Pyrrolide-Ligated Organoyttrium Complexes. Synthesis, Characterization, and Lactide Polymerization Behavior

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The *N,N*-bidentate ligand 2-{(*N*-2,6-diisopropylphenyl)iminomethyl)}pyrrole (**L^1**) and the *N,N,P*-tridentate ligand 2-{(*N*-2-diphenylphosphinophenyl)iminomethyl)}pyrrole (**L^2**) have been prepared. Their reactions with homoleptic yttrium tris(alkyl) compound $Y(CH_2SiMe_3)_3(THF)_2$ have been investigated. Treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with 1 equiv of **L^1** generated a THF-solvated bimetallic (pyrrolylaldiminato)yttrium mono(alkyl) complex (**1**) of central symmetry. In this process, **L^1** is deprotonated by metal alkyl and its imino C═N group is reduced to C−N by intramolecular alkylation, generating dianionic species that bridge two yttrium alkyl units in a unique $\eta^5/\eta^1:\kappa^1$ mode. The pyrrolyl ring behaves as a heterocyclopentadienyl ligand. Reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with 2 equiv of **L^1** afforded the monomeric bis(pyrrolylaldiminato)yttrium mono(alkyl) complex (**2**), selectively. Amination of **2** with 2,6-diisopropylaniline gave the corresponding yttrium amido complex (**3**). In **3** the pyrrolide ligand is monoanionic and bonds to the yttrium atom in a $\eta^1:\kappa^1$ mode. The homoleptic tris($\eta^1:\kappa^1$-pyrrolylaldiminato)-yttrium complex (**4**) was isolated when the molar ratio of **L^1** to $Y(CH_2SiMe_3)_3(THF)_2$ increases to 3:1. Reaction of **L^2** with equimolar $Y(CH_2SiMe_3)_3(THF)_2$ afforded an asymmetric binuclear complex (**5**). The dianionic *N,N,P* tridentate moieties derived from **L^2** coordinate to yttrium atoms in $\eta^5/\eta^1:\kappa^2$ modes, generating tetrahedron and trigonal/pyramidal geometry around the two metal centers, respectively. Both alkylation of the imino C═N group of ligand **L^2** and the pyrrole's ability to act similar to a heterocyclopentadienyl moiety were also found in complex **5**. Complexes **1**−**3** and **5** initiated polymerizations of D,L-lactide to give atactic polylactides with high molecular weights and narrow molecular weight distributions.

Introduction

The pyrrolide compounds have gathered particular research interest recently as spectator ligands by virtue of their strong metal−ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and catalytic activity toward polymerization.[1] Additionally, they can act as a versatile ligand due to η^5/κ^1 bonding capability of the pyrrolyl moiety, anticipated to be an alternative of cyclopentadiene.[2] Thus, quite a few complexes based on transition metals have been developed, which have exhibited high activity for olefin polymerization.[3] The pyrrolide-attached low-valent rare earth metal complexes originated by Gambarotta have also been demonstrated to possess unique reactivity such as N_2 reduction.[4] In contrast, these ligands have received scant attention in trivalent lanthanide chemistry. Some related examples are rare earth metal complexes supported by dipyrrolide[5] or porphyrinogen ligands, which usually aggregate to less predictable macrocyclic structures.[2a,6] Recently, Arnold reported a bis(pyrrolide)samarium complex where the pyrrolyl ligands coordinate to the central metal in η^1-modes, which showed interesting stereocontrol of the polymerization of methyl methacrylate.[7] Thus, synthesis of rare earth metal complexes bearing a η^5-coordinated pyrrolide moiety is therefore of obvious interest. On the other hand, rare earth metal alkyl complexes are highly active single-site catalysts or crucial precursors of the cationic counterparts after being activated by MAO or borates, having shown

