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Thiophene-NPN Ligand Supported Rare-Earth Metal Bis(alkyl) Complexes. Synthesis and Catalysis toward Highly *trans*-1,4 Selective Polymerization of Butadiene

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A series of new rare-earth metal bis(alkyl) complexes [$L^{1-3}Ln(CH_2SiMe_3)_2(THF)_n$] ($L^1$ = $MeC_4H_2SCH_2NC_6H_4(Ph)_2P{=}NC_6H_2Me_3$-2,4,6: Ln = Sc, n = 1 (**1a**); Ln = Lu, n = 1 (**1b**); L^2 = $MeC_4H_2SCH_2NC_6H_4(Ph)_2P{=}NC_6H_3Et_2$-2,6: Ln = Sc, n = 1 (**2a**); Ln = Lu, n = 1 (**2b**); Ln = Y, n = 1 (**2c**); L^3 = $MeC_4H_2SCH_2NC_6H_4(Ph)_2P{=}NC_6H_3{}^iPr_2$-2,6: Ln = Sc, n = 0 (**3a**)) and $L^4Sc(CH_2SiMe_3)_2(THF)$ (**4a**) (L^4 = $C_6H_5CH_2NC_6H_4(Ph)_2P{=}NC_6H_3Et_2$-2,6) have been prepared by reaction of rare-earth metal tris(alkyl)s with the corresponding HL^{1-4} ligands via alkane elimination. Complexes **1a**, **1b**, **2a**−**2c**, and **4a** are monomeric with a coordinating THF molecule. Each metal ion is coordinated by a NPN ligand, two *trans*-located alkyl groups, and a THF molecule, forming a distorted trigonal-bipyramidal geometry. Complex **3a** is THF-free, adopting a distorted tetrahedron geometry. In combination with AlR_3 and borate, these complexes have shown medium activity and good *trans*-1,4 selectivity for the polymerization of butadiene. The resultant polymer has moderate molecular weight (M_n = 10 000−18 000) with narrow molecular weight distribution ($M_w/M_n < 1.6$) and *trans*-1,4 regularity varying from 49.2% up to 91.3%. The catalyst performances are strongly dependent on the *ortho* substituent of the *N*-aryl ring and the presence of the thiophene moiety of the ligands and the type of aluminum alkyls and the lanthanide metal used. The scandium complex **2a** displays the highest *trans*-1,4 selectivity.

Introduction

During the past decades, many efforts have been made to develop new catalyst systems for regio- or stereoselective polymerization of conjugated dienes, providing an opportunity to create polymers widely applied in elastomer industry. In particular, many investigations have been devoted to investigate *cis*-1,4-selective catalyst systems because the resulting polydienes are the most important elastomers used for tires and other elastic materials.[1−7] In the meantime, an interest in *trans*-1,4-regulated polymer has emerged as a thermoplastic or an important component of high-performance rubbers. A variety of catalyst systems have been designed for the *trans*-1,4-selective polymerization of isoprene, such as Ziegler−Natta catalysts based on Ti and V metals,[8] $Ln(allyl)_2Cl(MgCl_2)_2/AlR_3$,[9] $Cp^*Nd(BH_4)_2(THF)_2/Mg(nBu)_2$,[10] $[(CMe_2C_5H_4)_2Sm(C_3H_5)MgCl_2(OEt_2)_2LiCl(OEt_2)]$,[11] and $Cp^*Ln(AlMe_4)_2/[Ph_3C][B(C_6F_5)_4]$/Al*i*-$Bu_3$.[12] *trans*-1,4-Regulated polybutadiene has been comparatively less well explored.[13] To date, the catalyst systems that can initiate the *trans*-1,4-selective polymerization of butadiene

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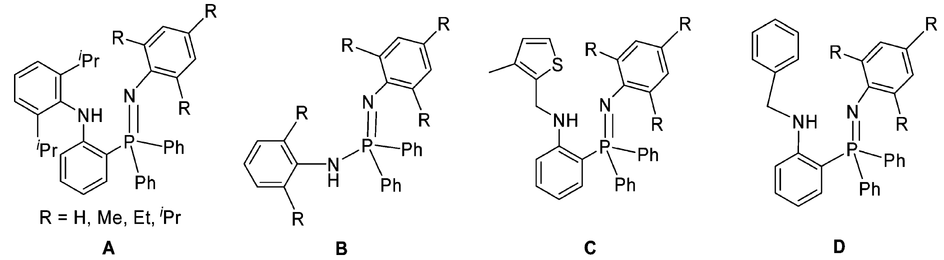
Chart 1



are Ziegler–Natta catalysts based mainly on transition metals, for instance Ti, V,[14] and Fe complexes chelated by tridentate N,N,N-donor ligands,[15] a Ti complex bearing an S,S-bidentate ligand,[16] and $VCl_3\{2,6\text{-bis}[(2,6\text{-}^iPr_2C_6H_3)N{=}C(Me)]_2\text{-}(C_5H_3N)\}$].[17] Rare-earth metal based catalyst systems are limited to $Cp^*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$, Ln = Ce)[5c] and lanthanide bis(allyl)s and neodymium alkoxides or aryl oxides, which need the activation of dialkylmagnesium.[18]

Because rare-earth metal bis(alkyl) complexes supported by monoanionic ancillary ligands have been demonstrated as highly active single-component catalysts or excellent precursors for the polymerizations of conjugated dienes and olefin under the activation of borates and aluminum alkyls,[19−22] our group has designed a series of non-Cp-ligated rare-earth metal bis(alkyl)s[23] and found that the ligands play distinctive roles in governing catalytic performance. As shown in Chart 1 the NPN ligand **A** reacted with rare-earth metal tris(alkyl)s to induce C−H activation,[23g] while **B**-stabilized bis(alkyl) species were excellent precursors for highly 3,4-selective polymerization of isoprene.[23d] Herein we wish to report the rare-earth metal bis(alkyl)s bearing ancillary ligands **C** and **D**, a new type of precursors for *trans*-1,4-selective polymerization of butadiene in the presence of borate and aluminum alkyls. The influence of the rare-earth metal, the sterics of ligands, and the polymerization conditions on the catalytic performance will be presented.

Results and Discussion

Synthesis and Characterization of NPN-Type Rare-Earth Metal Bis(alkyl) Complexes 1a−4a. The thiophene-NPN-type ligands HL^{1-4} (HL^{1-3}, Chart 1 **C**, HL^1: $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_2Me_3\text{-}2,4,6$; HL^2: $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_3Et_2\text{-}2,6$; HL^3: $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_3{}^iPr_2\text{-}2,6$; HL^4: Chart 1 **D**, $C_6H_5CH_2NHC_6H_4(Ph)_2P{=}NC_6H_3Et_2\text{-}2,6$) were prepared by the Staudinger reaction between thiophene-diphenylphosphinephenylamine $MeC_4H_2SCH_2NHC_6H_4P(Ph)_2$ or $C_6H_5CH_2NHC_6H_4P(Ph)_2$ with 1 equiv of the corresponding azides. Treatment of these ligands with rare-earth metal tris(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$, afforded the bis(alkyl) complexes $[L^{1-3}Ln(CH_2SiMe_3)_2(THF)_n]$ (L^1, Ln = Sc, $n = 1$ (**1a**); Ln = Lu, $n = 1$ (**1b**); L^2, Ln = Sc, $n = 1$ (**2a**); Ln = Lu, $n = 1$ (**2b**); Ln = Y, $n = 1$ (**2c**); L^3, Ln = Sc, $n = 0$ (**3a**)) and $L^4Sc(CH_2SiMe_3)_2(THF)$ ($L^4 = C_6H_5CH_2NC_6H_4(Ph)_2P{=}NC_6H_3Et_2\text{-}2,6$, **4a**) in quantitative yields (Schemes 1 and 2). All complexes were characterized by ^1H NMR spectroscopy. Complexes **1a**, **1b**, **2a**, **2b**, and **2c** displayed AB spins at the upfield region (δ 0.11 to −0.79) ($J_{H-H} = 11$ Hz) assignable to the diastereotopic methylene protons of the metal alkyl $Ln\text{-}CH_2SiMe_3$. In contrast, the resonances of the methylene protons of $Sc\text{-}CH_2SiMe_3$ in complex **3a** showed a doublet at δ 0.063, while complex **4a** exhibited a singlet at δ 0.076, suggesting that the two alkyl groups exchanged quickly in both complexes. The solid state structures of complexes **1b**, **2a**, **3a**, and **4a** were confirmed by X-ray diffraction analysis (Table 1, Figures 1−4). Complexes **1b**, **2a**, and **4a** are isostructural monomers with one coordinating THF molecule. The monoanionic thiophene-NPN ligand chelates to the central metal ion with N, N atoms, adopting meridional

