp	lex 1a	/[Ph	ı₃C_][B(C_6F	$_{5})_{4}$	/AliB	u ₃
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entry ^a	BD/IP (mmol/mmol)	PBD content (%)	cis-1,4/trans-1,4/1,2 BD microstructure(%) ^b	cis-1,4/trans-1,4/3,4 IP microstructure(%) ^b	$M_{n}^{c} \times 10^{-4}$	${M_{ m w}}_n^\prime / {M_{ m n}}^c$	$T_{\rm g}/T_{\rm m}~(^{\circ}{\rm C})^d$
1	0/20	0	-/-/-	3.1/87.3/9.6	3.96	1.80	-64.7/23.3
2	4/16	20	20.4/69.5/10.1	3.1/87.1/9.8	3.55	1.50	-66.3/-
3	8/12	40	21.7/69.8/8.5	5.2/84.2/10.6	4.04	1.42	-72.4/-
4	12/8	60	21.2/70.7/8.1	5.6/83.1/11.3	3.79	1.57	-75.5/-
5	16/4	80	20.3/71.8/7.9	5.9/82.6/11.5	3.99	1.54	-76.0/15.4
6	20/0	100	18.3/74.1/7.6	-/-/-	3.60	1.64	41.9/62.5 ^e

^{*a*}General conditions: 10^{-5} mol of complex 1a (Sc); toluene 5 mL; T_p 25 °C; $[Ph_3C][B(C_6F_5)_4]$:[Sc] = 1:1; $[Al]:AliBu_3$; [Al]/[Sc] = 10. Yield of copolymers: 100%. ^{*b*}Determined by ¹³C NMR and ¹H NMR. ^{*c*}Determined by GPC in THF at 40 °C against a polystyrene standard. ^{*d*}Determined from the second heating cycle of DSC measurements run at 10 °C min⁻¹. ^{*e*} T_t/T_m .

contrast, if the monomer η^2 -cis or η^4 -cis coordinates to the metal center to form mainly the anti Ln-allyl transition state species which is attached by monomer at the C1-Ln bond to give cis-1,4-regulated polyisoprene.^{1,14d,43} Therefore, the geometry of the ligand and the specific environment around the central metal play a significant role in governing the selectivity. For complex 1a, the the Sc^{3+} ion is so small that the ligand provides efficient steric shielding to the metal center, which only allows isoprene η^2 -trans coordination and favors the formation of trans-1,4-polyisoprene. With an increase of the ionic radius size,⁴⁴ the Y and Lu complexes 1b,c endowed a more open space for isoprene η^4 coordination. Thus, cis-1,4selectivity increased with the ionic radius. In the presence of AlEt₃, the catalytic system provided good activity and moderate trans-1,4-stereoselectivity (78.6%); however, on switching to AlMe₃, the trans-1,4-selectivity decreased significantly to 23.2%. Instead, the cis-1,4-selectivity increased to 67.3% (Table 1, entries 2 and 3). Similar results arising from a change of AIR_3 cocatalysts was found previously by Hou et al., who proved preliminarily that the generated cationic Ln-Al heteronuclear species might be attributed to the cis-1,4-polymerization of isoprene.^{45a} The trityl and anilinium borate activators A and B showed similar influences on the polymerization activity and selectivity (Table 1, entries 2 and 5), indicating that the resulting cationic active species had a weak connection with the counterion groups. The neutral borane compound C showed poor activity (Table 1, entry 5), which was observed in many systems reported previously.^{7c,10b} To date only a few organometallic complexes have been activated by neutral borane.^{45b} The catalytic system composed of complex 5 and $Mg(nBu)_2$ exhibited the highest trans-1,4-selectivity (97.0%) in this work at room temperature (Table 1, entry 10), in accordance with the formation of a Nd/Mg bimetallic compound bearing a bridging $Mg-BH_4$ group.^{4,45e}