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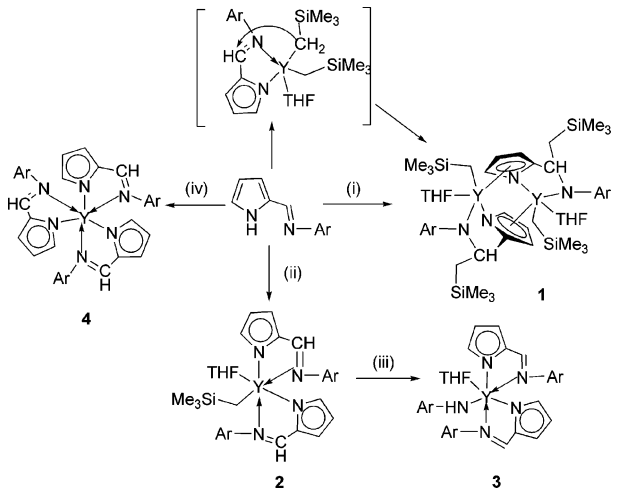
tremendous catalytic activities toward olefin polymerizations[8] and highly regio- or stereoselective polymerizations of conjugated monomers[9] and polar monomers.[10] However, the unstable property hinders the isolation and application of such complexes. Many ancillary ligands have been used in an attempt to stabilize metal alkyls. Up to date, they are dominated by cyclopentadienyl derivatives, including mono-, bis-, and ansa-auxiliaries.[11] Only recently have compounds containing heteroatoms such as bidentate amidinates,[12] guanidinates,[13] β-diketiminates,[14] and salicylaldiminates[15] been explored to support rare earth metal alkyls. The pyrolide ligands for such usage have been less investigated. Here we wish to report the synthesis, molecular structures, and coordination modes of the pyrrolide-ligated yttrium alkyl complexes and the amido derivative. The catalytic behavior of these complexes toward ring-opening polymerization of lactide is also presented.

Results and Discussion

Synthesis and Characterization of Complexes 1−4. The *N*,*N*-bidentate ligand 2-{(*N*-2,6-diisopropylphenyl)iminomethyl)}-pyrrole (**L^1**) was prepared by condensation reaction of pyrrole-2-carboxyaldehyde with 1 equiv of 2,6-diisopropylaniline. The reaction of **L^1** with 1 equiv of yttrium alkyls, $Y(CH_2SiMe_3)_3(THF)_2$, took place immediately upon addition at room temperature. The reaction mixture was kept stirring for 24 h to afford pyrrolylaldiminato yttrium mono(alkyl) complex **1** as the major product (55%) (Scheme 1). The neutral ligand **L^1** was first deprotonated by one metal alkyl of $Y(CH_2SiMe_3)_3(THF)_2$ with the release of tetramethylsilane, and then, the imino C═N group of which was alkylated via intramolecular migration of the metal alkyl, to generate dianionic species. ^{1}H NMR analysis of complex **1** displayed that the pyrrolyl protons showed a high-field shift at δ 6.25 compared to that at δ 6.54 of the η^1-N coordination mode,[5] suggesting that the pyrrolyl moiety coordinates to the yttrium atom in a η^5-fashion. The methylene protons of Y−CH_2SiMe$_3$ gave an AB spin around δ −0.4 (J_{Y-C-H} = 8 Hz), different from the singlet resonance at δ −0.6 in the yttrium tris(alkyl)s. The intramolecular alkyl migration was confirmed by the formation of a C(H)(CH_2SiMe$_3$)N group that exhibited discrete doublet resonances assigned to the methylene protons. The solid-state structure of complex **1**, as identified by X-ray analysis, is shown in Figure 1. Each yttrium atom bonds to an alkyl and a THF molecule to form a unit; dimerization via the dianionic pyrrolylaldiminate bridges forms a structure of central symmetry. The pyrrolide moiety coordinates to yttrium atoms in unique η^5/η^1:κ^1 modes like a cyclopantadienyl ligand to generate a distorted trigonal bipyramidal core. The pyrrolyl nitrogen N(2), THF oxygen, and alkyl carbon C(25) occupy the equatorial positions, while the center

Scheme 1 . Synthetic Pathway for Preparation of Complexes 1−4[a]



[a] Reagents and condition: Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$, toluene, rt, 24 h; (i) 1 equiv of $Y(CH_2SiMe_3)_3(THF)_2$; (ii) 1/2 equiv of $Y(CH_2SiMe_3)_3(THF)_2$; (iii) 2,6-^{i}Pr$_2$-C$_6$H$_3$NH$_2$, 6 h; (iv) 1/3 equiv of $Y(CH_2SiMe_3)_3(THF)_2$.

