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Pyrrolide-Supported Lanthanide Alkyl Complexes. Influence of Ligands on Molecular Structure and Catalytic Activity toward Isoprene Polymerization

Yi Yang,[†,‡] Bo Liu,[†,‡] Kui Lv,[†,‡] Wei Gao,[†] Dongmei Cui,*[,†] Xuesi Chen,[†] and Xiabin Jing[†]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, People's Republic of China, and Graduate School of
the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

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The *N*,*N*-bidentate ligands 2-{(*N*-2,6-R)iminomethyl)}pyrrole ($\mathbf{HL^1}$, R = dimethylphenyl; $\mathbf{HL^2}$, R = diisopropylphenyl) have been prepared. $\mathbf{HL^1}$ reacted readily with 1 equiv of lanthanide tris(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$, affording lanthanide bis(alkyl) complexes $L^1Ln(CH_2SiMe_3)_2(THF)_n$ (**1a**, Ln = Lu, $n = 2$; **1b**, Ln = Sc, $n = 1$) via alkane elimination. Reaction of the bulky ligand $\mathbf{HL^2}$ with 1 equiv of $Ln(CH_2SiMe_3)_3(THF)_2$ gave the bis(pyrrolylaldiminato) lanthanide mono(alkyl) complexes $L^2{}_2Ln(CH_2SiMe_3)(THF)$ (**2a**, Ln = Lu; **2b**, Ln = Sc), selectively. The *N*,*N*-bidentate ligand $\mathbf{HL^3}$, 2-dimethylaminomethylpyrrole, reacted with $Ln(CH_2SiMe_3)_3(THF)_2$, generating bimetallic bis(alkyl) complexes of central symmetry (**3a**, Ln = Y; **3b**, Ln = Lu; **3c**, Ln = Sc). Treatment of the *N*,*N*,*N*,*N*-tetradentate ligand $\mathbf{H_2L^4}$, 2,2′-bis(2,2-dimethylpropyldiimino)methylpyrrole, with equimolar $Lu(CH_2SiMe_3)_3(THF)_2$ afforded a C_2-symmetric binuclear complex (**4**). Complexes **3a**, **3b**, **3c**, and **4** represent rare examples of THF-free binuclear lanthanide bis(alkyl) complexes supported by non-cyclopentadienyl ligands. All complexes have been tested as initiators for the polymerization of isoprene in the presence of $AlEt_3$ and $[Ph_3C][B(C_6F_5)_4]$. Complexes **1a**, **1b**, and **3a** show activity, and **1b** is the most active initiator, whereas **2a**, **2b**, **3b**, **3c**, and **4** are inert. The microstructure of the resultant polyisoprene has a *cis*-1,4 or *trans*-1,4 configuration depending on the initiator applied.

Introduction

Over the past few years the synthesis of bis(alkyl) and tris(alkyl) complexes of group 3 metals supported by multidentate ligands has been a research area of increasing interest.[1] Recently, rare earth metal bis(alkyl) complexes supported by monoanionic ancillary ligands have also received much attention in organolanthanide chemistry because these complexes are highly active single-component catalysts or can be converted to the corresponding cationic mono(alkyl) species after being activated by borate, such as $[Ph_3C][B(C_6F_5)_4]$ or $[Me_2NHPh][B(C_6F_5)_4]$.[2] The thus resultant cationic species have demonstrated encouraging catalytic activities for a range of polymerizations, such as highly regio- or stereoselective polymerizations of conjugated monomers,[3] polar monomers,[4] and olefins.[5] In some cases, to reach high activity and high *cis*-1,4 selectivity, the addition of the third component AlR_2Cl, AlR_3, or MAO was needed,[3b,e,6]

[†] State Key Laboratory of Polymer Physics and Chemistry.

[‡] Graduate School of the Chinese Academy of Sciences.

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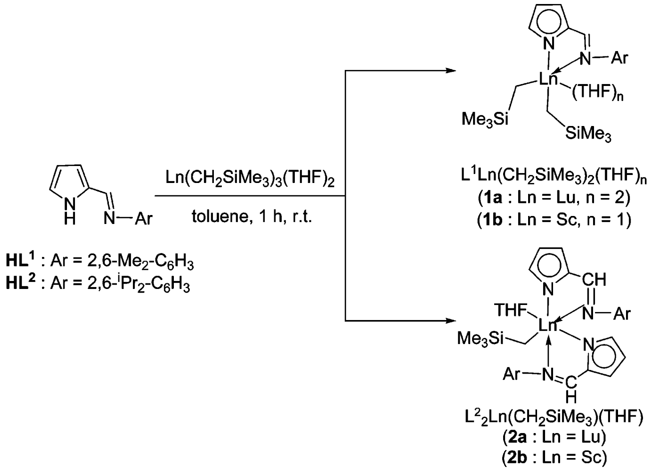
whereas rare earth metal bis(alkyl) species are highly reactive and usually less sterically hindered, which makes the isolation and application of the corresponding complexes more difficult due to ligand redistribution and formation of salt or solvent adducts. Tuning the ligand framework has been the efficient manner to adjust the stability as well as the catalytic activity of a complex.[7] Heteroatom compounds have been extensively explored to stabilize metal alkyl species by virtue of their strong metal−ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers, such as monodentate amides,[8] bidentate amidinates,[9] guanidinates,[10] β-diketiminates,[11] salicylaldiminates,[12] and crown ether or THF.[13] Comparatively, the pyrrolide ligands for such usage have remained less investigated. Up to date, Arnold reported a bis(pyrrolide) samarium mono(alkyl) complex initiating isospecific polymerization of MMA.[14] Our group also released several pyrrolide-ligated yttrium alkyl complexes that showed inter- or intramolecular migration of alkyl groups to generate mono(alkyl) or bimetallic bis(alkyl) species.[15] Here we wish to report the synthesis of lanthanide bis(alkyl) complexes bearing pyrrolide ligands and their catalytic behaviors for polymerization of isoprene in the presence of $AlEt_3$ and borate. We also present the significant effect of the ligand framework on the molecular structures and the catalytic performances of the complexes.

Results and Discussion

Scheme 1. Synthetic Pathway for Preparation of Complexes 1a, 1b, 2a, and 2b



Synthesis and Characterization of Complexes 1a, 1b, 2a, and 2b. The *N,N*-bidentate ligand 2-{(*N*-2,6-dimethylphenyl)-iminomethyl)}pyrrole (**HL^1**) was prepared by condensation reaction of pyrrole-2-carboxyaldehyde with 1 equiv of 2,6-dimethylaniline. Treatment of $Ln(CH_2SiMe_3)_3(THF)_2$ with 1 equiv of **HL^1** in toluene afforded pyrrolylaldiminato rare earth metal bis(alkyl) complexes $L^1Ln(CH_2SiMe_3)_2(THF)_n$ (**1a**, Ln = Lu, $n = 2$; **1b**, Ln = Sc, $n = 1$) (Scheme 1). The ^{1}H NMR spectrum of **1a** in C_6D_6 showed two sets of resonances indicating the existence of an enantiomer besides **1a**. Thus, methylene protons of four alkyl ligands, $Lu-CH_2SiMe_3$, gave three singlet resonances at δ −0.81, −0.70, and −0.64 with an integration ratio of 2:2:4, suggesting that two alkyl ligands were equivalent. Consistent with this, the imino proton $CH=N$ also displayed two singlets at δ 7.42 and 7.43, respectively. The pyrrolyl ring protons appeared in the olefinic region (δ 6.56), suggesting that the pyrrolyl anion might coordinate to the lutetium atom in η^1-N-coordination mode.[15] The molecular structure of **1a** (we did not isolate the single crystal of **1a**'s enantiomer) in the solid state has been confirmed by X-ray analysis as described in Figure 1. Selected bond distances and angles are listed in Table 1. The pyrrolide moiety chelates to the Lu ion via two nitrogen atoms in η^1/κ^1-coordination mode, which combines with two alkyl ligands and two solvated THF molecules to generate a distorted square-bipyramidal ligand core. The imino nitrogen N(1), the pyrrolyl nitrogen N(2), and the two alkyl carbon atoms (C(14) C(18)) define the equatorial position with the two THF oxygen atoms axial. The bond length of Lu−N(pyrrolyl) (Lu−

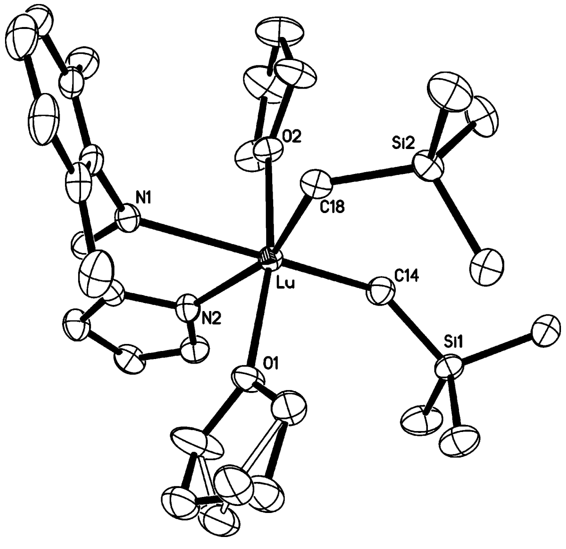


Figure 1. X-ray structure of **1a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 1a and 1b