The thermal behaviors of the obtained polymers were examined by DSC. Generally the trans-1,4-regulated polyisoprenes isolated from this work had a $T_{\rm g}$ value in the range of -50 to -70 °C, in agreement with the earlier literature.^{45c} Meanwhile, the melting transition temperature $T_{\rm m}$ could also be observed, which appears as a low value within the range 22–26 °C (with low intensity) for those polymers obtained by using complexes 1 as the precursors, while a much higher $T_{\rm m}$ value is found around 30–40 °C for the samples produced by the borohydrido catalytic system, which, as reported previously, depends on the molecular weights of polyisoprenes and their trans-1,4-contents as well as the length of the trans-1,4-sequences.^{14d,45c,d,g} Obviously, *trans*-1,4-polybutadiene having more regular polymeric chains in comparison to *trans*-1,4-polyisoprene (without side methyl groups) possesses crystalline-type (monoclinic-hexagonal) transition temperature (T_v 48.3 °C) and a much higher T_m value (90.6 °C).^{5c,17a,b}

Copolymerization of Isoprene and Butadiene. The copolymerization of butadiene with isoprene is usually adopted as an efficient way to reduce the crystallinity of the trans-1,4regulated polydiene homopolymers in order to improve their processing and mechanical properties.⁴⁶ We found that the system $la/[Ph_3C][B(C_6F_5)_4]/AliBu_3$ was able to initiate butadiene polymerization in a trans-1,4-selective manner with an activity similar to that for isoprene. Thus, the copolymerization of butadiene and isoprene was explored under various monomer feed ratios. The representative polymerization data are given in Table 2. It can be seen that all the copolymerizations could occur fluently to achieve complete conversions. The compositions of the copolymers were precisely consistent with the BD-to-IP feed ratios. In the copolymers, the trans-1,4-regularities of both the PIP and PBD sequences dropped slightly in comparison with the homopolymers, as evidenced by the ¹H NMR spectroscopy analysis. This was understandable, as the tacticity is usually lost at the joints of the polyisoprene and polybutadiene units in the copolymer, in particular when the two-type units are arranged randomly. The Fineman–Ross^{45f} plot for the copolymerization performed at 25 °C is depicted in Figure 4. A plot of F(f-1)/fas the ordinate and F^2/f as the abscissa is a straight line whose slope is r_{BD} and whose intercept is $-r_{IP}$ (F = [BD]/[IP] in feed, f = [BD]/[IP] in copolymer). The monomer competitive



Figure 4. Fineman–Ross plot for copolymerization of butadiene (BD) and isoprene (IP) with $1a/[Ph_3C][B(C_6F_5)_4]/AliBu_3$ at 25 °C (F = [BD]/[IP] in feed, f = [BD]/[IP] in copolymer, $r_{BD} = 2.89$, $r_{IP} = 0.41$).

polymerization rates were calculated to be $r_{\rm BD} = 2.89$ and $r_{\rm IP} = 0.41$, respectively, which is very close to the values for the copolymerization with the V(acac)₃/MAO system,^{46c} indicating an activity of butadiene slightly higher than that of isoprene and the random copolymerization tendency because of time value $r_{\rm BD} \times r_{\rm IP} = 1.18$.^{43c,46a-c} The thermal behavior of the obtained butadiene–isoprene copolymers was also examined by DSC. As shown in Figure 5, the crystalinity of the *trans*-1,4-polyisoprene



Figure 5. DSC curves of the resulting polymers given in Table 2: (1) 100% PIP (polyisoprene); (2) 20% PBD (polybutadiene); (3) 40% PBD; (4) 60% PBD; (5) 80% PBD; (6) 100% PBD.

was suppressed dramatically via incorporation of polybutadiene units over 20 mol %, as the endothermic peak (melting temperature $T_{\rm m}$) disappeared completely (traces 2–4), which was attributed to damage of the ordered arrangement of isoprene repeating units. When the content of the polybutadiene units increased up to 80 mol %, a broad endothermic peak appeared at 15.4 °C (trace 5), assigned to the overlapped monoclinic-hexagonal transition and melting temperatures ($T_{\rm t}$ and $T_{\rm m}$) of the highly trans-1,4-regulated PBD sequences,^{17b} which is much lower than $T_{\rm tr}$ = 41.5 °C and $T_{\rm m}$ = 62.5 °C of the homo-polybutadiene sample (trace 6). This indicates that the crystallinity of the trans-1,4-regulated polybutadiene and polyisoprene can be easily adjusted by the random copolymerization if a properly chosen catalytic precursor is employed.