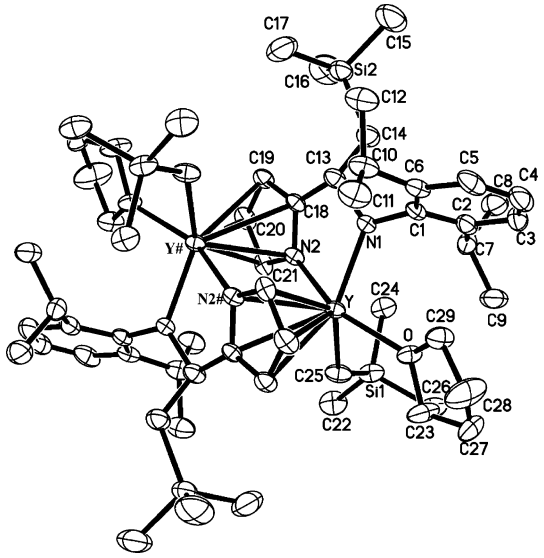


Figure 1. X-ray structure of **1** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

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

Y−N(1)	2.256(4)	Y#−C(20)	2.768(6)
Y−N(2)	2.382(5)	Y#−C(19)	2.851(6)
Y#−N(2)	2.646(5)	Y#−C(18)	2.800(6)
Y#−C(21)	2.631(6)	N(1)−C(13)	1.503(8)
N(1)−Y−N(2)	70.15(17)	Y−N(2)−Y#	103.73(17)
N(2)−Y−N(2)#	76.27(17)	C(13)−N(1)−Y	121.5(3)
N(1)−C(13)−C(18)	107.7(5)	N(2)−C(18)−C(13)	119.3(5)
C(18)−N(2)−Y	115.4(4)	N(1)−Y−N(2)#	100.75(16)

of the pyrrolyl ring and the anilido nitrogen N(1) are axial. The bond distances between yttrium and the pyrrolyl carbon, Y−η^5-C(pyr ring), ranging from 2.631(6) to 2.851(6) Å (Table 1), are comparable to Sm−η^5-C(pyr ring) (2.850(4)−2.928(4) Å) in a samarium dipyrrolide complex[6a] if the difference of the ionic radii is considered.[16] It is noteworthy that Y#−N(2) (2.646(5) Å) and Y#−C(21) (2.631(6) Å) are much shorter than Y#−C(18) (2.800(6) Å), Y#−C(19) (2.851(6) Å), and Y#−C(20) (2.768(6) Å). This is different from the lanthanocene complexes, where all Y−η^5-C(Cp ring) bond lengths are close, varying in a narrow range of 2.646(3)−2.674(4) Å. This could be due to the much stronger yttrium and nitrogen bond.[17] The bond distance of Y#−N(2) (2.646(5) Å) is longer than Y−N(2) (2.382(5) Å) and Y−N(1) (2.256(4) Å), well consistent with the η^5/η^1:κ^1 coordination mode of the pyrrolide ligand. The bond length of C(13)−N(1), 1.503(8) Å, is close to the normal C−N single bond (1.4904(17) Å),[18] indicating that the C═N bond of the ligand has been reduced to a single bond by intramolecular alkylation. The intramolecular alkylation has been found in *N,O* bidentate Salen titanium or zirconium bis(benzyl) complexes, which results in decomposition of the complexes and loss of catalytic activity for ethylene polymerization.[19] For *N,N* bidentate dipyrrolylimino or dipyridylimino compounds, the C═N bond is reduced to C−N by intermolecular alkyl migration to form a monanionic moiety that stabilizes lutetium bis(alkyl)s or even cationic alkyl species,[20] whereas alkylation of the C═N group of the pyrrolylaldiminato ligand affording dianionic species to support a complex such as **1** has not been known, as far as we are aware. Complex **1** also represents the first example of a rare earth metal bis(alkyl) complex bearing a η^5-coordinated pyrrolide, namely, a hetero-cyclopentadienyl ligand.