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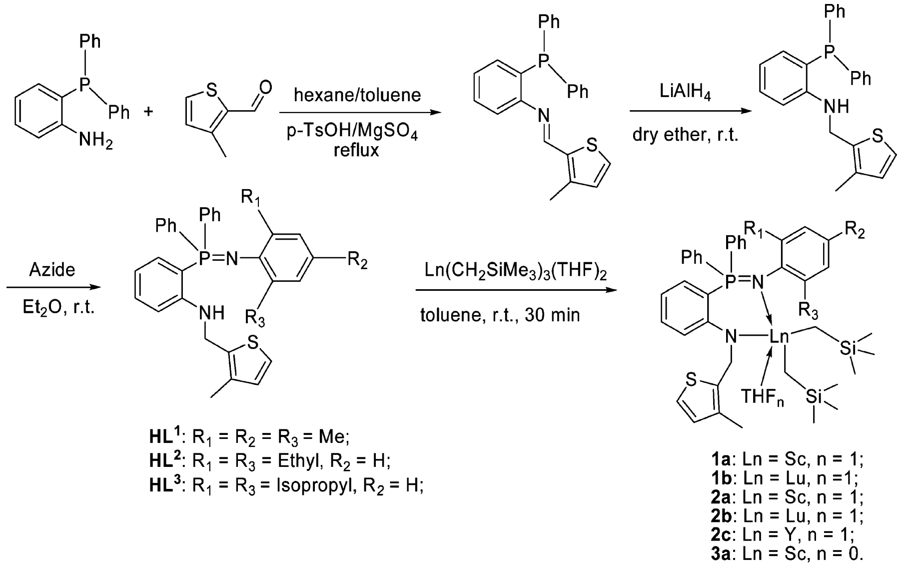
Scheme 1. Synthesis of Complexes 1−3



Scheme 2. Synthesis of Complex 4a

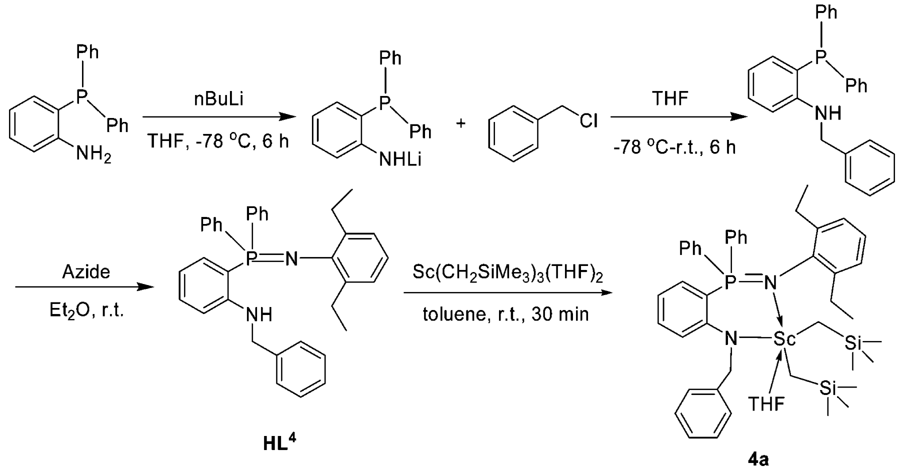


Table 1. Crystallographic Data and Refinements for Complexes 1b, 2a, 3a, and 4a

	1b·$(C_7H_8)_{0.5}$	**2a**	**3a**	**4a**·$(C_7H_8)_{0.5}$
formula	$C_{48.50}H_{66}LuN_2OPSSi_2$	$C_{46}H_{64}N_2OPSScSi_2$	$C_{44}H_{60}N_2PSScSi_2$	$C_{50.50}H_{68}N_2OPScSi_2$
fw	987.18	825.16	781.11	851.14
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$	$C2/c$	$P2(1)/n$
a/Å	12.0645(8)	12.2694(9)	41.905(3)	13.1455(7)
b/Å	14.3557(9)	26.4988(19)	11.7333(8)	25.6245(14)
c/Å	15.3451(1)	14.3383(1)	20.3477(14)	14.6598(8)
β/deg	96.8130(1)	93.1350(1)	115.1560(1)	91.2780(1)
V/Å^3	2533.5(3)	4654.8(6)	9055.8(11)	4936.9(5)
Z, D_c/g cm^{-3}	2, 1.289	4, 1.177	8, 1.146	4, 1.124
μ/mm^{-1}	2.102	0.323	0.327	0.265
F(000)	1010	1768	3344	1788
θ range/deg	1.81 to 26.03	1.62 to 26.07	1.82 to 26.06	1.59 to 26.08
h,k,l range	$-13 \le h \le 14$ $-17 \le k \le 16$ $-18 \le l \le 16$	$-15 \le h \le 10$ $-28 \le k \le 32$ $-16 \le l \le 17$	$-51 \le h \le 51$ $-14 \le k \le 9$ $-23 \le l \le 25$	$-16 \le h \le 16$ $-28 \le k \le 31$ $-18 \le l \le 12$
no. of reflns measd	14 209	26 048	24 922	27 624
no. of unique reflns	9741 [$R_{(\mathrm{int})} = 0.0711$]	9177 [$R_{(\mathrm{int})} = 0.0695$]	8911 [$R_{(\mathrm{int})} = 0.0855$]	9744 [$R_{(\mathrm{int})} = 0.0524$]
data/restraints/params	9741/52/579	9177/176/634	8911/0/471	9744/18/549
goodness-of-fit on F^2	1.014	0.877	0.963	1.025
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$ $wR_2 = 0.1179$	$R_1 = 0.0560$, $wR_2 = 0.0928$	$R_1 = 0.0631$ $wR_2 = 0.1178$	$R_1 = 0.0651$ $wR_2 = 0.1748$
R indices (all data)	$R_1 = 0.0564$ $wR_2 = 0.1228$	$R_1 = 0.1159$ $wR_2 = 0.1102$	$R_1 = 0.1321$ $wR_2 = 0.1453$	$R_1 = 0.1007$ $wR_2 = 0.1997$
largest diff peak and hole/e Å^{-3}	1.705 and −1.513	0.422 and −0.235	0.411 and −0.284	0.798 and −0.445

configuration, which leads to the thiophene ring (or phenyl) and *N*-aryl ring parallel to each other. The two alkyl species are located in *trans* positions. The geometry around the central metal is best described as distorted trigonal bipyramidal. Complex **3a**