1a		1b	
Lu−N(1)	2.540(3)	Sc−N(1)	2.2977(16)
Lu−N(2)	2.349(3)	Sc−N(2)	2.1872(16)
Lu−O(1)	2.313(2)	Sc−O	2.1990(14)
Lu−O(2)	2.326(2)		
Lu−C(14)	2.351(3)	Sc−C(14)	2.226(2)
Lu−C(18)	2.401(3)	Sc−C(18)	2.212(2)
O(1)−Lu−O(2)	169.04(7)		
N(1)−Lu−N(2)	68.87(8)	N(1)−Sc−N(2)	74.46(6)
C(14)−Lu−C(18)	106.09(11)	C(14)−Sc−C(18)	110.64(8)

N(2) = 2.349(3) Å) is comparable to that found in a lutetium−pyrrolyl complex, $Cp_2Lu(C_4H_4N)(THF)$ (2.289(4) Å).[16] The metal−imino nitrogen bond length (Lu−N(1) = 2.540(3) Å) is longer than the distance of the metal−pyrrolyl nitrogen (Lu−N(2) = 2.349(3) Å). The bond angle of C−Lu−C (106.09(11)°) is comparable to those in the rare earth metal bis(alkyl) complexes supported by triazacyclononane (99.41(8)°),[17] tri-amino-amide (101.96(6)°),[18] and β-diketiminate (108.90(13)°),[19] indicating the similar steric environment of these ligands, but it is smaller than those in a THF-solvated amidinato yttrium bis(alkyl) complex (119.5(2)°)[20] and in amido-phoshine-ligated lanthanide bis(alkyl) complexes (av 115.55°).[21]

Interestingly, under the same conditions, the reaction of $Sc(CH_2SiMe_3)_3(THF)_2$ with ligand **HL^1** gave the mono-THF-coordinated complex **1b**, $L^1Sc(CH_2SiMe_3)_2(THF)$, in contrast to the bis-THF-solvated **1a**, which could be attributed to the smaller ionic radii of the Sc atom. ^{1}H NMR of complex **1b** demonstrated that the methylene protons of the alkyl ligands, Sc−C*H*$_2$SiMe$_3$, gave a singlet resonance at a downfield region (δ 0.45), which was different from the three singlet resonances at upfield regions (δ −0.81, −0.70, and −0.64) in complex **1a** and its enantiomer. Accordingly, the geometry of the metal center in **1b** becomes a distorted square pyramid (Figure 2). The average Sc−C bond length (2.219(2) Å) (Table 1) is very close to those found in other scandium bis(alkyl) complexes, such as $[1,3\text{-}(SiMe_3)_2C_5H_3]Sc(CH_2SiMe_3)_2(THF)$ (2.215(1) Å),[3k] $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Sc(CH_2SiMe_3)_2(THF)$ (2.211(2) Å),[8] and $[PhC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2Sc(CH_2SiMe_3)_2(THF)$ (2.212(3) Å).[9d] The bond distances Sc−N and Sc−O are comparable to the corresponding ones in **1a**, if the difference of the ionic radii is considered,[22] whereas the bond angles (N(1)−Sc−N(2) 74.46(6)° and C(14)−Sc−C(18) 110.64(8)°) are much larger than those in complex **1a** (N(1)−Lu−N(2) 68.87(8)° and C(14)−Lu−C(18) 106.09(11)°) due to the less steric metal center and one THF coordination.

Surprisingly, switching from the sterically less demanding **HL^1** to the more bulky **HL^2** ligand, the analogous reaction with 1 equiv of $Ln(CH_2SiMe_3)_3(THF)_2$ generated the mono(alkyl) complexes **2a** (Ln = Lu) and **2b** (Ln = Sc) (Scheme 1), owing to ligand redistribution. The resonance for the pyrrolyl ring protons in the ^{1}H NMR spectrum of **2a** showed up in the olefinic region (δ 6.47). The singlet resonance at δ −0.49 was assignable to the equivalent methylene protons of Lu−C*H*$_2$SiMe$_3$. The methylene protons of Sc−C*H*$_2$SiMe$_3$ in complex **2b** gave a singlet resonance at a downfield region (δ 0.44), which was different from the singlet resonance at the upfield region (δ −0.49) in complex **2a**, but the same as the singlet resonance (δ 0.44) in complex **1b**. Complex **2a** adopts a distorted square-bipyramidal geometry (Figure 3) with the imino nitrogen atom N(4), two pyrrolyl nitrogen atoms N(1) and N(3), and the alkyl carbon C(35) occupying the equatorial positions, while the THF oxygen and another imino nitrogen atom, N(2), are axial. Selected bond distances and angles (Table 2) in complex **2a** are similar to the corresponding values in **1a** and need not be discussed further.

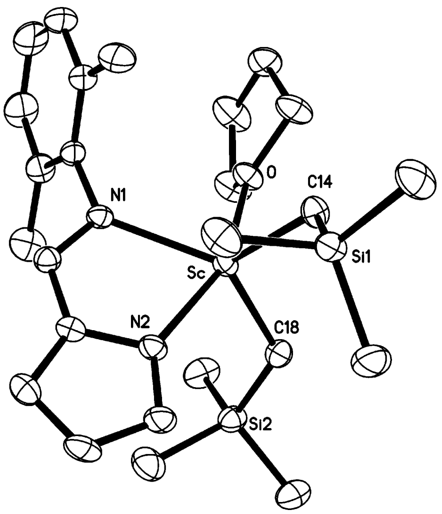

Figure 2. X-ray structure of **1b** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

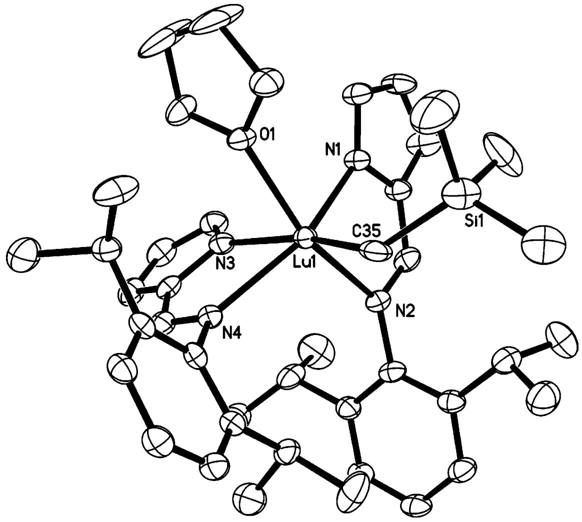

Figure 3. X-ray structure of **2a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2a

Lu(1)−N(1)	2.286(4)	Lu(1)−N(2)	2.437(4)
Lu(1)−N(3)	2.329(4)	Lu(1)−N(4)	2.433(4)
Lu(1)−O(1)	2.314(3)	Lu(1)−C(35)	2.344(6)
N(1)−Lu(1)−O(1)	83.29(13)	O(1)−Lu(1)−N(3)	84.02(13)
N(1)−Lu(1)−C(35)	108.69(17)	N(4)−Lu(1)−N(2)	108.13(14)

Synthesis and Characterization of Complexes 3a, 3b, and 3c. Treatment of $2\text{-}(Me_2NCH_2)\text{-}C_4H_3NH$ (**HL^3**) with 1 equiv of $Ln(CH_2SiMe_3)_3(THF)_2$ afforded the colorless complexes $[(2\text{-}(Me_2NCH_2)\text{-}C_4H_3N)Ln(CH_2SiMe_3)_2]_2$ (**3a**, Ln = Y; **3b**, Ln = Lu; **3c**, Ln = Sc) in moderate yields. Complexes **3a**, **3b**, and

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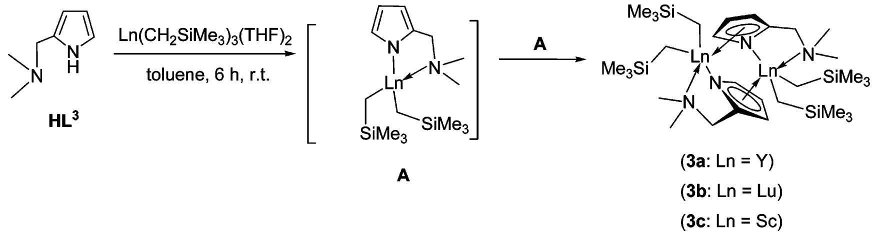
Scheme 2. Synthetic Pathway for Preparation of Complexes 3a, 3b, and 3c