Following a similar procedure, treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with 2 equiv of $\mathbf{L^1}$ generated complex **2** in high yield (82.3%) via abstractions of metal alkyls (Scheme 1). The ^{1}H NMR spectrum displayed that the pyrrolyl protons gave resonances in the olefinic region at δ 6.54, shifted downfield compared to δ 6.25 in complex **1**, indicating an η^1-N coordination mode of the pyrrolylaldiminato ligand. The singlet resonance at δ −0.50 was assignable to the equivalent methylene protons of YCH_2SiMe_3. The presence of a signal for the imino proton C*H*═N (δ 7.82) suggested the absence of alkylation. Although without X-ray analysis, the ^{1}H NMR spectrum is informative to figure out the molecular structure of complex **2**, being a bis(pyrrolylaldiminato)yttrium monoalkyl, analogous with samarium alkyl [2-(CH═NC_6H_3-2,6-^{i}Pr$_2$)-5-^{t}BuC_4H_2N]$_2$Sm(CH_2SiMe_3)(THF) reported by Anorld, albeit isolated by a different synthetic pathway.[7] This was further proved by amination of **2** with 2,6-diisopropylaniline to afford the corresponding amido complex **3** (80.3%) (Scheme 1). The molecular structure of **3** was resolved by X-ray diffraction analysis to be a monomer, adopting a six-coordinate octahedral geometry (Figure 2). The two pyrrolide ligands located in almost perpendicular positions coordinate to the yttrium atom in a η^1:κ^1-*N,N* bidentate fashion, leaving the THF molecule and anilido moiety in a *cis*-arrangement. No η^5-bonding mode of the pyrrolyl ring has been observed. The bond distances between yttrium and the chelate nitrogen of the pyrrolyl ring Y−N(pyr) (Y−N(1), 2.347(2) Å; Y−N(3), 2.367(2) Å) are shorter than those of yttrium and the imino nitrogen Y−N_{imino} (Y−N(2), 2.457(2) Å; Y−N(4), 2.491(2) Å) (Table 2). The bond length of yttrium and amino nitrogen Y−N(5) (2.260(2) Å) is the shortest, which is comparable to those found in bis(amido) yttrium complexes Y{N($SiMe_3$)$_2$}$_2${OSi^{t}Bu(2-C_6H_4(CH_2NMe_2))$_2$} (2.237(9) Å)[21] and Y{N($SiMe_3$)$_2$}$_2${*N*-isopropyl-2-(isopropylamino)troponiminato} (2.236(3) Å).[22] The acute N−Y−N angles (71.52(8)° and 69.46(8)°) and obtuse O−Y−N(2) angle (151.96(8)°) are comparable to those found in a related samarium alkyl complex mentioned previously (N−Sm−N, average 69.12°; O(1)−Sm1−N(5), 160.37(9)°).[7]

The homoleptic tris(η^1:κ^1-pyrrolylaldiminato)yttrium complex **4** was quantitatively isolated when 3 equiv of $\mathbf{L^1}$ reacted with

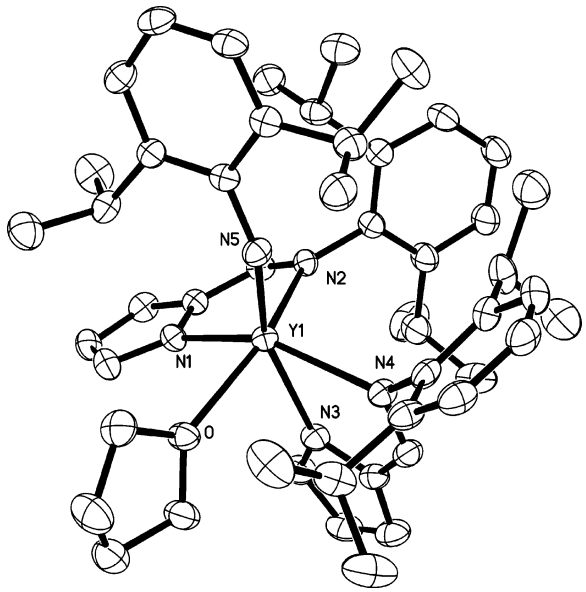

Figure 2. X-ray structure of **3** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3 and 4

	3	**4**
Y−N(1)	2.347(2)	2.493(2)
Y−N(2)	2.457(2)	2.326(2)
Y−N(3)	2.367(2)	2.487(2)
Y−N(4)	2.491(2)	2.334(2)
Y−N(5)	2.260(2)	2.471(2)
Y−N(6)		2.315(2)
N(1)−Y−N(2)	71.52(8)	71.35(8)
N(2)−Y−N(3)	85.56(8)	95.17(8)
N(3)−Y−N(4)	69.46(8)	71.26(8)
N(4)−Y−N(5)	85.93(8)	96.99(8)
N(5)−Y−N(6)		71.11(8)
N(6)−Y−N(1)		93.67(8)
N(5)−Y−N(1)	119.43(8)	105.08(8)
O(1)−Y−N(2)	151.96(8)	