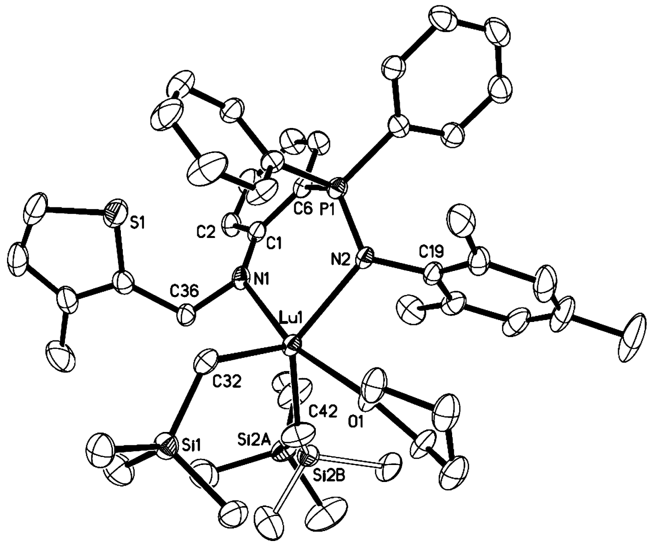


Figure 1. X-ray structure of **1b** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu(1)−N(1) = 2.260(4), Lu(1)−N(2) = 2.349(4), Lu(1)−C(32) = 2.366(6), Lu(1)−C(42) = 2.344(6), N(1)−C(1) = 1.357(7), P(1)−C(6) = 1.796(5), C(1)−C(6) = 1.434(8), N(1)−C(36) = 1.470(7), N(2)−P(1) = 1.610(4), N(1)−Lu(1)−N(2) = 82.8(2), P(1)−N(2)−Lu(1) = 117.0(2), C(1)−N(1)−Lu(1) = 137.6(3), C(36)−N(1)−Lu(1) = 101.4(3), C(42)−Lu(1)−C(32) = 109.2(2), N(2)−P(1)−C(6) = 115.3(2), N(1)−C(1)−C(6) = 120.5(5), C(1)−N(1)−C(36) = 116.6(4).

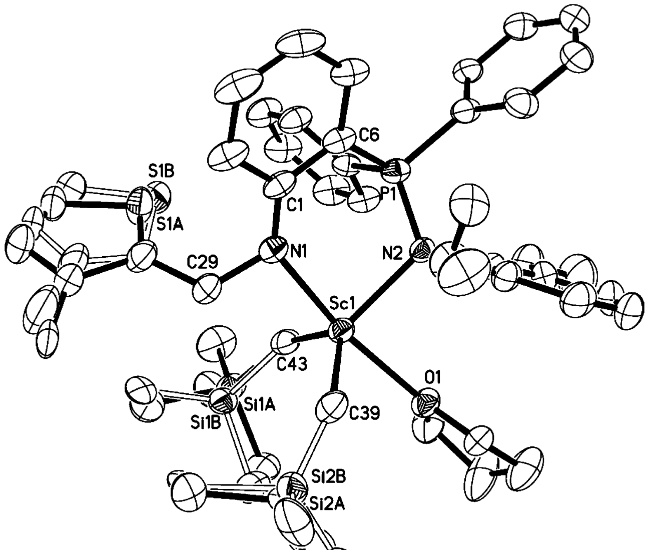


Figure 2. X-ray structure of **2a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) = 2.160(2), Sc(1)−N(2) = 2.198(2), Sc(1)−C(39) = 2.246(4), Sc(1)−C(43) = 2.235(4), C(1)−N(1) = 1.366(3), P(1)−C(6) = 1.779(3), C(1)−C(6) = 1.429(4), C(29)−N(1) = 1.462(3), N(2)−P(1) = 1.620(2), N(1)−Sc(1)−N(2) = 85.4(9), P(1)−N(2)−Sc(1) = 116.6(1), C(1)−N(1)−Sc(1) = 137.8(2), C(29)−N(1)−Sc(1) = 101.7(2), C(43)−Sc(1)−C(39) = 124.0(1), N(2)−P(1)−C(6) = 113.9(1), N(1)−C(1)−C(6) = 119.9(3), C(1)−N(1)−C(29) = 115.9(2).

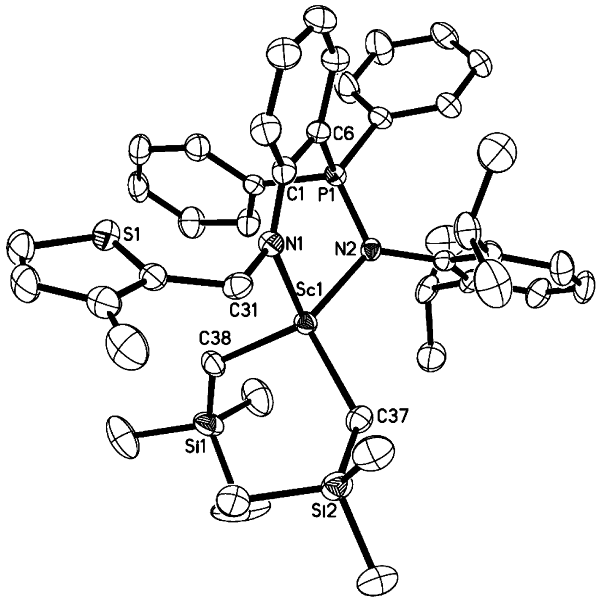


Figure 3. X-ray structure of **3a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) = 2.090(3), Sc(1)−N(2) = 2.147(3), Sc(1)−C(37) = 2.201(3), Sc(1)−C(38) = 2.218(4), N(1)−C(1) = 1.377(4), P(1)−C(6) = 1.786(4), C(1)−C(6) = 1.423(5), N(1)−C(31) = 1.464(4), N(2)−P(1) = 1.617(3), N(1)−Sc(1)−N(2) = 90.2(1), P(1)−N(2) −Sc(1) = 111.1(1), C(1)−N(1)−Sc(1) = 137.7(2), C(31)−N(1)−Sc(1) = 102.9(2), C(37)−Sc(1)−C(38) = 103.5(1), N(2)−P(1)−C(6) = 114.8(2), N(1)−C(1)−C(6) = 120.0(3), C(1)−N(1)−C(31) = 117.4(3).

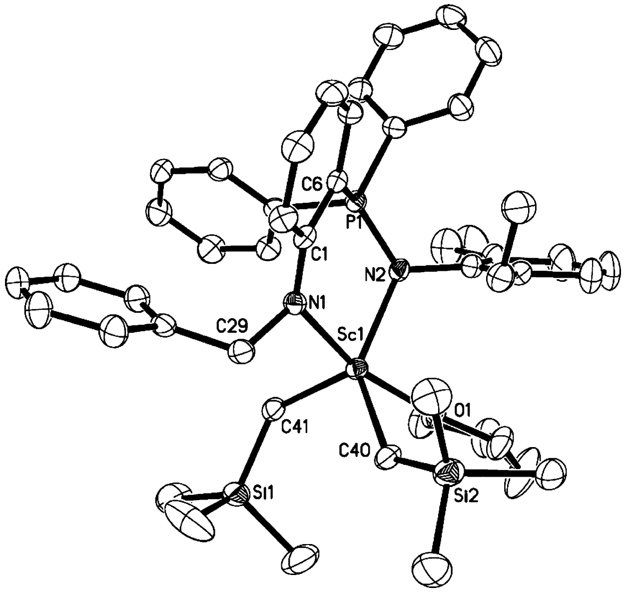
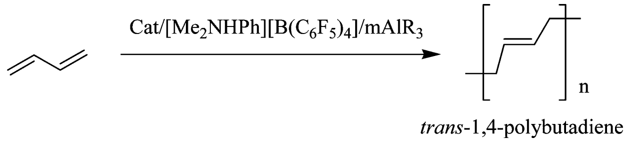