3c were extremely air- and moisture-sensitive and showed good solubility in THF and toluene but were insoluble in hexane. The probable reaction pathway is described as Scheme 2. The neutral ligand **HL^3** protonated one metal alkyl species of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ to give the bis(alkyl) intermediate **A**. Dimerization of two molecules of **A** via the pyrrolyl ring in one **A** attaching to the lanthanide ion in another **A** in a η^5-coordination mode afforded a binuclear tetra(alkyl) complex. Complexes **3a**, **3b**, and **3c** showed similar ^{1}H NMR spectra. The methylene protons of the alkyl ligand, Ln−C*H*$_2$SiMe$_3$, in both **3a** and **3b** exhibited four discrete AB spins, and the trimethylsilyl protons SiMe$_3$ also gave four singlet resonances, indicating molecular symmetry to some degree. The structure of **3a** is confirmed by X-ray analysis as a solvent-free dimer of central symmetry (C_i) (Figure 4). The yttrium ion bonds to two alkyl moieties arranged in *trans*-positions to form a unit. Such two units are bridged by two tridentate pyrrolyl anions in η^5/η^1:κ^1-modes, generating a dimer containing two distorted trigonal-bipyramidal cores. Interestingly, the two pyrrole rings are almost parallel, and the two nitrogen atoms combined with two yttrium atoms to form a plane. Two alkyl species locate the *endo* coordination of the plane, while the other two alkyl ligands are *exo*. Although the pyrrolyl ring coordinates to the lanthanide metal center in a η^5-mode like that found in the large cyclic or polymeric complexes[23] and in our previously reported imino pyrrolide complexes,[15] complex **3a** represents the first example of an amino pyrrolide-stabilized lanthanide bis(alkyl) complex with respect to the pyrrole ring as a η^5-heterocyclopentadinyl ligand. The bond distances between yttrium and the pyrrolyl carbon in **3a**, Y−η^5-C(pyr ring), ranging from 2.725(3) to 2.743(3) Å (Table 3), are comparable to that in [2-(2-Ph$_2$PC$_6$H$_3$NC(H)(CH$_2$SiMe$_3$))-C$_4$H$_3$N]$_2$Y$_2$(CH$_2$SiMe$_3$)$_2$(THF) (2.690(5) to 2.738(6) Å).[15] It is also noteworthy that all Y−η^5-C (pyr ring) bond lengths are close, varying in a narrow range that is compared with lanthanocene complexes (2.646(3)−2.674(4) Å).[24] The bond distance Y−N(1) (2.735(2) Å) is longer than Y−N(2A) (2.588(3) Å) and Y−N(1A) (2.446(2) Å), well consistent with the η^5/η^1:κ^1-coordination mode of the pyrrolide ligand, which is comparable to the bond length of Y−N in a η^1:κ^1-pyrrolyl yttrium amido complex.[25] The bond distances Y−C(8) (2.408(4) Å) and Y−C(9) (2.402(3) Å) have been found to be comparable to those in the previously reported yttrium bis(alkyl) complexes (Y−C, av 2.40 Å).[5h,7h,26] However, the corresponding bond angle (C(9)−Y−C(8) (91.99(13)°) is much smaller than the reported value (C−Y−C, av 101.5°),[5h,7h,26] and it is also much smaller than C−Lu−C (106.09(11)°) and C−Sc−C (110.64(8)°) found in complexes **1a** and **1b** discussed previously, suggesting the bulky environment around the central metal.

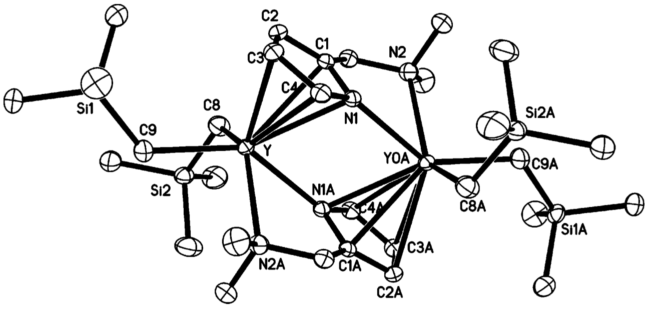


Figure 4. X-ray structure of **3a** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3a

Y−N(1)	2.735(2)	Y−C(1)	2.725(3)
Y−C(2)	2.738(3)	Y−C(3)	2.743(3)
Y−C(4)	2.735(3)	Y−N(1A)	2.446(2)
Y−N(2A)	2.588(3)	Y−C(8)	2.408(4)
Y−C(9)	2.402(3)		
C(9)−Y−C(8)	91.99(13)	N(1A)−Y−N(1)	71.47(9)
N(1A)−Y−N(2A)	66.55(8)	C(9)−Y−N(2A)	85.15(10)
C(8)−Y−N(1)#1	90.35(11)		

Synthesis and Characterization of Complex 4. Compound **H$_2$L^4**, containing two amino protons, was prepared by condensation reaction of pyrrole-2-carboxyaldehyde with 2,2-dimethyl-1,3-propanediamine without addition of formic acid. Treatment of **H$_2$L^4** by equimolar Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ afforded yellow crystals of complex **4** in a quantitative yield (65%). The probable reaction pathway could be described as follows (Scheme 3): Two alkyl ligands of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ were abstracted by the neutral ligand **H$_2$L^4** to give a mono(alkyl) intermediate **B**. **B** readily reacted with another molecule of **H$_2$L^4** to yield **C** via metal alkyl abstraction, which bore no alkyl ligand. The protonolysis reaction between the amino proton in **C** and another molecule of lutetium tris(alkyl)s accompanied by the coordination of the neutral pyrrole ring to Lu ions in η^5-mode afforded the final product **4**. The two discrete AB spins in the upfield region at δ −1.05 and −0.87 were attributed to the methylene protons of the metal alkyl species, indicating the symmetric character of the molecule. This is confirmed by an X-ray crystallographic diffraction study, suggesting that complex **4** is a C_2-symmetric dimer. The two dianionic *N,N,N,N*-tetradentate pyrrolide ligands bond to lutetium Lu(1) in η^5/η^5-modes to form reverse sandwich geometry, whereas they bond to Lu(2) in η^1:κ^1:η^1/η^1:κ^1:η^1-coordination modes to generate a twisted square-pyramidal geometry (Figure 5). The base of the pyramid is

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(23) (a) Dube, T.; Conoci, T.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3657. (b) Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716. (c) Dube, T.; Gambarotta, S.; Yap, G. P. A.; Conoci, S. *Organometallics* **2000**, *19*, 115. (d) Dube, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182. (e) Ganesan, M.; Lalonde, M. P.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2443. (f) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 766. (g) Berube C. D.; Yazdanbakhsh, M.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2003**, *22*, 3742.

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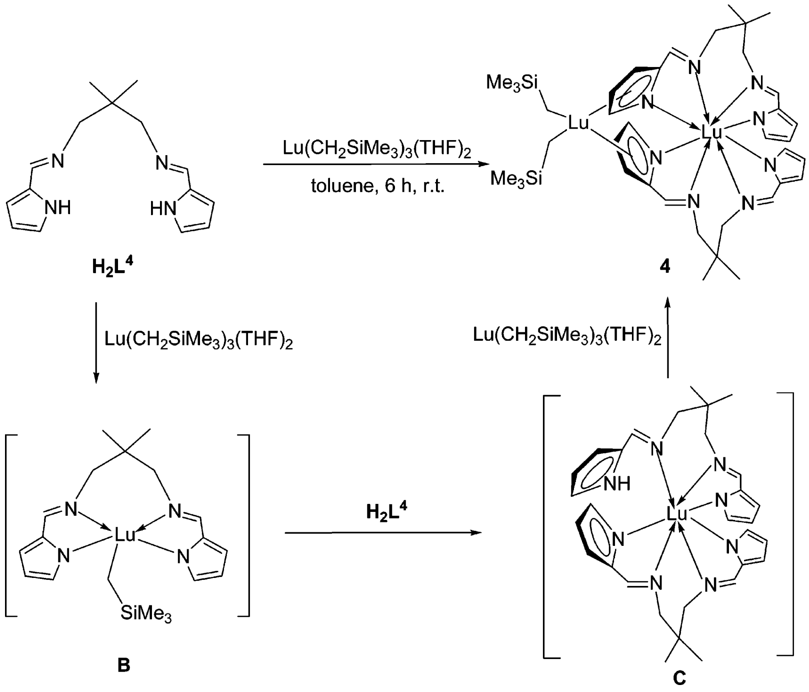
(26) (a) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.;. Noack, C. L.; Piers, W. E. Parvez, M. *Organometallics* **2003**, *22*, 1577. (b) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3486.