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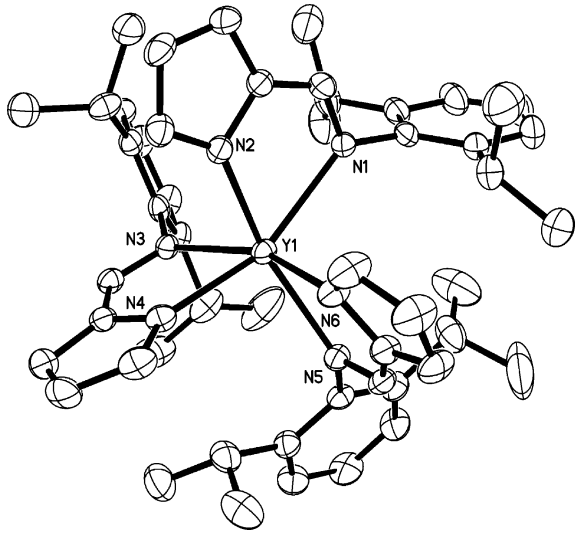
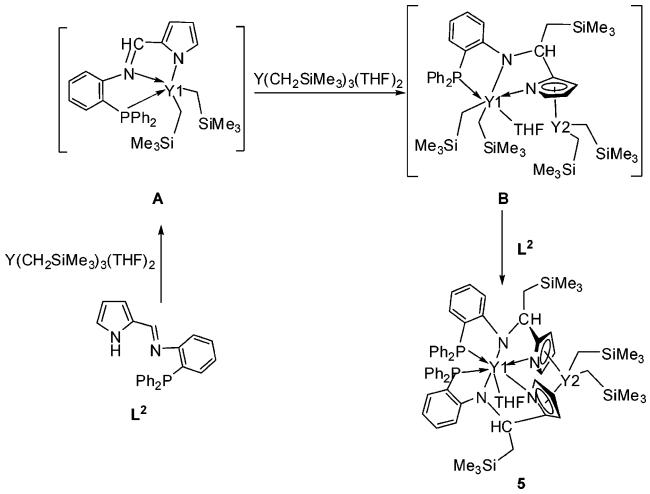


Figure 3. X-ray structure of **4** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 2 . Synthetic Pathway for Preparation of Complex 5



$Y(CH_2SiMe_3)_3(THF)_2$ at room temperature for 24 h (Scheme 1). Complex **4** was reported previously to be prepared by treatment of yttrium tris(amido) complex $Y\{N(SiMe_3)_2\}_3$ with 3 equiv of $\mathbf{L^1}$; however, no crystallographic information was provided.[5] We isolated single crystals of **4** and characterized its molecular structure by X-ray analysis, as shown in Figure 3. All three pyrrolide ligands coordinate to the yttrium in a η^1:κ^1-*N,N* bidentate mode. No coordination of THF is found. The bond lengths of $Y-N_{pyr}$ and $Y-N_{imino}$ are comparable to the corresponding ones found in complex **3** and do not need to be discussed further (Table 2).

Synthesis and Characterization of Complexes 5. The *N,N,P* tridentate ligand 2-{(N-2-diphenylphosphinophenyl)iminomethyl)}-pyrrole, $\mathbf{L^2}$, was prepared by condensation reaction of pyrrole-2-carboxyaldehyde with 2-diphenylphosphinophenylamine in the presence of a catalytic amount of formic acid. Treatment of $\mathbf{L^2}$ by equimolar $Y(CH_2SiMe_3)_3(THF)_2$ afforded yellow powders. Crystallization from a mixture of toluene and hexane gave yellow crystals of complex **5** in quantitative yield. The probable mechanistic pathway was described as Scheme 2. First, neutral ligand $\mathbf{L^2}$ protonates one metal alkyl species of $Y(CH_2SiMe_3)_3(THF)_2$ to give a bis(alkyl) intermediate **A**. Alkylation of the imino C═N group in **A** by the incoming $Y(CH_2SiMe_3)_3(THF)_2$ generates $C(H)(CH_2SiMe_3)N^-$ species attaching to Y(1), while the pyrrolyl ring η^5-coordinates to Y(2), to afford binuclear tetra-