CONCLUSION

We have demonstrated that the synthesis of a new family of bisarylated phosphazene (NPNPN-type) and imidodiphosphinate (OPNPO-type) rare-earth-metal bis(alkyl) and borohydrido complexes can be accessed by amino proton abstraction or sequential metathesis reactions. All these complexes are welldefined; in particular, the OPNPO-type yttrium bis(alkyl) complex **4b** adopts a rare zwitterionic structure. Furthermore, the catalytic performances of these complexes under the activation of proper metal alkyls or/and organoborate for isoprene or/and butadiene polymerization have been investigated. The zwitterionic yttrium alkyl complex **4b** bearing the imidodiphosphinate OPNPO-type ligand shows the highest activity, providing cis-1,4-enriched polyisoprene, while the complexes 1a-c bearing a bis-phenylated phosphazene NPNPN-type ligand exhibit higher activities; nevertheless, the analogues 2a and 3b,c with the sterically more bulky NPNPNtype ligands are totally inert, as the steric shielding around the metal center inhibits isoprene coordination. The microstructures of the polymers obtained are highly dependent on the central metals. Polyisoprene with very high trans-1,4content (90.0%) can be obtained from the smaller scandium precursor 1a, which is the first example of a scandium catalytic precursor initiating trans-1,4-selective polymerization of isoprene. With an increase of the metal ionic radius, which facilitates isoprene η^4 coordination, the cis-1,4-stereoselectivity obviously increases. The neutral system composed of complex 5 and $Mg(nBu)_2$ provides a much higher trans-1,4-selectivity toward homopolymerizations of both butadiene and isoprene (trans-1,4-contents 94.0% for butadiene and 97.0% for isoprene). The copolymerization of butadiene and isoprene by using the $la/[Ph_3C][B(C_6F_5)_4]/AliBu_3$ system yields random but noncrystalline copolymers with trans-1,4-regularity for both PBD and PIP sequences, which might find potential application for the preparation of low-rolling-resistance and high-slip-resistance tires.

EXPERIMENTAL SECTION

General Methods and Materials. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a MBraun glovebox. All solvents were purified with a MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for 1 H; 100 MHz for 13 C) or Bruker AV600 (FT, 600 MHz for 1 H; 150 MHz for ¹³C) spectrometer. ³¹P NMR spectra were recorded on a Bruker AV400 (FT, 162 MHz) spectrometer. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). Isoprene was dried over CaH₂ with stirring for 48 h and distilled under vacuum before use. Hexamethyldisilazane, MgnBu₂ (1.0 M in heptane), nBuLi (1.6 M in hexane), LnCl₃, and NaBH₄ were purchased from Aldrich or Fluka. Phenyl azide, ^{47a} 2,6-dimethylphenyl azide, ^{47b} 2,6-diisopropyl-phenyl azide, ^{47c,d} $Ph_2P-NH-PPh_2^{25}$ HN(PPh_2O)₂ (HL⁴),³⁹ Ln- $(CH_2SiMe_3)_3(THF)_2^{48} Nd(BH_4)_3(THF)_3^{49} [Ph_3C][B(C_6F_5)_4], and [PhNMe_2H][B(C_6F_5)_4]^{50}$ were synthesized as reported. The microstructure of polyisoprene was determined by ¹H NMR and ¹³C NMR spectra. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyisoprene were measured by a TOSOH HLC-8220 GPC instrument. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry. DSC was performed on a Mettler TOPEM TM DSC instrument under a nitrogen atmosphere. The thermal history difference in the polymers was eliminated by first heating the specimen to 120 °C, cooling at 10 °C min⁻¹ to -110 °C, and then a second heating from -110 to 120 $^\circ C$ at 10 $^\circ C$ min $^{-1}$ was performed. The reactivity ratios r_1 and r_2 were determined using the Fineman-Ross method and the linear relationship $F(f-1)/f = r_1(F^2/f) - r_2$, where F and f are the butadiene/isoprene molar ratios in the feed and the polymer (by ¹H NMR analysis), respectively.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at -88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ 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. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms

were placed at calculated positions and were included in the structure calculations without further refinement of the parameters.