Figure 4. X-ray structure of **4a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) = 2.153(3), Sc(1)−N(2) = 2.248(3), Sc(1)−C(41) = 2.242(3), Sc(1)−C(40) = 2.263(4), C(1)−N(1) = 1.377(4), P(1)−C(6) = 1.779(3), C(1)−C(6) = 1.425(4), N(1)−C(29) = 1.473(4), N(2)−P(1) = 1.618(3), N(1)−Sc(1)−N(2) = 85.2(9), P(1)−N(2)−Sc(1) = 116.51(14), C(1)−N(1)−Sc(1) = 135.5(2), C(29)−N(1)−Sc(1) = 105.65(18), C(41)−Sc(1)−C(40) = 107.0(1), N(2)−P(1)−C(6) = 114.1(1), N(1)−C(1)−C(6) = 119.9(3), C(1)−N(1)−C(29) = 115.0(3).

is THF-free, which could be attributed to the more crowded environment of the ligand. The Sc ion is coordinated by a monoanionic thiophene-NPN ligand and two alkyl ligands, adopting a distorted tetrahedral geometry. The average Ln−N bond length is 2.305(4) Å in **1b**, 2.179(2) Å in **2a**, 2.119(3) Å in **3a**, and 2.201(3) Å in **4a**, while the mean Ln−C bond length is 2.241(4) Å in **1b**, 2.241(4) Å in **2a**, 2.210(3) Å in **3a**, and 2.253(3) Å in **4a**. Both fall within the normal values.[22,23c,d] The

Table 2. Polymerization of Butadiene by Using Various Complexes[a]



entry	cat.	AlR_3	activator[b]	conv (%)	M_n (× 10^{-4})[c]	M_w/M_n	microstructures[d](%)			T_{m1}[e](°C)	T_{m2}[e](°C)
							trans-1,4	*cis*-1,4	1,2-		
1	**1a**	Al^iBu_3	**C**	65	1.26	1.52	90.9	1.3	7.8	45.9	89.8
2	**2a**	Al^iBu_3	**C**	41	1.34	1.44	91.3	2.6	6.1	43.2	84.5
3[f]	**3a**	Al^iBu_3	**C**	23	0.57	1.28	81.2	3.4	15.4	43.3	
4	**1a**	$AlEt_3$	**C**	76	1.27	1.49	84.1	5.2	10.7	44.7	89.9
5	**1a**	$AlMe_3$	**C**	30	1.62	1.57	77.4	13.7	8.9	45.3	81.9
6	**2a**	$AlEt_3$	**C**	73	1.10	1.49	89.4	2.4	8.2	43.8	86.8
7	**2a**	$AlMe_3$	**C**	20	1.71	1.43	81.5	8.6	9.8	42.1	80.7
8	**1a**	Al^iBu_3	**A**	70	1.56	1.45	89.4	3.3	7.3	43.6	91.2
9	**1a**	Al^iBu_3	**B**	65	1.48	1.44	83.7	5.7	10.6	43.5	93.0
10	**2a**	Al^iBu_3	**A**	50	0.98	1.46	89.8	2.0	8.2	43.4	82.2
11	**2a**	Al^iBu_3	**B**	52	0.93	1.51	90.3	1.1	8.6	43.1	83.5
12	**2b**	Al^iBu_3	**C**	46	0.63	1.79	59.2	21.2	19.6		
13	**2c**	Al^iBu_3	**C**	90	2.49	1.57	49.2	43.0	7.8		
14	**4a**	$AlMe_3$	**B**	70	1.13	1.54	84.6	3.4	12.0	42.7	80.4
15	**4a**	$AlMe_3$	**C**	73	1.32	1.51	88.5	2.3	9.2	42.3	83.1
16	**4a**	$AlEt_3$	**C**	80	0.76	1.35	80.1	4.4	15.5	40.0	
17	**4a**	Al^iBu_3	**C**	80	1.31	1.47	84.0	3.7	12.3	42.0	79.9

[a] Conditions: complex (20 μmol), butadiene (0.54 g, 10.00 mmol) in toluene, $[AlR_3]$:[Ln]:[activator] = 10/1/1, Tp: 25 °C, 12 h. [b] Activiator = $[Ph_3C][B(C_6F_5)_4]$ (**A**), $B(C_6F_5)_3$ (**B**), $[PhNHMe_2][B(C_6F_5)_4]$ (**C**). [c] Determined by GPC against polystyrene standard. [d] Determined by IR spectroscopy. [f] The reaction time is 24 h. [g] Determined by differential scanning calorimetry.

angle of N−Ln−N is 82.8(2)° in **1b**, 85.4(9)° in **2a**, 90.2(1)° in **3a**, and 85.2(9)° in **4a**. It is noteworthy that the angle of N−Sc−N in **3a** is much larger than those in **1b**, **2a**, and **4a** owing to the tetrahedral geometry.

Polymerization of Butadiene. The catalytic performance of all complexes **1a**−**4a** for the polymerization of butadiene (BD) had been investigated. Although these complexes alone were inert, on activation by AlR_3 and borates they showed medium activity and varied *trans*-1,4 selectivity at room temperature. The polymerization data are summarized in Table 2.

The activity of complex **1a**, bearing an *ortho*-methyl substituent of the *N*-aryl ring of the ligand, was higher than that of complex **2a**, with an *ortho*-ethyl substituent, under the same conditions. When the *ortho* substituent was replaced by the more bulky isopropyl group in the case of complex **3a**, a much more obvious decrease in the catalytic activity was observed (entries 1−3). These results indicated that the precursors with ligands that are too bulky showed low catalytic activity since the steric environment of the metal center hindered the coordination of the monomer. Such influence of the bulkiness of *ortho* substituents on the activity of complexes has been found previously.[7a,23d] We also noted that the catalytic activity was strongly affected by the type of aluminum alkyls, in the sequence $AlEt_3$ ≥ Al*i*Bu_3 > $AlMe_3$, but less influenced by the type of borate and borane (entries 1−2, 4−11).

The *trans*-1,4 selectivity of this system varied with the *ortho* substituents of the *N*-aryl moiety of the ligand, which reached 91.3% for **2a**, bearing *ortho*-ethyl, and dropped slightly for **1a**, bearing *ortho*-methyl (90.9%). It should be noted that a significant decrease in *trans*-1,4 selectivity in the case of **3a** (81.2%), with the much bulkier *ortho*-isopropyl group, was observed. This might be attributed to the more crowded metal center, which influenced the orientation of the incoming butadiene monomer and the active allyl species, resulting in the insertion of the incoming butadiene monomer at C3 of the allyl species with consequent formation of a 1,2 unit (entries 1−3).[23a,d] This could be proved by the increase of the 1,2-regularity of polybutadiene obtained (entry 3, 1,2-% = 15.4). Meanwhile, the *trans*-1,4 selectivity was also strongly affected by the bulkiness of the aluminum alkyls, in the sequence Al^iBu_3(91.3%) > $AlEt_3$(89.4%) > $AlMe_3$(81.5%) (entries 2, 6, and 7), as observed in other lanthanide metal based systems, such as $[(C_5Me_5)_2Sm(THF)_2]/AlR_3/[Ph_3C][B(C_6F_5)_4]$[4] and $Cp^*_2Gd[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2GdCp^*_2/AlR_3/[Ph_3C][B(C_6F_5)_4]$.[5c] In contrast, the *trans*-1,4 selectivity of this catalytic system was slightly influenced by the type of borate or borane, $[PhNHMe_2][B(C_6F_5)_4]$ (91.3%) ≥ $[B(C_6F_5)_3]$ (90.3%) ≥ $[Ph_3C][B(C_6F_5)_4]$ (89.8%) (entries 2, 10, and 11).