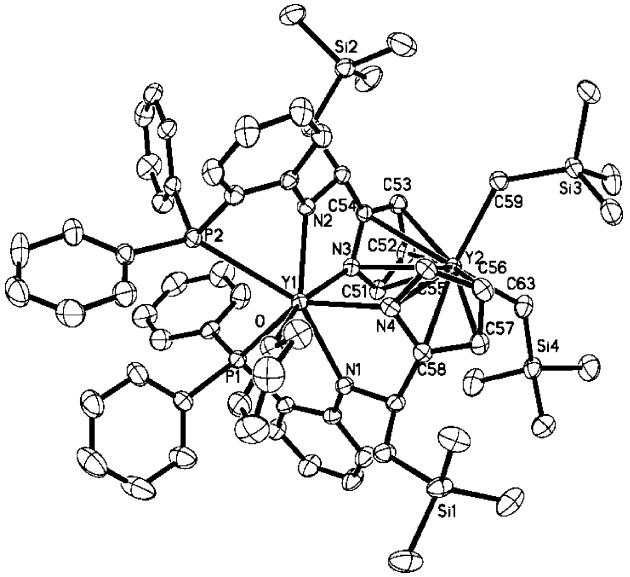


Figure 4. X-ray structure of **5** with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

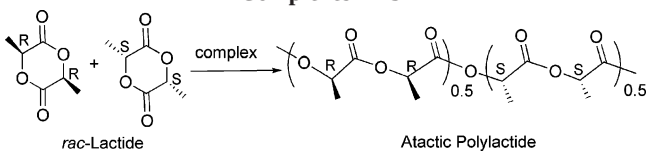
(alkyl) intermediate **B**. **B** reacts with another molecule of neutral ligand $\mathbf{L^2}$ to yield complex **5** via metal alkyl abstraction and intramolecular alkylation as described previously for the formation of **1** (Scheme 2). The ^{1}H NMR spectrum of complex **5** was complicated and difficult to assign until the resolution of the solid structure. The four discrete doublet−doublet signals in the upfield region δ −1.07 to −0.17 were attributed to the diastereotopic protons of the metal alkyls. The methylene protons of the newly formed $C(H)(CH_2SiMe_3)N$ species were also nonequivalent, giving separate resonances at δ 0.27, 0.77, and 1.67. This indicated the structurally asymmetric character of complex **5** in solution. Moreover, complex **5** belongs to the rare examples of bis(alkyl) complexes based on rare earth metals, as the highly active character of the two metal alkyls and the relatively less steric environment make the isolation of such complexes difficult.[23] The solid structure of complex **5** is far from those reported previously. For instance, a lutetium bis-(alkyl) complex bearing a monoanionic *N,N,N* tridentate anilido-pyridine-amido ligand is monomeric. The two alkyl moieties are arranged in *trans*-positions. The geometry about the metal center is described as twisted square pyramidal. The base of the pyramid is defined by the nitrogen atoms, which contribute to stabilize the complex,[20] while complex **5** is an asymmetric dimer (Figure 4). The two *N,N,P* tridentate pyrrolide ligands, bearing dianionic species, coordinate to Y(1) in a η^1:κ^2/η^1:κ^2 fashion along with a solvated THF moiety to generate seven-coordinate trigonal/pyramidal geometry around Y(1), whereas the pyrrolyl rings bond to Y(2) in a η^5/η^5 mode to form a reverse-sandwich geometry between the Y(1) and Y(2) atoms. The two alkyl moieties coordinate to Y(2) in *cis*-positions to the two pyrrolyl rings. The pyrrolyl rings and alkyl carbon atoms form an eight-coordinate tetrahedron geometry around Y(2). It seems at first glance that the Y(2) unit is a metallocene bis-(alkyl). In fact, it is noteworthy that one pyrrolyl ring coordinates to Y(2) as a neutral ligand, while another bears one negative charge. Thus, the resulting bond lengths formed by Y(2) with η^5-C and η^5-N of the two rings are different. The bond lengths of the C and N atoms of one pyrrolyl ring to the Y(2) ion are