Scheme 3. Synthetic Pathway for Preparation of Complex 4



defined by the eight nitrogen atoms, which contributes to stabilize the complex.[27] The two alkyl moieties coordinate to Lu(1) in *cis*-positions against the two pyrrolyl rings. It is noteworthy that the pyrrolyl rings coordinate to Lu(1) as a neutral ligand and negatively charged species, respectively. The bond lengths of Lu(1) to η^5-C and η^5-N of each pyrrolyl ring are unequal, varying in a wide range (Lu(1)−N(1), 2.593(2) Å; Lu(1)−C(1), 2.650(3) Å; Lu(1)−C(2), 2.759(3) Å; Lu(1)−C(3), 2.749(3) Å; Lu(1)−C(4), 2.627(3) Å) (Table 4), which is consistent with Y−η^5-C (pyr ring) (2.631(6) to 2.851(6) Å) in {[2-(2,6-*i*Pr$_2$C$_6$H$_3$NC(H)(CH$_2$SiMe$_3$))-C$_4$H$_3$N]Y(CH$_2$SiMe$_3$)-(THF)}$_2$.[15] The bond distances between Lu(2) and nitrogen atoms N(1), N(2), N(3), and N(4), averaging 2.434 Å, are within the range typically observed for Lu−N bonds.[28] The Lu−CH$_2$SiMe$_3$ bond length in **4** (2.312(4) Å) is comparable with those found in (C$_5$Me$_5$)Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.332(4) Å),[29] (C$_5$Me$_4$SiMe$_3$)Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.335(3) Å),[30] and **1a** (2.351(3) and 2.401(3) Å). The bond angle C(16)−Lu(1)−C(16A) (104.47(19)°) is close to that in **1a** (C−Lu−C = 106.09(11)°) and **1b** (C−Sc−C = 110.64(8)°), showing the similar steric environment of the ligands; however, it is much larger than that in **3a** (C−Y−C = 91.99(13)°) and the values (C−Y−C = 96.4(2)°) we reported previously.[15]

Table 4. Selected Bond Distances (Å) and Angles (deg) for 4

Lu(1)−N(1)	2.593(2)	Lu(2)−N(1)	2.448(3)
Lu(1)−C(1)	2.650(3)	Lu(2)−N(2)	2.416(3)
Lu(1)−C(2)	2.759(3)	Lu(2)−N(3)	2.483(3)
Lu(1)−C(3)	2.749(3)	Lu(2)−N(4)	2.389(3)
Lu(1)−C(4)	2.627(3)	Lu(1)−C(16)	2.312(4)
C(16)−Lu(1)−C(16A)	104.47(19)	N(1)−Lu(1)−N(1A)	65.81(11)
N(1)−Lu(2)−N(3A)	68.79(8)	N(2A)−Lu(2)−N(3A)	70.21(9)
N(4)−Lu(2)−N(2A)	69.77(10)		

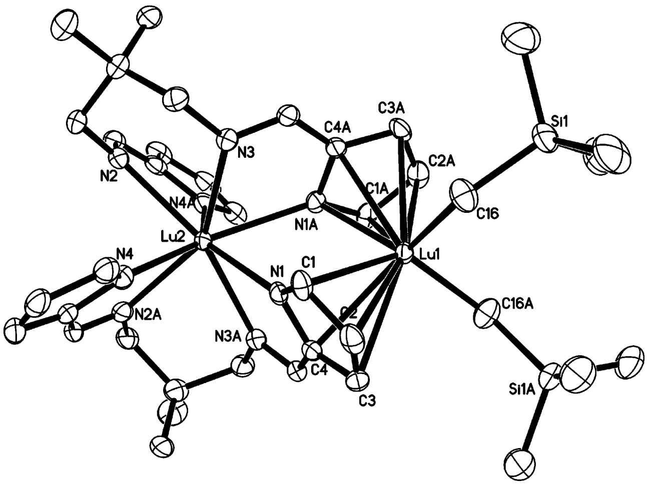


Figure 5. X-ray structure of **4** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Isoprene Polymerization. All complexes had been tested as initiators for the polymerization of isoprene activated by AlEt$_3$ and borate ([Ph$_3$C][B(C$_6$F$_5$)$_4$]). Representative data are summarized in Table 5.

Complex **1a** was inactive in the polymerization of isoprene and when treated with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] was also inert (Table 5, entry 1). Upon addition of the third component, AlEt$_3$, the system showed versatile activity depending on the molar ratio of [Al]/[Ln].[3b,e,6] When the ratio was 1:1, no polymerization took place (Table 5, entry 2). Increasing the ratio to 2:1, complete conversion could be reached in 5 h at room temperature, and the resulting polyisoprene had high molecular weight but broad molecular weight distribution (Table 5, entry 3). In order to investigate the nature of the initiator, the reaction of **1a** and 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$D$_6$ was monitored by ^{1}H NMR technique. The spectrum showed that the resonances for one metal alkyl species disappeared accompanied by the quantitative formation of Ph$_3$CCH$_2$SiMe$_3$;[3h] the methylene protons from the other alkyl species shifted downfield to δ 0.01 and 0.03, indicating the generation of cation [L^{1}Lu(CH$_2$SiMe$_3$)-

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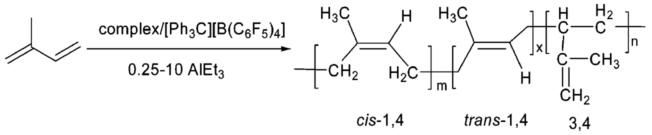
Table 5. Isoprene Polymerization with Alkyl Complexes/[Ph_3C][$B(C_6F_5)_4$] with Various Amounts of $AlEt_3$[a]



entry	cat.	[Ip]/[Ln]	[Al]/[Ln]	time (min)	conv (%)	M_{calcd} (10^4)[b]	M_n (10^4)[c]	PDI[c]	1,4[d](%) cis	1,4[d](%) trans	3,4[d] (%)	eff[e] (%)
1	**1a**	1000:1	0	300	0							
2	**1a**	1000:1	1:1	300	0							
3	**1a**	1000:1	2:1	300	99	6.81	10.7	4.39	75.0	16.5	8.5	64
4	**1a**	1000:1	3:1	300	100	6.81	6.89	3.16	62.0	27.1	10.9	99
5	**1a**	1000:1	5:1	300	100	6.81	4.59	3.03	65.3	25.3	9.4	148
6	**1a**	1000:1	10:1	300	100	6.81	3.70	3.47	69.1	23.2	7.7	184
7	**1a**	500:1	3:1	300	100	3.41	3.56	3.71	74.3	16.2	9.5	96
8	**1a**	1500:1	3:1	300	100	10.2	11.5	3.42	70.2	21.2	8.6	89
9	**1a**	2000:1	3:1	300	100	13.6	15.9	3.59	63.0	27.9	9.1	86
10[f]	**1a**	3000:1	3:1	1200	96	19.6	22.6	3.39	65.9	24.2	9.9	87
11	**1b**	1000:1	0	1	0							
12	**1b**	1000:1	0.25:1	1	100	6.81	36.5	2.15	75.9	15.0	9.1	19
13	**1b**	1000:1	0.5:1	1	100	6.81	29.5	1.94	75.6	15.6	8.8	23
14	**1b**	1000:1	1:1	1	100	6.81	29.8	2.03	76.0	14.5	9.5	23
15	**1b**	1000:1	1.5:1	1	100	6.81	10.1	1.55	76.7	14.3	9.0	67
16	**1b**	1000:1	2:1	1	100	6.81	12.8	1.70	73.7	17.7	8.6	53
17	**1b**	1000:1	5:1	1	100	6.81	10.8	1.85	76.4	14.4	9.2	63
18	**2a**	1000:1	5:1	500	0							
19	**2b**	1000:1	5:1	500	0							
20[g]	**3a**	1000:1	5:1	300	99	3.37	1.34	1.37	15.2	70.4	14.4	251
21[g]	**3b**	1000:1	5:1	500	0							
22[g]	**3c**	1000:1	5:1	500	trace							
23	**4**	1000:1	5:1	500	0							

[a] General condition: 20 °C, toluene; $[Ip]_0 = 2.0$ mol/L, [Ln] = 2.0 mmol/L, [B]/[Ln] = 1.0 (B = [Ph_3C][$B(C_6F_5)_4$]). [b] M_{calcd} = ([Ip]/[Ln]) × 68.12 × X (X = conversion). [c] Measured by GPC calibrated with standard polystyrene samples. [d] Determined by ^1H NMR. [e] Catalyst efficiency = M_n(calculated)/M_n(measured). [f] [Ln] = 0.5 mmol/L. [g] [B]/[Ln] = 2.0.