Synthesis of [C₆H₅N=PPh₂HNPh₂P= $\bar{N}C_6H_5$] (HL¹). Phenyl azide (2.86 g, 24 mmol) in 10 mL of toluene was added dropwise to a toluene solution (50 mL) of bis(diphenylphosphine)amine (Ph₂PNHPPh₂) (3.85 g, 10 mmol) at 60 °C by releasing nitrogen gas. The reaction mixture was refluxed until the evolution of nitrogen gas ceased. Finally, the solution was concentrated to approximately 20 mL and was kept at -30 °C for 2 h. Filtering, washing with hexane, and evaporating the residual solvents afforded HL¹ as a pale yellow solid (5.36 g, 90%). ¹H NMR (300 MHz, CDCl₃, 7.26 ppm, 25 °C): δ 3.00–5.00 (very broad s, 1H, NH), 6.62–6.70 (m, 6H, *o*-NC₆H₅ and *p*-NC₆H₅), 6.94 (t, ³J_{HH} = 7.5 Hz, 4H, *o*-NC₆H₅), 7.30–7.42 (m, 12H, *m*-PC₆H₅ and *p*-PC₆H₅), 7.82 (quart, ³J_{HH} = 7.2 Hz, 8H, *o*-PC₆H₅). ³¹P NMR (162 MHz, CDCl₃, 25 °C): δ 6.51 ppm (s). Anal. Calcd for C₂₄H₃₁N₃P₂: C, 68.09; H, 7.33; N, 9.93. Found: C, 68.35; H, 7.20; N, 9.79.

Synthesis of [2,6-Me₂C₆H₃N=PPh₂HNPh₂P=NC₆H₃Me₂-2,6] (HL²). 2,6-Dimethylphenyl azide (3.53 g, 24 mmol) in 10 mL of toluene was added dropwise to a toluene solution (50 mL) of bis(diphenylphosphine)amine (Ph₂PNHPPh₂) (3.85 g, 10 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 2 h and then heated to 70 °C for 12 h for the complete evolution of nitrogen gas. Removal of the volatiles gave a reddish solid, which was further purified by washing with hexane to afford reddish solids (5.05 g, 81%). ¹H NMR (400 MHz, CDCl₃, 7.26 ppm, 25 °C): δ 1.99 (s, 12H, CH₃), 4.06 (br s, 1H, NH), 6.69 (t, ³J_{HH} = 7.6 Hz, 2H, *p***-NC₆H₃), 6.82 (d, ³J_{HH} = 3.6 Hz, 4H,** *m***-NC₆H₃), 7.19–7.23 (m, 8H,** *m***-PC₆H₅), 7.32 (t, ³J_{HH} = 7.2 Hz, 4H,** *p***-PC₆H₅), 7.66 (quart, ³J_{HH} = 7.2 Hz, 8H,** *o***-PC₆H₅). ³¹P NMR (162 MHz, CDCl₃, 25 °C): δ 1.85 ppm (s). Anal. Calcd for C₂₈H₃₉N₃P₂: C, 70.15; H, 8.14; N, 8.77. Found: C, 69.80; H, 8.31; N, 8.87.**

Synthesis of $[2,6-Pr_2C_6H_3N = PPh_2HNPh_2P = NC_6H_3'Pr_2-2,6]$ (HL³). Following a similar procedure described for the preparation of ligand HL², the ligand HL³ was isolated from the Staudinger reaction of Ph_2PNHPPh_2 (3.85 g, 10 mmol) with 2.4 equiv of 2,6-diisopropylphenyl azide (4.87 g, 24 mmol) as a pale white powder (6.47 g, 88%). ¹H NMR (300 MHz, CDCl₃, 7.26 ppm, 25 °C): δ 0.76 (d, ³J_{HH} = 6.9 Hz, 24H, CH(CH_3)_2), 3.55 (sept, ³J_{HH} = 6.9 Hz, 44H, CH(CH_3)_2), 6.91 (s, 6H, *p*-C₆H₃ and *m*-NC₆H₃), 7.20–7.30 (m, 8H, *m*-PC₆H₅), 7.38 (t, ³J_{HH} = 7.2 Hz, 4H, *p*-PC₆H₅), 7.49 (quart, ³J_{HH} = 7.2 Hz, 8H, *o*-PC₆H₅) (the NH signal did not appear). ³¹P NMR (162 MHz, CDCl₃, 25 °C): δ 6.26 ppm (s). Anal. Calcd for C₃₆H₅₅N₃P₂: C, 73.10; H, 9.31; N, 7.11. Found: C, 73.48; H, 9.38; N, 6.95.