To investigate the role of the central metal, complexes based on scandium (**2a**), lutetium (**2b**), and yttrium (**2c**) were examined. The activity was governed strongly by the central metal type, Y > Sc > Lu. A *trans*-1,4 selectivity as high as 91.3% could be obtained with the scandium precursor, 59.2% with the lutetium analogue, and 49.2% with yttrium (entries 2, 12, and 13). Obviously, the stereoselectivity depends on the size of the metal ion, Sc > Lu > Y, the inverse of the ionic radii (Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å)).[24]

In order to evaluate the influence of thiophenyl group of the ligand, scandium complex **4a**, with a benzyl group of the ligand, was synthesized. The activity of complex **4a** was higher than the scandium analogues **1a**, **2a**, and **3a**, bearing the thiophenyl group of the ligand, under the same conditions (entries 14−16). However, the *trans*-1,4 selectivity of **4a** (84.0%) (entry 17) was close to that of **3a** but lower than those of **1a** (90.9%) and **2a** (91.3%). This was attributed to the probable presence of an interaction between the sulfur of the thiophenyl moiety and the metal center in the active species in the cases of using complexes **1a**, **2a**, and **3a** as initiators but the absence in the case of **4a**, which increased the spacial crowding of the metal center to some degree.

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[24] Effective ionic radius of Ln^{3+} for coordination number 6: Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

Conclusion

A series of new rare-earth metal bis(alkyl)s stabilized by NPN-type ligands was synthesized via alkane elimination, which in combination with aluminum alkyls and borate established a new type of catalyst system. This catalytic system provided medium activity and predominant *trans*-1,4 selectivity for the polymerization of butadiene. The central metal, the spacial crowding of the *ortho* substituent of the *N*-aryl ring, and the presence of the thiophenyl moiety, as well as the type of aluminum alkyl, played significant roles in controlling the catalytic activity and selectivity that were, in contrast, influenced slightly by the type of borate (or borane).

Experimental Section

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 an MBraun glovebox. All solvents were purified from an MBraun SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed with paraffin film. ^{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. IR spectra were recorded on a Vertex 70 FT-IR. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere. The instrument was calibrated for temperature and enthalpy using pure indium (mp = 156.6 °C) and sapphire before experiment. Measurements during the first heating from 10 to 150 °C and then the first cooling from 150 to 10 °C as well as the second heating from 10 to 150 °C at 10 °C/min were performed. Polymer molecular weight was measured on a Tosoh HLC 8220 GPC with THF as eluent. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). 3-Methylthiophene-2-carboxyaldehyde, etc., were purchased from the National Medicine Company (China) and were used without further purification. (2-Diphenylphosphino)aniline, mesityl azide, 2,6-diethylphenyl azide, 2,6-diisopropylphenyl azide, and Ln(CH_2SiMe_3)(THF)$_2$ (Ln = Y, Lu, Sc) were prepared according to published literature.[25]

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 −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. 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 calculation without further refinement of the parameters.

Synthesis of $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_2Me_3$-2,4,6 (HL^1). Under an N_2 atmosphere, 3-methylthiophene-2-carboxyaldehyde (1.40 g, 10 mmol) and 2-diphenylphosphino aniline (2.78 g, 10 mmol) were dissolved in a hexane/toluene solution (20 mL/20 mL), and then anhydrous $MgSO_4$ (10 g) and the catalyst *p*-TsOH (0.25 g) were added. The reaction mixture was stirred under reflux for 24 h. After filtration, the solution was cooled to −30 °C to afford a yellowish-brown solid of $MeC_4H_2SCH{=}NC_6H_4P(Ph)_2$ within 12 h (3.08 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.31 (s, 3H, C*H*$_3$-thienyl), alkyl 6.94 (d, *J* = 5.0 Hz, 1H, 4*H*-thienyl), 7.26 (d, *J* = 5.0 Hz, 1H, 5*H*-thienyl), 7.35−7.59 (m, 14H, PPh$_2$ and PC$_6$*H*$_4$N), 8.15 ppm (s, 1H, C*H*=N). An ether solution of $MeC_4H_2SC{=}NC_6H_4P(Ph)_2$ (2.0 g, 5.2 mmol) was treated with excess $LiAlH_4$ (1.5 ratio) at room temperature for 12 h. When the color of the mixture changed from yellowish-green to yellowish-brown, 100 mL of water containing 3 mL of HCl was added slowly. Then, the aqueous layer was extracted by diethyl ether three times (50 mL × 3). The combined organic portion was dried over anhydrous $NaSO_4$. Removal of solvent afforded $MeC_4H_2SCH_2NHC_6H_4P(Ph)_2$ as a white solid (1.80 g, 91%), which reacted with 1 equiv of mesitylazide in an ether solution at room temperature overnight. The resultant solution was concentrated to 5 mL, and 5 mL of hexane was added. The solution was stored at −30 °C overnight to afford HL^1 as a brown solid (3.65 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$ 25 °C): δ 1.93 (s, 6H, *o*-C*H*$_3$-N-aryl), 2.05 (s, 3H, *p*-C*H*$_3$-N-aryl), 2.15 (s, 3H, C*H*$_3$-thienyl), 4.32(d, *J* = 5.0 Hz, 2H, C*H*$_2$), 6.53 (m, 1H, *p*-PC$_6$*H*$_4$*N*), 6.70 (s, 2H, *m*-NC$_6$*H*$_2$), 6.80 (m, 2H, *p*-P*Ph*$_2$), 6.93 (d, *J* = 5.0 Hz, 1H, thienyl), 7.26 (d, *J* = 5.0 Hz, 1H, thienyl), 7.38−7.41(m, 4H, *m*-PPh$_2$), 7.47−7.60 (m, 6H, *o*-PPh$_2$, *m*-PC$_6$*H*$_4$N), 7.90 ppm (m, 1H, *o*-PC$_6$*H*$_4$N).

Synthesis of $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_3Et_2$-2,6 (HL^2). Following a similar procedure to that described for the formation of HL^1 but replacing mesitylazide by 2,6-diethylphenyl azide gave HL^2 in a 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$ 25 °C): δ 0.83 (t, *J* = 7.5 Hz, 6H, *o*-CH$_2$C*H*$_3$-*N*-aryl), 1.96 (s, 3H, C*H*$_3$-thienyl), 2.32 (q, *J* = 7.5 Hz, 4H, *o*-C*H*$_2$CH$_3$-*N*-aryl), 4.22 (d, *J* = 5 Hz, 2H, C*H*$_2$), 6.45 (m, 1H, *p*-PC$_6$*H*$_4$N), 6.57 (m, 1H, *m*-PC$_6$*H*$_4$N), 6.61 (d, *J* = 5 Hz, 1H, 4-thienyl), 6.66 (m, 1H, *m*-NC$_6$*H*$_3$), 6.73 (m, 1H, *p*-NC$_6$*H*$_3$), 6.80 (m, 2H, *p*-P*Ph*$_2$), 6.86 (d, *J* = 5.0 Hz, 1H, 5-thienyl), 7.19 (m, 1H, *m*-NC$_6$*H*$_3$), 7.30 (m, 4H, *m*-PPh$_2$), 7.39 (m, 1H, *m*-PC$_6$*H*$_4$N), 7.47 (m, 4H, *o*-P*Ph*$_2$), 7.64 ppm (m, 1H, *o*-PC$_6$*H*$_4$N).