$(THF)_2]^+$.[31] Then, excess $AlEt_3$ was added to the above cationic system. The resonances arising from the ligand remained unchanged, while that from metal alkyl protons shifted slightly (δ 0.02). Obvious changes were found for the signals from solvated THF molecules, which gave a triplet resonance at δ 3.45 upfield-shifted compared to the singlet resonance at δ 3.78 in complex **1a**. Analysis of the NMR spectrum of a mixture of **1a** and $AlEt_3$ in C_6D_6 excluded the possibility of cleavage of the ligand from the metal center and the alkylation of the imino function CH═N of the ligand by $AlEt_3$ (C*H*═N proton still peaked at δ 7.31 compared with δ 7.42 in complex **1a**). Thus, we assumed that the cation $[L^1Lu(CH_2SiMe_3)(THF)_2]^+$ was the initiator of the polymerization of isoprene. The role of $AlEt_3$ was that it could trap and coordinate to a THF molecule,[32] which reduced the electron density of the metal center and decreased the competitive coordination ability of THF with the monomer isoprene.[33] Hessen has reported that a bis-THF-solvated yttrium bis(alkyl) complex showed no activity if activated only by borate; addition of AlR_3 is crucial.[20] In our system, $AlEt_3$ also removed impurities and behaved as a chain transfer agent if excess $AlEt_3$ was added, as shown in Table 5 (entries 4−6). When the [Al]/[Ln] ratio was 10:1, the molecular weight of polyisoprene, M_n = 37 000, was much smaller than that (M_n = 107000) when the ratio was 2:1, consistent with a previous result.[34]

The effect of monomer-to-initiator ratio on the polymerization was also investigated. At an [Al]/[Ln] of 3:1, the polymerization of isoprene was performed under various [Ip]/[Ln] ratios ranging from 500 to 2000. With an increase in the ratio, the molecular weight of polyisoprene increased close to the theoretical value M_{calcd} and the catalytic efficiency was high (86−96%) (Table 5, entries 7−9). When the ratio was 3000:1, the polymerization became sluggish due to the too low concentration of the initiator (0.5 mmol/L) compared to that when the ratio was 500:1 (2.0 mmol/L), whereas a complete conversion could also be reached if the polymerization time was prolonged to 20 h, to afford polyisoprene with a molecular weight as high as 22.6 × 10^4 (96%, Table 5, entry 10). On the whole, the molecular weight distribution of polyisoprene was broad, which might be attributed to the faster chain transfer reaction than propagation.

It is surprising that the combination of **1b**/[Ph_3C][$B(C_6F_5)_4$] with a small amount of $AlEt_3$ was highly active (T_p = 1 min) compared to its analogous **1a** (T_p = 300 min), although no polymerization was observed without $AlEt_3$ (the major role of which might be removal of impurities). This high catalytic activity of **1b** could be attributed to the smaller Sc ionic radius, allowing mono-THF coordination. Thus, the metal center was

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(31) ^1H NMR monitoring of the reaction of complex **1a** with 1 equiv of [Ph_3C][$B(C_6F_5)_4$] in C_6D_6 at 25 °C showed almost quantitative formation of $Ph_3CCH_2SiMe_3$ (δ 7.42−7.43 (m, 6H, *o*-Ph), 7.19−7.21 (m, 9H, *m,p*-Ph), 2.17 (s, 2H, CH_2), −0.10 (s, 9H, SiMe_3)). Additional signals were observed at δ 6.95−7.03 (m, 3H, *m,p*-C_6H_3), 6.44, 6.80, 6.82 (s, 3H, pyr), 3.26 (s, 8H, THF), 1.68 (s, 6H, $C_6H_3Me_2$), 1.25 (s, 8H, THF), 0.11 (s, 9H, Lu−CH_2SiMe_3), 0.01, 0.03 (s, 2H, Lu−C$H_2$$SiMe_3$), which may be assigned to $[L^1Lu(CH_2SiMe_3)(THF)_2][B(C_6F_5)_4]$, although the proton in the ligand C*H*═N could not be unequivocally assigned due to possible overlap with the other signals (*o*-Ph).

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Table 6. Summary of Crystallographic Data for 1−4

	1a	**1b**	**2a**	**3a**	**4**-C_7H_8
formula	$C_{29}H_{51}N_2O_2Si_2Lu$	$C_{25}H_{43}N_2OSi_2Sc$	$C_{42}H_{59}N_4OSiLu$	$C_{30}H_{66}N_4Si_4Y_2$	$C_{45}H_{66}N_8Si_2Lu_2$
cryst size, mm	0.18 × 0.15 × 0.13	0.25 × 0.18 × 0.16	0.18 × 0.13 × 0.11	0.18 × 0.15 × 0.13	0.13 × 0.09 × 0.07
fw	690.87	488.75	838.99	773.05	1125.18
cryst syst	monoclinic	monoclinic	triclinic	triclinic	tetragonal
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P4(3)2(1)2$
a (Å)	9.4569(6)	11.5805(8)	10.3754(6)	9.4442(8)	14.9571(7)
b (Å)	16.4263(10)	14.0152(10)	19.2503(11)	10.4910(9)	14.9571(7)
c (Å)	21.2020(13)	17.7458(13)	20.9445(12)	11.4717(10)	21.8098(14)
α (deg)	90	90	88.3420(10)	77.9230(10)	90
β (deg)	92.3310(10)	90.5080(10)	89.6590(10)	84.3380(10)	90
γ (deg)	90	90	88.0490(10)	65.7770(10)	90
V (Å^3)	3290.8(4)	2880.1(4)	4179.0(4)	1013.49(15)	4879.2(4)
Z	4	4	4	1	4
D_{calcd} (g/cm^3)	1.394	1.127	1.334	1.267	1.532
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$ (deg)	52.06	52.08	52.00	52.08	52.08
μ (cm^{-1})	30.98	3.56	24.26	29.90	41.10
F(000)	1416	1056	1728	408	2248
no. of obsd reflns	6444	5680	16 002	3900	4826
no. of params refnd	352	288	905	189	266
GOF	0.928	1.021	0.870	0.996	0.965
R_1	0.0252	0.0416	0.0405	0.0389	0.0184
wR_2	0.0515	0.1114	0.0860	0.0987	0.0411

electronically much more positive than that of **1a**, which was favored by the coordination and insertion of the nonpolar monomer isoprene, in agreement with the previous results that mono-THF-coordinated bis(alkyl) complexes displayed high activity under the presence of equimolar borate without $AlEt_3$.[3h,20] The molecular weight of the resulting polyisoprene was much higher compared to the theoretic value, which was attributed to the extremely rapid propagation rather than initiation, leading to the reduction of the catalyst efficiency (Table 5, entries 11−14).[35] If the ratio was raised in the range 1.5:1−5:1, the molecular weight of polyisoprene decreased due to the transfer-agent role of $AlEt_3$ (Table 5, entries 15−17).

The microstructures of polymers obtained were *cis*-1,4 ranging from 62% to 75% by using system **1a**, which varied within a narrow range of 74%−77% with system **1b**.

The catalytic activities of THF-free bimetallic tetra(alkyl) complexes **3a**−**c** with cocatalysts $AlEt_3$ and $[Ph_3C][B(C_6F_5)_4]$ were relatively low compared with monosolvated complexes **1a**,**b** (Table 5, entries 20−22). However, the effect of the ionic radius of the central metal ion on the catalytic activity was consistent with **1a**,**b** in the trend Y >> Sc ≥ Lu. In contrast, the polyisoprene isolated was dominated by 1,4-*trans*-regularity (70%), which might be attributed to the spatial environment of the metal center.

The monoalkyl complexes **2a**,**b** and the bimetallic bis(alkyl) complex **4** were inert to the polymerization of isoprene even when activated by borate and $AlEt_3$ due to the absence of a metal alkyl initiator in the former two cases and the very electron negative metal center in the latter case (Table 5, entries 18, 19, and 23).

Conclusion

We have demonstrated a series of rare earth metal bis(alkyl) complexes bearing η^1- or η^5-coordinated pyrrolide moieties, which have been well-defined with novel structures dependent strongly on the ligand framework and the ionic radius of the central metal. In the presence of $AlEt_3$ and borate ($[Ph_3C][B(C_6F_5)_4]$), the monomeric mono-THF-solvated bis(alkyl) complex has exhibited a higher activity toward polymerization of isoprene than the bis-THF-solvated counterpart and the THF-free bimetallic bis(alkyl)s. The resulting polyisoprene has a predominant *cis*- or *trans*-configuration depending on the initiator employed.

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 by paraffin film. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by $^1H-^1H$ COSY and $^1H-^{13}C$ HMQC experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR. The molecular weight and molecular weight distribution of the polymers were measured by a TOSOH HLC-8220 GPC. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Pyrrole-2-carboxyaldehyde was prepared according to the literature.[36]

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 ($\lambda = 0.71073$ 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 the calculated positions and were included in the structure calculation without further refinement of the parameters. The crystallographic data and the refinement of complexes **1a**, **1b**, **2a**, **3a**, and **4** are summarized in Table 6.

2-(2,6-$Me_2C_6H_3N$=CH)-C_4H_3NH (HL^1). To a dried MeOH solution (20 mL) of pyrrole-2-carboxyaldehyde (1.90 g, 20 mmol) were added 2,6-dimethylaniline (2.42 g, 20 mmol) and a catalytic

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(35) Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 1909.