(23) The first monocyclopentadienyl rare metal bis(alkyl) complexes were reported by Lappert 30 years ago; see: Lappert, M. F.; Pearce, R. *Chem. Commun.* **1973**, 126. Recently, rare earth alkyl complexes have demonstrated unique catalytic activities; see refs 9h,i.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 5

Y(1)−N(1)	2.419(4)	Y(1)−N(2)	2.292(4)
Y(1)−N(3)	2.369(4)	Y(1)−N(4)	2.359(5)
Y(1)−P(1)	2.8901(15)	Y(1)−P(2)	3.0289(15)
Y(2)−N(3)	2.632(4)	Y(2)−N(4)	2.701(4)
Y(2)−C(51)	2.686(5)	Y(2)−C(52)	2.795(5)
Y(2)−C(53)	2.792(6)	Y(2)−C(54)	2.692(5)
Y(2)−C(55)	2.690(5)	Y(2)−C(56)	2.726(6)
Y(2)−C(57)	2.738(6)	Y(2)−C(58)	2.731(5)
Y(2)−C(59)	2.402(5)	Y(2)−C(63)	2.381(6)
C(59)−Y(2)−C(63)	96.4(2)	Y(1)−N(3)−Y(2)	104.90(16)
N(4)−Y(1)−N(3)	81.39(15)		

Table 4. Ring-Opening Polymerization of D,L-Lactide by Complexes 1−5[a]



rac-Lactide Atactic Polylactide

entry	cat.	[LA]/[Ln]	solvent	conv (%)	M_{calcd} ($\times 10^4$)[b]	M_n ($\times 10^4$)[c]	PDI
1	**1**	300	THF	100	4.32	5.21	1.53
2	**2**	150	THF	100	2.16	2.21	1.31
3	**2**	300	THF	93	4.02	3.82	1.26
4	**2**	500	THF	91	6.56	5.31	1.18
5	**2**	800	THF	92	10.6	6.46	1.12
6	**2**	1000	THF	100	14.4	9.00	1.12
7	**2**	300	CH_2Cl_2	100	4.32	2.66	1.75
8	**2**	800	CH_2Cl_2	85	9.80	9.04	1.63
9	**3**	300	THF	96	4.15	3.32	1.56
10	**3**	800	THF	96	11.1	12.8	1.63
11	**4**	300	THF	trace	n.d.[d]	n.d.	n.d.
12	**5**	300	THF	93	4.02	2.44	1.49
13	**5**	800	THF	93	10.7	7.62	1.49

[a] General conditions: 20 °C, 1 h, [LA] = 1.0 mol/L. [b] M_{cal} = ([LA]/[Ln]) × 144.13 × X (X = conversion). [c] Measured by GPC calibrated with standard polystyrene samples. [d] n.d. = not determined.

unequal, varying in a wide range of 2.632(4)−2.795(5) Å (Table 3), which are comparable to those in **1**. Comparatively, the distances between Y(2) and the atoms N(4), C(55), C(56), C(57), and C(58) from the other pyrrolyl ring are uniform, varying within a narrow range from 2.690(5) to 2.738(6) Å. These bond distances are strongly reminiscent of those Dy−η^5-C(Cp ring), ranging from 2.638(2) to 2.704(3) Å) in complex ($C_5Me_4SiMe_3$)Dy(CH_2SiMe_3)$_2$(THF),[10e] suggesting that the pyrrolyl ring can be an ideal alternative to the cyclopentadienyl ancillary ligand. The bond distances between Y(1) and nitrogen atoms N(1), N(2), N(3), and N(4), averaging 2.360 Å, are comparable to Y−N (2.204(4)−2.449(5) Å) reported by Mashima.[5] The bond distances Y(2)−C(59) (2.402(5) Å) and Y(2)−C(63) (2.381(6) Å) and the corresponding bond angle C(59)−Y(2)−C(63) (96.4(2)°) have been found to be not obviously different from those in the previously reported yttrium bis(alkyl) complexes (Y−C, av 2.40 Å; C−Y−C, av 101.5°).[9h,10e,24]