Synthesis of $L^{1}Sc(CH_{2}SiMe_{3})_{2}$ (1a). To a hexane solution (2.0 mL) of Sc(CH₂SiMe₃)₃(THF)₂ (0.225 g, 0.5 mmol) was added dropwise 1 equiv of HL¹ (0.297 g, 0.5 mmol in 2 mL of THF) at room temperature. The mixture was stirred for 3 h at room temperature and then concentrated to about 0.5 mL. Addition of 1 mL of hexane and cooling to -30 °C for 2 days afforded crystalline solids, which were washed with a small amount of hexane to remove impurities and dried in vacuo to give pale yellow solids of 1a (0.236 g, 60%). Single crystals suitable for X-ray analysis were obtained from a THF/toluene mixture at -30 °C within 2 days. ¹H NMR (400 MHz, C₆D₆, 7.16 ppm, 25 °C): δ 0.39 (s, 18H, CH₂SiMe₃), 0.91 (s, 4H, CH₂SiMe₃), 6.71-6.82 (m, 10 H, NC₆H₅), 6.88 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, *m*-PC₆H₅), 7.09 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 4H, *m*-PC₆H₅), 7.38 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 4H, *p*-PC₆H₅), 7.52 (m, 8H, *o*-PC₆H₅). 13 C NMR (100 MHz, C₆D₆) 128.06 ppm, 25 °C): δ 4.19 (s, 6C, CH₂SiMe₃), 44.62 (br s, 2C, CH₂SiMe₃), 121.63 (s, aromatic CH), 123.10 (m, aromatic CH), 128.60 (m, aromatic CH), 129.33 (s, aromatic CH), 129.60 (d, J_{PC} = 4.3 Hz, 2C, aromatic ipso-C), 130.75 (d, J_{PC} = 4.3 Hz, 2C, aromatic *ipso-C*), 132.11–132.28 (m, aromatic CH), 147.07 (s, aromatic ipso-C). Anal. Calcd for C32H52N3P2Si2Sc: C, 48.85; H, 6.62; N, 5.34. Found: C, 48.53; H, 6.52; N, 5.57.

Synthesis of L¹Y(CH₂SiMe₃)₂ (1b). By a procedure similar to that described for the preparation of **1a**, treatment of Y-(CH₂SiMe₃)₃(THF)₂ (0.247 g, 0.50 mmol) with HL¹ (0.297 g, 0.50 mmol) gave yellow solids of **1b** (0.241 g, 58%). Single crystals suitable for X-ray analysis were not obtained. ¹H NMR (600 MHz, C_6D_{67} 7.16

ppm, 25 °C): δ 0.30 (d, J_{YH} = 2.8 Hz, 4H, CH_2SiMe_3), 0.40 (s, 18H, CH_2SiMe_3), 6.72–6.83 (m, 10H, NC_6H_5), 6.90 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, m-PC₆H₅), 7.06 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 4H, m-PC₆H₅), 7.20 (d, ${}^{3}J_{HH}$ = 8.0 Hz, 4H, p-PC₆H₅), 7.50 (m, 8H, o-PC₆H₅). ${}^{13}C$ NMR (150 MHz, C₆D₆, 128.06 ppm, 25 °C): δ 4.84 (s, 6C, CH_2SiMe_3), 39.22 (d, J_{YC} = 41 Hz, 2C, CH_2SiMe_3), 121.74 (s, aromatic CH), 122.70 (m, aromatic CH), 129.68 (s, aromatic CH), 129.97 (s, aromatic CH), 130.43 (d, J_{PC} = 7.2 Hz, 2C, aromatic *ipso*-C), 131.16 (d, J_{PC} = 7.2 Hz, 2C, aromatic *ipso*-C), 132.51 (s, aromatic CH), 147.36 (s, aromatic *ipso*-C). Anal. Calcd for $C_{32}H_{52}N_3P_2Si_2Y$: C, 46.27; H, 6.27; N, 5.06. Found: C, 46.49; H, 6.12; N, 4.90.