(36) Wallace, D. M.; Leung, S. H.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1993**, *58*, 7245.

amount of formic acid (0.25 mL) under stirring. The reaction mixture was stirred for 4 h at room temperature. Subsequently, the yellow solution was concentrated and cooled to −30 °C. Then some colorless crystals precipitated, separated by filtration, and then washed with cold methanol. Removal of the solvents afforded product in 63% yield (2.50 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.18 (s, 6H, $C_6H_3Me_2$), 6.26 (m, 1H, 4-pyr), 6.63 (m, 1H, 3-pyr), 6.67 (s, 1H, 5-pyr), 6.98−7.11 (m, 3H, *m,p*-C_6H_3), 7.99 (s, 1H, N═C−*H*), 10.35 ppm (br, 1H, N−*H*). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 18.89 (2C, $C_6H_3Me_2$), 110.41 (1C, 5-pyr), 117.38 (1C, 4-pyr), 124.47 (1C, 3-pyr), 128.68 (3C, *m,p*-C_6H_3), 128.88 (1C, *ipso*-pyr), 130.42 (2C, *o*-C_6H_3), 151.19 (1C, *ipso*-C_6H_3), 153.81 ppm (1C, N═CH). IR (KBr pellets): ν 3202, 2977, 2905, 2863, 1633, 1590, 1554, 1475, 1446, 1415, 1378, 1338, 1313, 1253, 1246, 1188, 1162, 1137, 1088, 1035, 973, 916, 883, 860, 833, 793, 767, 743, 731, 607, 527, 502, 422 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_2$ (%): C, 78.75; H, 7.12; N, 14.13. Found: C, 78.54; H, 7.07; N, 14.33.

2-(2,6-$^iPr_2C_6H_3N$═CH)-C_4H_3NH (HL^2). To a dried MeOH solution (20 mL) of pyrrole-2-carboxyaldehyde (1.90 g, 20 mmol) were added 2,6-diisopropylaniline (3.6 g, 20 mmol) and a catalytic amount of formic acid (0.25 mL) under stirring. The reaction mixture was stirred for 4 h at room temperature. Subsequently, the white precipitate was separated by filtration and then washed with cold methanol. Removal of the solvents afforded **HL^2** in 74% yield (3.75 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.12 (d, J_{H-H} = 6.9 Hz, 12H, CH*Me*$_2$), 3.06 (hepta, J_{H-H} = 6.9 Hz, 2H, C*H*Me$_2$), 6.20 (m, 1H, 4-pyr), 6.49 (s, 1H, 3-pyr), 6.60 (t, 1H, 5-pyr), 7.15 (m, 3H, *m,p*-C_6H_3), 7.95 (s, 1H, N═C−*H*), 10.39 ppm (br, 1H, N−*H*). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 24.03 (4C, CH*Me*$_2$), 28.35 (2C, *C*HMe$_2$), 110.31 (1C, 5-pyr), 117.14 (1C, 4-pyr), 123.65 (1C, 3-pyr), 124.61 (2C, *m*-C_6H_3), 124.97 (1C, *p*-C_6H_3), 130.33 (1C, *ipso*-pyr), 139.43 (2C, *o*-C_6H_3), 148.92 (1C, *ipso*-C_6H_3), 153.16 ppm (1C, N═CH). IR (KBr pellets): ν 3235, 3060, 2964, 2926, 2869, 1628, 1586, 1554, 1458, 1418, 1384, 1363, 1338, 1311, 1253, 1181, 1133, 1108, 1089, 1056, 1033, 932, 883, 860, 832, 803, 781, 760, 746, 607 cm^{-1}. Anal. Calcd for $C_{17}H_{22}N_2$ (%): C, 80.27; H, 8.72; N, 11.01. Found: C, 80.54; H, 8.07; N, 10.93.

2-(Me_2NCH_2)-C_4H_3NH (HL^3). A solution of 17 g (0.21 mol) of dimethylamine hydrochloride in 15.8 g (0.21 mol) of 40% formalin was added slowly to 13.4 g (0.20 mol) of pyrrole over 60 min. Stirring was continued for 1 h after the addition was completed. It was then poured into 100 mL of 25% sodium hydroxide solution and extracted with ether (3 × 50 mL). The combined ether extracts were washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. The ether was removed, and the residue was distilled at reduced pressure. The product was collected at 60−80 °C (0.5 mm) and crystallized in the receiver in the form of white crystals. The yield was 9.6 g (39%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.24 (s, 6H, N*Me*$_2$), 3.43 (s, 2H, C*H*$_2$N), 6.03 (s, 1H, 3-pyr), 6.10 (m, 1H, 4-pyr), 6.70 (s, 1H, 5-pyr), 9.40 ppm (br, 1H, N−*H*). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 45.41 (2C, N*Me*$_2$), 57.17 (1C, *C*H$_2$N), 107.83 (1C, 3-pyr), 108.27 (1C, 4-pyr), 118.63 (1C, 5-pyr), 129.32 ppm (1C, *ipso*-pyr). IR (KBr pellets): ν 3184, 3090, 2981, 2949, 2909, 2861, 2826, 2782, 2707, 2609, 1714, 1586, 1507, 1469, 1456, 1407, 1355, 1306, 1264, 1252, 1237, 1176, 1155, 1131, 1095, 1038, 1022, 1011, 968, 885, 842, 717, 639, 614, 461, 408 cm^{-1}. Anal. Calcd for $C_7H_{12}N_2$ (%): C, 67.70; H, 9.74; N, 22.56. Found: C, 67.45; H, 9.88; N, 22.83.

2-C_4H_3NH−CH═$NCH_2CMe_2CH_2N$═CH-2-C_4H_3NH (H_2L^4). To a dried MeOH solution (10 mL) of pyrrole-2-carboxyaldehyde (3.10 g, 32.6 mmol) was added 2,2-dimethyl-1,3-propanediamine (1.66 g, 16.3 mmol) under stirring. The reaction mixture was stirred for 4 h at room temperature. Subsequently, the white precipitate was separated by filtration and then washed with cold methanol. Removal of the solvents afforded **H_2L^4** in 76% yield (3.2 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.93 (s, 6H, C*Me*$_2$), 3.41 (s, 4H, NC*H*$_2$), 6.22 (m, 2H, 4-pyr), 6.44 (m, 2H, 3-pyr), 6.85 (m, 2H, 5-pyr), 7.96 (s, 2H, N═C*H*), 9.06 ppm (br, 2H, N−*H*). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 24.87 (2C, C*Me*$_2$), 37.71 (1C, *C*Me$_2$), 70.24 (2C, N*C*H$_2$), 109.86 (2C, 5-pyr), 114.92 (2C, 4-pyr), 122.66 (2C, 3-pyr), 130.69 (2C, *ipso*-pyr), 153.26 ppm (2C, N═*C*H). IR (KBr pellets): ν 3131, 3085, 2971, 2892, 2844, 1739, 1639, 1553, 1464, 1452, 1436, 1420, 1384, 1358, 1332, 1317, 1299, 1257, 1244, 1196, 1164, 1139, 1129, 1058, 1036, 992, 974, 941, 929, 881, 850, 788, 736, 608, 534, 445 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_4$ (%): C, 70.28; H, 7.86; N, 21.86. Found: C, 70.10; H, 7.69; N, 21.94.

[2-(2,6-$Me_2C_6H_3N$═CH)-C_4H_3N]Lu(CH_2SiMe_3)$_2$(THF)$_2$ (1a). To a toluene solution (5.0 mL) of Lu(CH_2SiMe_3)$_3$(THF)$_2$ (0.210 g, 0.362 mmol), equivalent **HL^1** (0.071 g, 0.360 mmol in 2 mL toluene) was dropwise added at room temperature. The mixture was then stirred for 1 h. Removal of the volatiles gave a deep red oily residue. The residue was dissolved with 3 mL of hexane and then cooled to −30 °C for 12 h to give colorless solids, which were washed carefully by a small amount of hexane (0.5 mL) and then dried under vacuum to afford complex **1a** in 64% yield (0.160 g). Colorless single crystals for X-ray analysis grew from hexane at −30 °C within a day. ^{1}H NMR (400 MHz, C_6D_6, 25 °C, **1a** and its enantiomer): −0.81, −0.70 (s, 4H, C*H*$_2$SiMe$_3$), −0.64 (s, 4H, C*H*$_2$SiMe$_3$), 0.18 (s, 6H, CH$_2$Si*Me*$_3$), 0.37 (s, 30H, CH$_2$Si*Me*$_3$), 1.34 (s, 16H, THF), 1.98, 2.14 (s, 12H, $C_6H_3Me_2$), 3.78 (s, 16H, THF), 6.56, 6.63 (s, 2H, 4-pyr), 6.92 (m, 2H, 3-pyr), 6.99 (s, 4H, *m*-C_6H_3), 7.05 (m, 2H, *p*-C_6H_3), 7.13, 7.68 (s, 2H, 5-pyr), 7.42, 7.43 ppm (s, 2H, N═C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 5.13 (m, 12C, CH$_2$Si*Me*$_3$), 18.87, 19.31 (s, 4C, $C_6H_3Me_2$), 25.71 (s, 8C, THF), 39.58, 42.23 (s, 4C, *C*H$_2$SiMe$_3$), 71.07 (s, 8C, THF), 113.76, 113.82 (s, 2C, 4-pyr), 121.99 (s, 2C, 3-pyr), 122.90 (s, 2C, 5-pyr), 125.45, 125.77 (s, 2C, *p*-C_6H_3), 129.08 (s, 4C, *m*-C_6H_3), 130.76, 131.72 (s, 4C, *o*-C_6H_3), 139.38, 139.51 (s, 2C, *ipso*-pyr), 150.56 (s, 2C, *ipso*-C_6H_3), 163.58, 164.46 ppm (s, 2C, *C*H═N). IR (KBr pellets): ν 2949, 1598, 1575, 1463, 1440, 1390, 1340, 1305, 1234, 1198, 1174, 1094, 1036, 1018, 981, 857, 779, 746, 705, 667, 610, 575, 533, 494 cm^{-1}. Anal. Calcd for $C_{29}H_{51}N_2O_2Si_2Lu$ (%): C, 50.42; H, 7.44; N, 4.05. Found: C, 50.19; H, 7.23; N, 4.29.