Synthesis of $MeC_4H_2SCH_2NHC_6H_4(Ph)_2P{=}NC_6H_3{}^iPr_2$-2,6 (HL^3). Following a similar procedure to that described for the formation of HL^1 but replacing mesitylazide by 2,6-diisopropylphenyl azide gave HL^3 in high yield (80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.74 (d, *J* = 6.8 Hz, 12H, *o*-CH*Me*$_2$-N-aryl), 1.96 (s, 3H, C*H*$_3$-thienyl), 3.20 (m, 2H, *o*-C*H*Me$_2$-N-aryl), 4.23 (d, *J* = 5.0 Hz, 2H, C*H*$_2$), 6.46 (m, 1H, *p*-PC$_6$*H*$_4$N), 6.56 (m, 1H, *m*-PC$_6$*H*$_4$N), 6.61(d, *J* = 5.0 Hz, 1H, 4-thienyl), 6.70 (m, 2H, *m*-NC$_6$*H*$_3$), 6.82 (m, 2H, *p*-PPh$_2$), 6.86 (d, *J* = 5.0 Hz, 1H, 5-thienyl), 7.18(m, 1H, *p*- NC$_6$*H*$_4$), 7.32 (m, 4H, *m*-PPh$_2$), 7.38 (m, 1H, *m*-PC$_6$*H*$_4$N), 7.46 (m, 4H, *o*-PPh$_2$), 7.60 ppm (m, 1H, *o*-PC$_6$*H*$_4$N).

Synthesis of $C_6H_5CH_2NHC_6H_4(Ph)_2P{=}NC_6H_3Et_2$-2,6 (HL^4). Under a nitrogen atmosphere, ^{n}BuLi (1.6 M in hexane, 6.6 mL, 10.5 mmol) was added dropwise to a THF solution (25 mL) of the 2-diphenylphosphinoaniline (2.78 g, 10 mmol) at −78 °C. The reaction mixture remained stirring at −78 °C for 6 h, and then 1 equiv of $ClCH_2Ph$ was added slowly. The reaction mixture was allowed to warm to room temperature slowly and remained stirring for 6 h. Then 100 mL of water containing 3 mL of HCl was added to the reaction mixture. The aqueous layer was extracted with ether three times. The combined organic portion was dried by anhydrous Na_2SO_4. Volatiles were removed under reduced pressure to afford white solids of $C_6H_5CH_2NHC_6H_4(Ph)_2P$ (2.31 g, 63%). To the dry ether solution of $C_6H_5CH_2NHC_6H_4P(Ph)_2$ was added 1 equiv of 2,6-diethylphenylazide, and the mixture reacted at room temperature overnight. The reaction solution was concentrated to 5 mL, 5 mL of hexane was added, and the mixture then was kept at −30 °C to afford brown solids of HL^4 within 12 h (3.59 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.83 (t, *J* = 7.5 Hz, 6H, *o*-CH$_2$C*H*$_3$-*N*-aryl), 2.34 (m, 4H, *o*-C*H*$_2$CH$_3$-*N*-aryl), 4.19 (d, *J* = 5.0 Hz, 2H,

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CH_2), 6.43−6.41 (m, 3H, *m,p*-NC_6H_3), 6.82−6.80 (m, 2H, *p*-PPh_2), 7.04−7.03 (m, 3H, PC_6H_4N), 7.26−7.16 (m, 4H, C_6H_5), 7.34−7.30 (m, 1H, C_6H_5), 7.43−7.42 (m, 4H, *m*-PPh_2), 7.51−7.47 (m, 4H, *o*-PPh_2), 7.51 ppm (m, 1H, *o*-PC_6H_4N).

Synthesis of $L^1Sc(CH_2SiMe_3)_2(THF)$ (1a). A toluene (2 mL) solution of HL^1 (0.26 g, 0.50 mmol) was added dropwise to a toluene (2 mL) solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.29 g, 0.50 mmol) at room temperature, and the mixture was stirred for 30 min. The solution was concentrated to 2 mL under reduced pressure, 2 mL of hexane was added, and the solution was cooled to −30 °C to give **1a** as a colorless solid (0.33 g, 80%) within 12 h. Crystals suitable for X-ray analysis were grown from a mixture of hexane/toluene. ^1H NMR (400 MHz, C_6D_6): δ 0.20 (AB, J = 11 Hz, 2H, CH_2SiMe_3), 0.23 (AB, J = 11 Hz, 2H, CH_2SiMe_3), 0.38 (s, 18H, CH_2SiMe_3), 1.47 (br, 4H, THF), 2.13(s, 3H, CH_3-thienyl), 2.20 (s, 3H, *p*-CH_3-NPh), 2.38 (s, 3H, *o*-CH_3-*N*Ph), 2.39 (s, 3H, *o*-CH_3-*N*Ph), 3.74 (br, 4H, THF), 5.70 (s, 2H, CH_2), 6.42(m, 1H, *p*-PC_6H_4N), 6.75 (s, 2H, NC_6H_2), 6.77 (d, J = 5.0 Hz, 1H, 4-thienyl), 6.87 (d, J = 5.0 Hz, 1H, 5-*thienyl*), 6.93 (m, 1H, *m*-NC_6H_4P), 6.95 (m, 1H, *m*-PC_6H_4N), 7.02−7.07 (m, 4H, *m*-PPh_2), 7.11−7.13 (m, 2H, *p*-PPh_2), 7.21 (m, 1H, *o*-PC_6H_4N), 7.63 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6): δ 4.35 (6C, Si*Me*$_3$), 14.52 (1C, CH_3-thienyl), 21.14 (1C, *p*-CH_3-Ph), 21.85 (2C, *o*-CH_3-Ph), 25.96 (2C, THF), 41.51, 42.13 (1C, CH_2SiMe_3), 43.52 (1C, CH_2), 70.03 (2C, THF), 114.28 (d, 1C, *p*-PPh), 114.70 (d, 1C, *m*-PPh), 122.69 (1C, 4-*thienyl*), 122.81 (1C, 5-thienyl), 126.13 (1C, *ipso*-NPh), 126.58 (1C, *ipso*-thienyl), 127.14, 127.57 (2C, *ipso*-Ph), 128.74 (2C, *m*-PPh_2), 129.05, 129.17 (2C, *m*-PPh_2), 129.76 (1C, *ipso*-thienyl), 130.40, 130.80 (2C, *m*-NPh), 132.64 (2C, *ipso*-Ph), 133.34 (2C, *p*-PPh_2), 133.99 (1C, *p*-PPh), 134.58−134.68 (4C, *o*-PPh_2), 135.49 (1C, *m*-PPh), 136.93 (1C, *ipso*-PPh_2), 139.08 (1C, *ipso*-Ph), 139.79 ppm (1C, *ipso*-Ph), 159.48 ppm (d, J = 5.0 Hz,1C, *ipso*-PPh). Anal. Calcd for $C_{45}H_{62}ScN_2OPSSi_2$ (%): C, 66.63; H, 7.70; N, 3.45. Found: C, 66.27; H, 7.196; N, 3.01.