Synthesis of $L^{1}Lu(CH_{2}SiMe_{3})_{2}$ (1c). By a procedure similar to that described for the preparation of 1a, treatment of Lu- $(CH_2SiMe_3)_3(THF)_2$ (0.290 g, 0.50 mmol) with HL¹ (0.297 g, 0.50 mmol) gave yellow crystals of 1b (0.330 g, 72%). Single crystals suitable for X-ray analysis were obtained from a THF/toluene mixture at -30 °C within 2 days. ¹H NMR (600 MHz, C₆D₆, 7.16 ppm, 25 °C): δ 0.16 (s, 4H, CH₂SiMe₃), 0.41 (s, 18H, CH₂SiMe₃), 6.72–6.79 (m, 10H, NC₆H₅), 6.90 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, *m*-PC₆H₅), 7.06 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 4H, *m*-PC₆H₅), 7.23 (d, ${}^{3}J_{HH}$ = 8.4 Hz, 4H, *p*-PC₆H₅), 7.50 (m, 8H, *o*-PC₆H₅). 13 C NMR (150 MHz, C₆D₆, 128.06 ppm, 25 °C): δ 4.68 (s, 6C, CH₂SiMe₃), 46.03 (s, 2C, CH₂SiMe₃), 121.43 (s, aromatic CH), 122.55 (m, aromatic CH), 128.35 (s, aromatic CH), 128.63 (m, aromatic CH), 129.34 (s, aromatic CH), 129.48 (s, aromatic CH), 130.08 (d, J_{PC} = 7.0 Hz, 2C, aromatic *ipso-C*), 130.86 (d, J_{PC} = 7.0 Hz, 2C, aromatic ipso-C), 131.96 (m, aromatic CH), 132.22 (s, aromatic CH), 146.83 (s, aromatic ipso-C). Anal. Calcd for C32H52N3P2Si2Lu: C, 41.92; H, 5.68; N, 4.59. Found: C, 41.67; H, 5.82; N, 4.73.

Synthesis of L²Sc(CH₂SiMe₃)₂ (2a). By a procedure similar to that described for the preparation of 1a, treatment of Sc- $(CH_2SiMe_3)_3(THF)_2$ (0.225 g, 0.50 mmol) with HL² (0.312 g, 0.50 mmol) gave yellow solids of 2a (0.232 g, 55%). Single crystals suitable for X-ray analysis were obtained from a THF/toluene mixture at -30 $^{\circ}$ C overnight. ¹H NMR (400 MHz, C₆D₆, 7.16 ppm, 25 $^{\circ}$ C): δ 0.24 (s, 18H, CH₂SiMe₃), 0.60 (s, 4H, CH₂SiMe₃), 2.37 (s, 12H, C₆H₃CH₃), 6.78 (t, ${}^{3}J_{HH} = 8.0$ Hz, 8H, m-PC₆ H_{5}), 6.88 (t, ${}^{3}J_{HH} = 6.8$ Hz, 4H, m-NC₆H₃), 6.95 (t, ${}^{3}J_{HH}$ = 6.8 Hz, 2H, *p*-NC₆H₃), 7.04 (d, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, p-PC₆H₅), 7.52 (m, 8H, o-PC₆H₅). ¹³C NMR (150 MHz, C₆D₆) 128.06 ppm, 25 °C): δ 4.09 (s, 6C, CH₂SiMe₃), 21.79 (s, 4C, C₆H₃CH₃), 46.95 (s, 2C, CH₂SiMe₃), 124.43 (s, aromatic CH), 122.55 (m, aromatic CH), 128.35 (s, aromatic CH), 128.63 (m, aromatic CH), 129.34 (s, aromatic CH), 129.59 (s, aromatic CH), 131.61 (s, aromatic CH), 131.79 (s, aromatic CH), 132.91 (d, $J_{PC} = 6.0$ Hz, 2C, aromatic ipso-C), 134.01 (d, J_{PC} = 6.0 Hz, 2C, aromatic ipso-C), 135.54 (s, aromatic CH), 142.81 (s, aromatic ipso-C). Anal. Calcd for C36H60N3P2Si2Sc: C, 51.31; H, 7.13; N, 4.99. Found: C, 51.66; H, 7.02; N, 4.84.