[2-(2,6-$Me_2C_6H_3N$═CH)-C_4H_3N]Sc(CH_2SiMe_3)$_2$(THF) (1b). Following a procedure similar to that described for the preparation of **1a**, treatment of a toluene solution (5.0 mL) of Sc(CH_2SiMe_3)$_3$(THF)$_2$ (0.205 g, 0.455 mmol) with 1 equiv of **HL^1** (0.090 g, 0.455 mmol in 2 mL of toluene) afforded complex **1b** (0.185 g, 83%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.33 (s, 18H, CH$_2$Si*Me*$_3$), 0.45 (s, 4H, C*H*$_2$SiMe$_3$), 1.12 (s, 4H, THF), 2.10 (s, 6H, $C_6H_3Me_2$), 3.68 (s, 4H, THF), 6.61 (m, 1H, 4-pyr), 6.90 (m, 1H, 3-pyr), 6.92 (m, 3H, *m*, *p*-C_6H_3), 7.13 (s, 1H, 5-pyr), 7.95 ppm (s, 1H, N═C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.11 (s, 6C, CH$_2$Si*Me*$_3$), 19.69 (s, 2C, $C_6H_3Me_2$), 25.09 (s, 2C, THF), 47.21 (br, 2C, *C*H$_2$SiMe$_3$), 71.66 (s, 2C, THF), 114.03 (s, 1C, 4-pyr), 122.67 (s, 1C, 3-pyr), 125.87 (s, 1C, 5-pyr), 126.55 (s, 1C, *p*-C_6H_3), 128.95 (s, 2C, *m*-C_6H_3), 131.54 (s, 2C, *o*-C_6H_3), 140.45 (s, 1C, 2-pyr), 149.66 (s, 1C, *ipso*-C_6H_3), 163.86 ppm (s, 1C, *C*H═N). IR (KBr pellets): ν 3649, 3218, 2950, 2895, 2855, 1628, 1598, 1577, 1496, 1467, 1444, 1390, 1342, 1297, 1263, 1248, 1178, 1134, 1091, 1037, 984, 896, 883, 860, 795, 769, 745, 683, 605, 577, 536, 473, 433 cm^{-1}. Anal. Calcd for $C_{25}H_{43}N_2OSi_2Sc$ (%): C, 61.42; H, 8.87; N, 5.73. Found: C, 61.53; H, 8.61; N, 5.70.

[2-(2,6-$^iPr_2C_6H_3N$═CH)-C_4H_3N]$_2$Lu(CH_2SiMe_3)(THF) (2a). To a toluene solution (5.0 mL) of Lu(CH_2SiMe_3)$_3$(THF)$_2$ (0.235 g, 0.405 mmol) was added dropwise 1 equiv of **HL^2** (0.103 g, 0.405 mmol in 2 mL of toluene) at room temperature. The mixture was then stirred for 1 h. Removal of the volatiles gave a deep yellow, oily residue. The residue was dissolved with 3 mL of hexane and then cooled to −30 °C for 12 h to give colorless solids, which were washed carefully by a small amount of hexane (0.5 mL) and then dried under vacuum to afford complex **2a** in 36% yield (0.121 g). Colorless single crystals for X-ray analysis grew from hexane at −30 °C within a day. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.49 (s, 2H, CH_2SiMe_3), 0.18 (s, 9H, CH_2SiMe_3), 0.98−1.33 (m, 24H, $CHMe_2$), 1.36 (s, 4H, THF), 3.25 (m, 4H, $CHMe_2$), 3.79 (s, 4H, THF), 6.47 (br, 2H, 3-pyr), 6.88 (br, 2H, 4-pyr), 7.17 (s, 2H, 5-pyr), 7.19 (s, 6H, *m,p*-C_6H_3), 7.83 ppm (s, 2H, N=C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.87 (s, 3C, $SiMe_3$), 23.50, 29.00 (s, 4C, $CHMe_2$), 26.02, 26.58 (s, 8C, $CHMe_2$), 26.34 (s, 2C, THF), 32.63 (s, 1C, CH_2SiMe_3), 71.14 (br, 2C, THF), 114.17 (s, 4C, 3,4-pyr), 123.48 (br, 2C, 5-pyr), 124.37 (s, 4C, *m*-C_6H_3), 127.00 (s, 2C, *p*-C_6H_3), 137.38 (2C, *ipso*-pyr), 140.18 (s, 2C, *o*-C_6H_3), 142.61 (s, 2C, *o*-C_6H_3), 148.27 (s, 2C, *ipso*-C_6H_3), 164.45 ppm (s, 2C, N=*C*H). IR (KBr pellets): ν 2963, 1594, 1575, 1485, 1461, 1441, 1391, 1362, 1343, 1321, 1299, 1260, 1235, 1168, 1109, 1033, 1012, 983, 934, 881, 857, 804, 786, 748, 708, 668, 607, 564, 469, 434 cm^{-1}. Anal. Calcd for $C_{42}H_{59}N_4OSiLu$ (%): C, 60.13; H, 7.09; N, 6.68. Found: C, 60.16; H, 7.23; N, 6.50.

$[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3N{=}CH)\text{-}C_4H_3N]_2Sc(CH_2SiMe_3)(THF)$ (2b). Following a procedure similar to that described for the preparation of **2a**, treatment of a toluene solution (5.0 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.176 g, 0.390 mmol) with 1 equiv of **HL^2** (0.099 g, 0.390 mmol in 2 mL of toluene) afforded complex **2b** (0.105 g, 38%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.28 (s, 9H, CH_2SiMe_3), 0.44 (s, 2H, CH_2SiMe_3), 0.72, 0.96, 0.98, 1.08, 1.10, 1.14, 1.24, 1.55 (d, *J* = 6.8 Hz, 24H, $CHMe_2$), 1.32 (s, 4H, THF), 3.26, 3.77 (sept, *J* = 6.8 Hz, 4H, $CHMe_2$), 3.96 (s, 4H, THF), 6.15, 6.40 (m, 2H, 3-pyr), 6.48, 6.68 (s, 2H, 4-pyr), 6.82, 7.07 (s, 2H, 5-pyr), 7.20−7.26 (m, 6H, *m,p*-C_6H_3), 7.67 ppm (s, 2H, N=C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 3.38 (s, 3C, $SiMe_3$), 23.06, 23.50, 23.81, 26.65 (s, 4C, $CHMe_2$), 14.79, 21.90, 24.32, 25.98, 26.27, 28.41, 29.22, 30.40 (s, 8C, $CHMe_2$), 25.65 (s, 2C, THF), 32.41 (s, 1C, CH_2SiMe_3), 72.45 (br, 2C, THF), 114.11 (s, 2C, 3-pyr), 123.19 (s, 2C, 4-pyr), 124.23 (s, 2C, 5-pyr), 124.48 (s, 4C, *m*-C_6H_3), 127.49 (s, 2C, *p*-C_6H_3), 139.81 (2C, *ipso*-pyr), 142.51 (s, 2C, *o*-C_6H_3), 143.10 (s, 2C, *o*-C_6H_3), 145.86 (s, 2C, *ipso*-C_6H_3), 163.81 ppm (s, 2C, N=*C*H). IR (KBr pellets): ν 3225, 3064, 2962, 2927, 2868, 1627, 1595, 1576, 1461, 1445, 1419, 1392, 1363, 1340, 1325, 1296, 1247, 1172, 1135, 1108, 1092, 1058, 1036, 985, 960, 934, 898, 883, 861, 803, 781, 746, 680, 605, 473 cm^{-1}. Anal. Calcd for $C_{42}H_{59}N_4OSiSc$ (%): C, 71.15; H, 8.39; N, 7.90. Found: C, 71.53; H, 8.11; N, 8.01.