Synthesis of $L^1Lu(CH_2SiMe_3)_2(THF)$ (1b). Following a similar procedure, treatment of the solution of HL^1 (0.26 g, 0.50 mmol) with $Lu(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.50 mmol) in toluene (2 mL) afforded complex **1b** (0.58 g, 70%). The single crystals were obtained from a mixture of hexane/toluene. ^1H NMR (400 MHz, C_6D_6): δ −0.70 (AB, J = 11 Hz, 2H, CH_2SiMe_3), −0.44 (AB, J = 11 Hz, 2H, CH_2SiMe_3), 0.46 (s, 18H, CH_2SiMe_3), 1.26 (br, 4H, THF), 2.11 (br, 3H, CH_3), 2.29 (s, 6H, $2CH_3$), 2.53 (s, 3H, CH_3-thienyl), 3.66 (br, 4H, THF), 5.49 (s, 2H, CH_2), 6.39 (m, 1H, *p*-PC_6H_4N), 6.61 (s, 2H, NC_6H_2), 6.79 (d, J = 5.0 Hz, 1H, 4-thienyl), 6.89 (d, J = 5.0 Hz, 1H, 5-*thienyl*), 7.01 (m, 1H, *m*-NC_6H_4P), 7.05 (m, 1H, *o*-NC_6H_4P), 7.10 (m, 4H, *m*-PPh_2), 7.16 (m, 2H, *p*-PPh_2), 7.23 (m, 1H, *o*-PC_6H_4N), 7.62 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6): δ 5.22 (6C, Si*Me*$_3$), 14.79 (1C, CH_3-thienyl), 21.05 (1C, *p*-CH_3-Ph), 21.62 (2C, *o*-CH_3-Ph), 25.56 (2C, THF), 41.77 (2C, CH_2SiMe_3), 42.62 (1C, CH_2), 71.19 (2C, THF), 112.72 (1C, *p*-PPh), 115.38 (1C, *m*-PPh), 122.40 (1C, 4-*thienyl*), 126.13 (1C, *ipso*-thienyl), 127.06 (1C, *ipso*-Ph), 127.48 (1C, *ipso*-Ph), 128.60 (2C, *m*-PPh_2), 128.88, 129.00 (2C, *m*-PPh_2), 129.77 (1C, *ipso*-thienyl), 130.08 (1C, 5-*thienyl*), 130.15, 130.29 (2C, *m*-NPh), 132.85 (2C, *p*-PPh_2), 133.27 (2C, *ipso*-Ph), 133.51 (1C, *p*-PPh), 134.37, 134.45, 134.56, 134.65 (4C, *o*-PPh_2), 135.28 (1C, *m*-PPh), 136.46 (1C, *ipso*-PPh_2), 140.61 (1C, *ipso*-Ph), 143.21 (1C, *ipso*-Ph), 161.25 ppm (d, 1C, J = 4.4 Hz, *ipso*-PPh). Anal. Calcd for $C_{45}H_{62}LuN_2OPSSi_2$ (%): C, 57.43; H, 6.64; N, 2.98. Found: C, 56.58; H, 6.07; N, 2.72.

Synthesis of $L^2Sc(CH_2SiMe_3)_2(THF)$ (2a). Following a similar procedure, treatment of a solution of HL^2 (0.27 g, 0.50 mmol) with $Sc(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.50 mmol, in 2 mL of toluene) afforded complex **2a** (0.29 g, 70%). The single crystals were obtained from a mixture of hexane/toluene. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.00 (AB, J = 10.0 Hz, 2H, CH_2SiMe_3), 0.16 (AB, J = 10.0 Hz, 2H, CH_2SiMe_3), 0.35 (s, 18H, CH_2SiMe_3), 1.10 (t, J = 8.0 Hz, 6H, CH_2CH_3), 1.50 (br, 4H, THF), 2.45 (s, 3H, CH_3-thienyl), 2.75 (q, J = 8.0 Hz, 2H, CH_2CH_3), 3.01 (q, J = 8.0 Hz, 2H, CH_2CH_3), 3.69 (m, 4H, THF), 5.72 (s, 2H, CH_2), 6.38 (m, 1H, *m*-PC_6H_4N), 6.77 (d, J = 5.0 Hz, 1H, 4-thienyl), 6.91 (d, J = 5.0 Hz, 1H, 5-thienyl), 6.95 (m, 2H, *o, m*-NC_6H_4P), 7.04 (m, 3H, *m, p*-NC_6H_3), 7.08 (m, 4H, *m*-PPh_2), 7.16 (m, 1H, *o*-PC_6H_4N), 7.24 (m, 2H, *p*-PPh_2), 7.58 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.49 (6C, Si*Me*$_3$), 14.21(2C, CH_2CH_3), 14.64 (1C, CH_3-thienyl), 25.93 (1C, CH_2CH_3), 29.19(1C, CH_2CH_3), 41.49(1C, CH_2SiMe_3), 43.39 (1C, CH_2SiMe_3), 68.81 (4C, THF), 114.16 (1C, *p*-PPh), 114.60 (1C, *m*-PPh), 122.55 (1C, 4-*thienyl*), 125.62 (2C, *ipso*-thienyl), 126.60 (2C, *m*-NPh), 126.85 (1C, *p*-NPh), 127.84 (2C, *ipso*-Ph), 128.26 (2C, *m*-PPh_2), 128.95, 129.07 (2C, *m*-PPh_2), 130.26 (1C, 5-thienyl), 133.17 (2C, *p*-PPh_2), 133.40 (1C, *ipso*-Ph), 133.95 (1C, *o*-PPh), 134.01, 134.89 (4C, *o*-PPh_2), 135.33 (1C, *m*-PPh), 140.24 (1C, *ipso*-Ph), 142.04, 142.10 (2C, *ipso*-PPh_2), 159.69 ppm (d, J = 4.0 Hz,1C, *ipso*-PPh). Anal. Calcd for $C_{46}H_{64}N_2OPSScSi_2$ (%): C, 66.95; H, 7.82; N, 3.39. Found: C, 66.35; H, 7.34; N, 3.23.

Synthesis of $L^2Lu(CH_2SiMe_3)_2(THF)$ (2b). Following a similar procedure, treatment of a solution of HL^2 (0.27 g, 0.50 mmol) with $Lu(CH_2SiMe_3)_3(THF)_2$ (0.29 g, 0.50 mmol) in toluene (2 mL) afforded complex **2b** (0.36 g, 75%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −0.75 (AB, J = 11 Hz, 2H, CH_2SiMe_3), −0.50 (AB, J = 11 Hz, 2H, CH_2SiMe_3), 0.45 (s, 18H, CH_2SiMe_3), 1.05 (t, J = 7.4 Hz, 6H, CH_2CH_3), 1.39 (br, 4H, THF), 2.57(s, 3H, CH_3-thienyl), 2.79 (q, J = 7.4 Hz, 2H, CH_2CH_3), 2.93 (q, J = 7.4 Hz, 2H, CH_2CH_3), 3.66 (br, 4H, THF), 5.53 (s, 2H, CH_2), 6.36 (m, 1H, *m*-PC_6H_4N), 6.79 (d, J = 5.0 Hz, 1H, 4-thienyl), 6.90 (d, J = 5.0 Hz, 1H, 5-thienyl), 6.98 (m, 4H, *o, m*-NC_6H_4P, *m*-NC_6H_3), 7.11 (m, 1H, *p*-NC_6H_3), 7.11 (m, 4H, *m*-PPh_2), 7.17 (m, 1H, *o*-PC_6H_4N), 7.28 (m, 2H, *p*-PPh_2), 7.61 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 5.22 (6C, Si*Me*$_3$), 14.00 (2C, CH_2CH_3), 14.83 (1C, CH_3-thienyl), 25.64 (1C, CH_2CH_3), 25.97 (1C, CH_2CH_3), 26.10 (2C, THF), 41.89 (s, 1C, CH_2SiMe_3), 42.68 (1C, CH_2SiMe_3), 69.01 (2C, THF), 112.73 (1C, *p*-PPh), 115.32 (1C, *m*-PPh), 122.30 (1C, 4-thienyl), 124.61 (2C, *ipso*-thienyl), 126.14 (2C, *m*-NPh), 126.83 (1C, *p*-NPh), 127.42 (2C, *ipso*-Ph), 128.26 (2C, *m*-PPh_2), 128.87, 128.99 (2C, *m*-PPh_2), 130.02 (1C, 5-thienyl), 132.86 (2C, *p*-PPh_2), 133.27 (1C, *ipso*-Ph), 133.77, 133.89 (1C, *o*-PPh), 134.55, 134.64 (4C, *o*-PPh_2), 135.28 (1C, *m*-PPh), 140.68 (1C, *ipso*-Ph), 141.67, 141.72 (2C, *ipso*-PPh_2), 161.30 ppm (d, J = 4.2 Hz, 1C, *ipso*-PPh). Anal. Calcd for $C_{46}H_{64}N_2OPSLuSi_2$ (%): C, 57.84; H, 6.75; N, 2.93. Found: C, 57.30; H, 6.25; N, 2.37.