Synthesis of L³Y(CH₂SiMe₃)₂ (3b). By a procedure similar to that described for the preparation of 1a, treatment of Y-(CH₂SiMe₃)₃(THF)₂ (0.247 g, 0.50 mmol) with HL³ (0.368 g, 0.50 mmol) gave yellow solids of 3b (0.335 g, 67%). Single crystals suitable for X-ray analysis were not obtained. ¹H NMR (400 MHz, C₆D₆, 7.16 ppm, 25 °C): δ 0.10 (d, J_{YH} = 2.8 Hz, 4H, CH_2SiMe_3), 0.34 (s, 18H, CH_2SiMe_3), 0.63 (d, ${}^{3}J_{HH}$ = 5.6 Hz, 12H, $C_6H_3CH(CH_3)_2$), 1.55 (d, ${}^{3}J_{\text{HH}} = 5.6 \text{ Hz}, 12 \text{H}, C_{6}\text{H}_{3}\text{CH}(\text{CH}_{3})_{2}), 3.81 \text{ (sept, } {}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, 4 \text{H},$ $C_6H_3CH(CH_3)_2$, 6.78–6.88 (m, 12H, m-PC₆H₅ and p-PC₆H₅), 7.15 (s, 6H, m-NC₆H₃ and p-NC₆H₃), 7.38 (m, 8H, o-PC₆H₅). ¹³C NMR (100 MHz, C₆D₆, 128.06 ppm, 25 °C): δ 4.48 (s, 6C, CH₂SiMe₃), 23.30 (s, 4C, C₆H₃CH(CH₃)₂), 27.75 (s, 4C, C₆H₃CH(CH₃)₂), 29.20 (s, 4C, $C_6H_3CH(CH_3)_2$), 46.95 (d, $J_{YC} = 27.7$ Hz, 2C, CH_2SiMe_3), 124.66 (s, aromatic CH), 124.90 (s, aromatic CH), 125.70 (s, aromatic CH), 129.33 (s, aromatic CH), 131.48 (s, aromatic CH), 132.12 (m, aromatic CH), 132.78 (d, J_{PC} = 5.4 Hz, 2C, aromatic ipso-C), 133.51 (d, J_{PC} = 5.4 Hz, 2C, aromatic ipso-C), 139.16 (s, aromatic ipso-C), 145.67 (s, aromatic *ipso-C*). Anal. Calcd for C₄₄H₇₆N₃P₂Si₂Y: C, 52.80; H, 7.60; N, 4.20. Found: C, 53.05; H, 7.49; N, 4.08.

Synthesis of L³Lu(CH₂SiMe₃)₂ (3c). Following a procedure similar to that described for the preparation of 1a, treatment of

 $Lu(CH_2SiMe_3)_3(THF)_2$ (0.290 g, 0.50 mmol) with HL³ (0.368 g, 0.50 mmol) gave yellow solids of 3c (0.348 g, 64%). Single crystals suitable for X-ray analysis were obtained from a THF/toluene mixture at -30°C overnight. ¹H NMR (400 MHz, C_6D_{64} 7.16 ppm, 25 °C): δ –0.10 (s, 4H, CH_2SiMe_3), 0.35 (s, 18H, CH_2SiMe_3), 0.66 (d, ${}^{3}J_{HH} = 6.8$ Hz, 12H, $C_6H_3CH(CH_3)_2$), 1.56 (d, ${}^{3}J_{HH} = 6.8$ Hz, 12H, C_6H_3CH - $(CH_3)_2$), 3.87 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 4H, $C_6H_3CH(CH_3)_2$), 6.75–6.84 (m, 12H, m-PC₆H₅ and p-PC₆H₅), 7.16 (s, 6H, m-NC₆H₃ and p-NC₆H₃), 7.40 (m, 8H, o-PC₆H₅). ¹³C NMR (150 MHz, C₆D₆, 128.06 ppm, 25 °C): δ 4.62 (s, 6C, CH₂SiMe₃), 23.50 (s, 4C, C₆H₃CH-(CH₃)₂), 27.80 (s, 4C, C₆H₃CH(CH₃)₂), 29.11 (s, 4C, C₆H₃CH-(CH₃)₂), 47.31 (s, 2C, CH₂SiMe₃), 124.69 (s, aromatic CH), 125.07 (s, aromatic CH), 130.73 (s, aromatic CH), 131.51 (s, aromatic CH), 132.22 (m, aromatic CH), 132.77 (d, J_{PC} = 5.4 Hz, 2C, aromatic ipso-C), 133.50 (d, J_{PC} = 5.4 Hz, 2C, aromatic *ipso-C*), 139.04 (s, aromatic ipso-C), 145.89 (s, aromatic ipso-C). Anal. Calcd for C44H76N3P2Si2Lu: C, 48.57; H, 6.99; N, 3.86. Found: C, 48.95; H, 6.74; N, 3.75.