$[(2\text{-}(Me_2NCH_2)\text{-}C_4H_3N)Y(CH_2SiMe_3)_2]_2$ (3a). To a toluene solution (5.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.185 g, 0.374 mmol) was dropwise added 1 equiv of **HL^3** (0.046 g, 0.374 mmol in 2 mL of toluene) at room temperature. The mixture was then stirred for 5 h. Removal of the volatiles gave white solids, which were washed carefully by a small amount of hexane (0.5 mL) and then dried under vacuum to afford complex **3a** in 59% yield (0.086 g). Colorless single crystals for X-ray analysis grew from toluene at −30 °C within a day. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.86, −0.70, −0.64, −0.44 (d, J_{Y-C-H} = 8.0 Hz, 8H, CH_2SiMe_3), 0.33, 0.41, 0.43, 0.49 (s, 36H, CH_2SiMe_3), 1.94, 1.97, 2.08, 2.29 (s, 12H, NMe_2), 2.89, 2.95, 3.76, 4.14 (d, *J* = 15.2 Hz, 4H, CH_2N), 6.48, 6.55 (s, 2H, 3-pyr), 6.60, 6.70 (s, 2H, 5-pyr), 6.73, 6.88 ppm (s, 2H, 4-pyr). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.83, 5.10, 5.20 (s, 12C, CH_2SiMe_3), 31.41 (d, J_{Y-C} = 41.4 Hz, 1C, CH_2SiMe_3), 35.00 (d, J_{Y-C} = 36.8 Hz, 1C, CH_2SiMe_3), 35.77 (d, J_{Y-C} = 40.8 Hz, 1C, CH_2SiMe_3), 38.16 (d, J_{Y-C} = 38.4 Hz, 1C, CH_2SiMe_3), 43.37, 45.16, 48.35, 50.16 (s, 4C, NMe_2), 59.90, 61.27 (s, 2C, CH_2N), 112.19, 113.35 (s, 2C, 3-pyr), 115.91, 116.50 (s, 2C, 5-pyr), 126.80, 127.99 (s, 2C, 4-pyr), 135.71, 139.84 ppm (s, 2C, *ipso*-pyr). IR (KBr, pellets): ν 3098, 2945, 2885, 2867, 2817, 2798, 1583, 1468, 1438, 1424, 1409, 1350, 1299, 1267, 1248, 1236, 1176, 1157, 1146, 1100, 1037, 1005, 977, 964, 854, 789, 740, 714, 671, 625, 453 cm^{-1}. Anal. Calcd for $C_{30}H_{66}N_4Si_4Y_2$ (%): C, 46.61; H, 8.61; N, 7.25. Found: C, 46.50; H, 8.33; N, 7.36.

$[(2\text{-}(Me_2NCH_2)\text{-}C_4H_3N)Lu(CH_2SiMe_3)_2]_2$ (3b). Following a procedure similar to that described for the preparation of **3a**, treatment of a toluene solution (5.0 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.210 g, 0.361 mmol) with 1 equiv of **HL^3** (0.046 g, 0.367 mmol in 2 mL of toluene) afforded complex **3b** (0.247 g, 72%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −1.10, −1.08 (s, 2H, CH_2SiMe_3), −0.93, −0.91 (s, 2H, CH_2SiMe_3), −0.86, −0.83 (s, 2H, CH_2SiMe_3), −0.71, −0.68 (s, 2H, CH_2SiMe_3), 0.31, 0.41, 0.43, 0.49 (s, 36H, CH_2SiMe_3), 1.91, 1.98, 2.08, 2.32 (s, 12H, NMe_2), 2.91, 2.95, 3.78, 4.10 (d, *J* = 12.0 Hz, 4H, CH_2N), 6.42 (s, 1H, 3-pyr), 6.54 (s, 2H, 3-pyr, 5-pyr), 6.69 (s, 2H, 4-pyr, 5-pyr), 6.84 ppm (s, 1H, 4-pyr). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.94, 5.31 (s, 12C, CH_2SiMe_3), 35.93 (s, 1C, CH_2SiMe_3), 39.45, 39.64 (s, 2C, CH_2SiMe_3), 42.34 (s, 1C, CH_2SiMe_3), 43.53, 46.08, 48.43, 50.41 (s, 4C, NMe_2), 60.19, 61.58 (s, 2C, CH_2N), 111.62, 113.41 (s, 2C, 3-pyr), 115.82, 116.84 (s, 2C, 5-pyr), 126.65, 127.72 (s, 2C, 4-pyr), 135.03, 139.68 ppm (s, 2C, *ipso*-pyr). IR (KBr, pellets): ν 3095, 2947, 2880, 2865, 2816, 2799, 1583, 1465, 1434, 1424, 1408, 1350, 1297, 1267, 1245, 1233, 1171, 1157, 1146, 1102, 1035, 1004, 977, 963, 858, 782, 746, 714, 673, 629, 450 cm^{-1}. Anal. Calcd for $C_{30}H_{66}N_4Si_4Lu_2$ (%): C, 38.12; H, 7.04; N, 5.93. Found: C, 38.03; H, 7.33; N, 5.66.

$[(2\text{-}(Me_2NCH_2)\text{-}C_4H_3N)Sc(CH_2SiMe_3)_2]_2$ (3c). Following a procedure similar to that described for the preparation of **3a**, treatment of a toluene solution (5.0 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.178 g, 0.395 mmol) with 1 equiv of **HL^3** (0.049 g, 0.395 mmol in 2 mL of toluene) afforded complex **3c** (0.179 g, 66%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.65, −0.46, −0.22, −0.12 (s, 8H, CH_2SiMe_3), 0.46 (s, 36H, CH_2SiMe_3), 2.13, 2.25, 2.31, 2.38 (s, 12H, NMe_2), 3.00, 3.10, 3.89, 4.12 (s, 4H, CH_2N), 6.49 (s, 1H, 3-pyr), 6.72 (br, 4H, 3, 4, 5-pyr), 7.05 ppm (s, 1H, 4-pyr). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.53, 4.81 (s, 12C, CH_2SiMe_3), 60.70 (s, 2C, CH_2N), 106.75 (s, 2C, 3-pyr), 109.08 (s, 2C, 5-pyr), 126.06 (s, 2C, 4-pyr), 134.79 (s, 2C, *ipso*-pyr). IR (KBr, pellets): ν 3092, 2949, 2868, 2833, 1560, 1466, 1444, 1405, 1347, 1305, 1248, 1237, 1178, 1157, 1135, 1098, 1038, 1026, 1002, 969, 881, 854, 792, 743, 721, 672, 619, 456, 426, 410 cm^{-1}. Anal. Calcd for $C_{30}H_{66}N_4Si_4Sc_2$ (%): C, 52.59; H, 9.71; N, 8.18. Found: C, 52.16; H, 9.33; N, 8.47.

$[2\text{-}C_4H_3N{-}CH{=}NCH_2CMe_2CH_2N{=}CH\text{-}2\text{-}C_4H_3N]_2Lu_2(CH_2SiMe_3)_2$ (4). To a toluene solution (5.0 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.230 g, 0.396 mmol) was dropwise added 1 equiv of **H_2L^4** (0.101 g, 0.394 mmol in 2 mL of toluene) at room temperature. The mixture was then stirred for 5 h. Removal of the volatiles gave a yellow oil, which was dissolved in a small amount of hexane (0.5 mL) and then cooled to −30 °C to afford complex **4** (yellow solids) in 65% yield (0.265 g). Colorless single crystals for X-ray analysis grew from hexane at −30 °C within a few days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −1.06, −1.03, −0.88, −0.85 (s, 4H, CH_2SiMe_3), 0.29 (s, 6H, $C(CH_3)_2$), 0.42 (s, 18H, CH_2SiMe_3), 0.67 (s, 6H, $C(CH_3)_2$), 2.38, 2.58, 2.66, 1.54 (d, *J* = 12.0 Hz, 8H, NCH_2), 6.60 (m, 4H, 3-pyr), 6.72, 6.84 (m, 4H, 4-pyr), 7.09, 7.20 (s, 4H, 5-pyr), 7.46, 7.77 (s, 4H, N=C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 5.12 (s, 6C, CH_2SiMe_3), 22.35, 26.76 (s, 4C, $C(CH_3)_2$), 25.67 (s, 2C, $C(CH_3)_2$), 36.70, 38.12 (s, 2C, CH_2SiMe_3), 68.56, 72.27 (s, 4C, NCH_2), 111.51, 116.40 (s, 4C, 3-pyr), 117.46, 119.94 (s, 4C, 4-pyr), 131.87, 137.16 (s, 4C, 5-pyr), 135.49, 138.71 (s, 4C, *ipso*-pyr), 160.30, 160.64 ppm (s, 4C, *C*H=N). IR (KBr, pellets): ν 3602, 3246, 3100, 2954, 2894, 2842, 1626, 1606, 1508, 1470, 1440, 1397, 1389, 1366, 1355, 1324, 1293, 1249, 1078, 1034, 977, 894, 862, 811, 794, 742, 694, 613 cm^{-1}. Anal. Calcd for $C_{45}H_{66}N_8Si_2Lu_2$ (%): C, 48.04; H, 5.91; N, 9.96. Found: C, 48.40; H, 5.53; N, 10.05.

Isoprene Polymerization. A detailed polymerization procedure (Table 5, entry 4) is described as a typical example. In a glovebox, the monomer (1.0 mL, 10 mmol) was added into a 25 mL flask. Then, 3 equiv of $AlEt_3$ (4.1 μL, 0.05 mmol), a toluene solution (5.0 mL) of **1a** (6.9 mg, 0.01 mmol), and 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (9.6 mg, 0.01 mmol) were added to the flask. After the reaction was stirred for 5 h, the flask was moved outside. Methanol was injected to terminate the polymerization. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at ambient temperature to constant weight.

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Supporting Information Available: CIF files and crystallographic data for **1a**, **1b**, **2**, **3a**, and **4** including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters are available free of charge via the Internet at http://pubs.acs.org.

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