Synthesis of $L^3Sc(CH_2SiMe_3)_2(THF)$ (3a). Following a similar procedure, treatment of a solution of HL^3 (0.28 g, 0.50 mmol) with $Sc(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.50 mmol) in toluene (2 mL) afforded complex **3a** (0.29 g, 75%). The single crystals were obtained from a mixture of hexane/toluene. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.061 (s, 2H, CH_2SiMe_3), 0.066 (s, 2H, CH_2SiMe_3), 0.30 (s, 18H, CH_2SiMe_3), 0.82 (d, J = 6.8 Hz, 6H, CH*Me*$_2$), 1.51 (d, J = 6.8 Hz, 6H, CH*Me*$_2$), 2.38 (s, 3H, CH_3-thienyl), 3.85 (m, 2H, $CHMe_2$), 5.71 (s, 2H, CH_2), 6.35 (m, 1H, *m*-PC_6H_4N), 6.71 (m, 1H, *m*-PC_6H_4N), 6.79 (d, J = 5.0 Hz, 1H, 4-thienyl), 6.92 (m, 1H, *p*-PC_6H_4N), 6.97 (d, J = 5.0 Hz, 1H, 5-thienyl), 7.06 (m, 4H, *m*-PPh_2), 7.14 (m, 2H, *p*-PPh_2), 7.22 (m, 3H, *m, p*-NC_6H_3), 7.24 (m, 1H, *o*-PPh), 7.55 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.49 (6C, Si*Me*$_3$), 14.21 (4C, CH_2CH_3), 14.64 (1C, CH_3-thienyl), 25.93 (1C, CH_2CH_3), 29.19 (1C, CH_2CH_3), 41.49(1C, CH_2SiMe_3), 43.39 (1C, CH_2SiMe_3), 68.81 (s, 4C, THF), 114.16 (1C, *p*-PPh), 114.60 (1C, *m*-PPh), 122.55 (1C, 4-thienyl), 125.62 (2C, *ipso*-thienyl), 126.60 (2C, *m*-NPh), 126.85 (1C, *p*-NPh), 127.84 (2C, *ipso*-Ph), 128.26 (2C, *m*-PPh_2), 128.95, 129.07 (2C, *m*-PPh_2), 130.26 (1C, 5-thienyl), 133.17 (2C, *p*-PPh_2), 133.40 (1C, *ipso*-Ph), 133.95 (1C, *o*-PPh), 134.01, 134.89 (4C, *o*-PPh_2), 135.33 (1C, *m*-PPh), 140.24 (1C, *ipso*-Ph), 142.04,142.10 (2C, *ipso*-PPh_2), 159.69 ppm (1C, *ipso*-PPh). Anal. Calcd for $C_{44}H_{60}N_2PSScSi_2$ (%): C, 67.65; H, 7.74; N, 3.59. Found: C, 67.29; H, 7.51; N, 3.11.

Synthesis of $L^4Sc(CH_2SiMe_3)_2(THF)$ (4a). Following a similar procedure, treatment of the solution of HL^4 (0.26 g, 0.50 mmol) with $Sc(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.50 mmol) in toluene (2 mL) afforded complex **4a** (0.30 g, 75%). The single crystals were obtained from a mixture of hexane/toluene. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.076 (s, 4H, CH_2SiMe_3), 0.32 (s, 18H, CH_2SiMe_3), 1.15 (t, $J = 7.0$ Hz, 6H, CH_2CH_3), 1.47 (br, 4H, THF), 2.80 (t, 2H, $J = 7.0$ Hz, CH_2CH_3), 3.10 (t, 2H, $J = 7.0$ Hz, CH_2CH_3), 3.70 (br, 4H, THF), 5.59 (s, 2H, CH_2), 6.36 (m, 1H, *m*-PC_6H_4N), 6.81−6.91 (m, 2H, C_6H_5), 7.02−7.06 (m, 2H, *m,p*-PC_6H_4N), 7.08−7.11 (m, 7H, C_6H_5, *m,p*-NC_6H_3, *o*-PC_6H_4N), 7.13−7.17 (m, 6H, *m,p*-PPh_2), 7.57 ppm (m, 4H, *o*-PPh_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.45 (6C, $SiMe_3$), 14.36 (2C, CH_2CH_3), 26.05 (1C, CH_2CH_3), 26.38 (1C, CH_2CH_3), 41.37 (1C, CH_2SiMe_3), 48.08 (1C, CH_2SiMe_3), 69.39 (4C, THF), 114.23, 114.37 (1C, *p*-PPh), 114.96, 115.05 (2C, *m*-PPh), 125.94 (2C, *ipso*-Ph), 126.66 (1C, *ipso*-Ph), 126.84 (3C, Ph), 127.03 (2C, Ph), 127.65 (1C, *ipso*-Ph), 128.27 (2C, *m*-PPh_2), 128.50, 128.74 (2C, *m*-PPh_2), 128.87, 129.04, 129.16 (3C, Ph), 133.28 (2C, *p*-PPh_2), 133.65, 133.77 (1C, *o*-PPh), 134.48, 134.57 (4C, *o*-PPh_2), 135.41 (1C, *m*-PPh), 141.18 (1C, *ipso*-Ph), 142.06, 142.11 (2C, *ipso*-PPh_2), 159.06 ppm (d, $J = 4.0$ Hz, 1C, *ipso*-PPh). Anal. Calcd for $C_{47}H_{64}N_2OPScSi_2$ (%): C, 70.11; H, 8.01; N, 3.48. Found: C, 69.30; H, 8.29; N, 3.01.

A Typical Polymerization Procedure. To a 25 mL flask were added a toluene solution of butadiene (0.54 g) and 200 μmol of Al^iBu_3. Then, 20 μmol of **2a** and equimolar borate ($[Me_2NHPh][B(C_6F_5)_4]$) were added to initiate the polymerization. After a designated time, the mixture was poured into a large quantity of ethanol. A white precipitate of polybutadiene was collected and dried under vacuum at 40 °C for 24 h to a constant weight.

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Supporting Information Available: CIF files for complexes **1b**, **2a**, **3a**, and **4a** are available free of charge via the Internet at http://pubs.acs.org.

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