Synthesis of L⁴Y(CH₂SiMe₃)₂(THF)₂ (4b). Following a procedure similar to that described for the preparation of 1a, treatment of $Y(CH_2SiMe_3)_3(THF)_2 \ (0.247 \ g, \ 0.50 \ mmol)$ with $HL^4 \ (0.208 \ g, \ 0.50 \ mmol)$ mmol) gave yellow solids of 4b (0.268 g, 65%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane mixture at -30 °C overnight. ¹H NMR (400 MHz, C₆D₆, 7.16 ppm, 25 °C): δ -0.69 (d, ² J_{YH} = 2 Hz, 2H, CH₂SiMe₃), -0.30 (s, 2H, CH₂SiMe₃), 0.29 (s, 18H, CH₂SiMe₃), 1.31 (m, 8H, THF), 3.80 (m, 8H, THF), 7.00-7.11 (m, 12H, m-PC₆H₅ and p-PC₆H₅), 7.95-8.01 (m, 8H, o- PC_6H_5). ¹³C NMR (100 MHz, C_6D_6 , 128.06 ppm, 25 °C): δ 4.64 (s, 6C, CH₂SiMe₃), 25.25 (s, 4C, THF), 29.73 (d, J_{YC} = 39.5 Hz, 1C, CH₂SiMe₃), 33.73 (d, J_{YC} = 35.3 Hz, 1C, CH₂SiMe₃), 69.78 (s, 4C, THF), 125.70 (s, aromatic CH), 128.57 (s, aromatic CH), 129.33 (s, aromatic CH), 130.50 (s, aromatic CH), 131.04 (s, aromatic CH), 131.22–131.65 (m, aromatic CH), 136.82 (d, J_{PC} = 2.9 Hz, 2C, aromatic ipso-C), 137.62 (d, J_{PC} =3.2 Hz, 2C, aromatic ipso-C), 138.18 (d, J_{PC} = 3.0 Hz, 2C, aromatic *ipso-C*), 138.97 (d, J_{PC} = 3.0 Hz, 2C, aromatic *ipso-C*), Anal. Calcd for C₄₀H₅₈O₄NP₂Si₂Y: C, 58.25; H, 7.04; N, 1.70. Found: C, 58.57; H, 6.91; N, 1.60.

Synthesis of L¹Nd(BH₄)₂(THF)₂ (5). 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 HL¹ at 0 °C (0.595 g, 1 mmol), and the mixture was stirred for 1 h. Then the reaction solution was added to a THF suspension (15 mL) of Nd(BH₄)₃(THF)₃ (0.404 g, 1 mmol) at 0 °C. The mixture was warmed to 50 °C for 12 h. Removal of THF in vacuo was followed by addition of toluene and then filtration to remove LiCl. Yellow-green crystals were obtained from the concentrated toluene solution at -30 °C overnight (0.59 g, 48%). Anal. Calcd for C₄₄H₅₄O₂N₃P₂B₂Nd: C, 57.70; H, 5.90; N, 4.59. Found: C, 57.52; H, 6.03; N, 4.77.

Polymerization of Isoprene. A typical procedure for the polymerization was as follows (Table 1, entry 1): in a glovebox, a toluene solution of **1a** (2.0 mL, 10 μ mol, 6.4 mg), a toluene solution of [Ph₃C][B(C₆F₅)₄] (1.0 mL, 10 μ mol, 9.2 mg), 0.1 mmol of Al*i*Bu₃, and a toluene solution of isoprene (10 mmol, 0.68 g) were added into a 15 mL reactor. After a designated time, methanol was injected into the system to quench the polymerization, and the reaction mixture was poured into a large quantity of methanol containing a small amount of hydrochloric acid to precipitate the white solids. The precipitated polymer was collected by filtration, washed with methanol, and dried under vacuum at 40 °C to a constant weight to afford 0.68 g (100% yield) of polyisoprene. The copolymerization of butadiene and isoprene was carried out by a similar procedure.

ASSOCIATED CONTENT

Supporting Information

Figures, a table, and CIF files giving ¹H and ¹³C NMR spectra of all complexes and the crystallographic data and structure refinement details for complexes 1a,c, 2a, 3c, 4b, and 5. This material is available free of charge via the Internet at http:// pubs.acs.org. CCDC 904968 (1a), 899206 (1c), 899207 (2a), 899208 (3c), 899209 (4b), and 899210 (5) also contain

supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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Notes

The authors declare no competing financial interest.

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