Polymerization of D,L-Lactide Initiated by Complexes 1−5. Complexes **1**−**5** were used to initiate the ring-opening polymerizations (ROP) of D,L-lactide (D,L-LA), respectively. Representative results are summarized in Table 4. The polymerization initiated by complex **1** was carried out at room temperature smoothly to reach almost complete conversion in 1 h in THF media (Table 4, entry 1). However, the molecular weight distribution of the resultant polylactide (PLA) was relatively broad. This could be attributed to the mutual effects of the two metal alkyls upon the monomer approach and insertion during polymerization. Thus, although each metal center bears one reaction site (Y−σ-C), complex **1** was not a real "single-site" catalyst. When using complex **2** as initiator, high catalytic activity and much more controllable polymerization were found. The molecular weight of the resultant PLA increased with the increase of monomer-to-initiator ratio that was close to the theoretic value (calculated on the assumption that each metal alkyl initiates the polymerization). The deviation was obvious at ratios higher than 800. Nevertheless, in all cases the molecular weight distribution was very narrow over the entire monomer-to-initiator ratio range, indicating a single-site catalyst system (Table 4, entries 2−6). However, the polymerization performed in CH_2Cl_2 afforded PLA with a much broader molecular weight distribution (Table 4, entries 7, 8). This might be due to the coordination of CH_2Cl_2, which changed the steric environment and the Lewis acidity of the central metal, which was consistent with the previously reported bis(phenolate)yttrium amide system.[25] The amido complex **3** was comparable to its precursor **2** in terms of catalytic activity. Due to the above-mentioned reason, the polydispersity of the isolated PLA was broadened (Table 4, entries 9, 10).[25a] In contrast, no obvious polymerization at room temperature was observed by using homoleptic complex **4**, which might be due to the chelate Y−η^1-N initiator in **4** being less active than the Y−σ-C in **1** and **2** or Y−σ-N in **3** (Table 4, entry 11). Bis(alkyl) complex **5**, as expected, demonstrated to be as efficient an initiator as the mono(alkyl) counterparts. Also, it was not surprising that the resultant PLA had a lower molecular weight and broader molecular weight distribution, as both alkyl species participated in the initiation, resulting in multiple sites in the complex **5** system (Table 4, entries 12, 13).

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. ^{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 the ^{1}H−^{1}H COSY and ^{1}H−^{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 GPC Waters 410. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). 2,6-Diisopropylaniline was obtained from Aldrich and purified by distillation before use. Pyrrole-2-carboxyaldehyde and 2-diphenylphosphanylphenylamine were prepared according to the literature.[26,27]

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 −80 °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

(24) (a) Bambirra, S.; Boot, S. J.; Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 1898. (b) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3486. (c) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E. *Organometallics* **2003**, *22*, 1577.

(25) (a) Ma, H.; Okuda. J. *Macromolecules* **2005**, *38*, 2665. (b) Ma, H.; Spaniol, T.; Okuda, J. *Dalton Trans.* **2003**, 4770.

(26) David, M. W.; Leung, S. H.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1993**, *58*, 7245.

(27) (a) Dai, X.; Wong, A.; Virgil, S. C. *J. Org. Chem.* **1998**, *63*, 259. (b) Cooper, M. K. *Inorg. Synth.* **1989**, *25*, 129.

Table 5. Summary of Crystallographic Data for 1, 3, 4, and 5

	1·0.5C_6H_{14}	**3**·C_7H_8	**4**	**5**
formula	$C_{30.5}H_{47}N_2OSi_2Y$	$C_{57}H_{76}N_5OY$	$C_{51}H_{63}N_6Y$	$C_{66}H_{88}N_4OP_2Si_4Y_2$
cryst size, mm	0.25 × 0.19 × 0.09	0.33 × 0.24 × 0.15	0.26 × 0.23 × 0.16	0.47 × 0.23 × 0.18
fw	602.79	936.14	848.98	1305.52
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.1563(12)	11.5198(8)	11.6880(7)	20.3821(8)
b (Å)	20.818(2)	12.3059(9)	16.6699(10)	19.3542(7)
c (Å)	17.4417(19)	38.706(3)	24.4478(15)	22.0003(9)
α (deg)	90	90	90	90
β (deg)	99.432(2)	106.323(2)	100.5320(10)	116.1680(10)
γ (deg)	90	90	90	90
V (Å^3)	3638.0(7)	5265.9(7)	4683.1(5)	7789.1(5)
Z	4	4	4	4
D_{calcd} (g/cm^3)	1.101	1.181	1.204	1.113
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
$2\theta_{max}$, deg	52.14	52.14	52.12	52.06
μ (cm^{-1})	16.90	11.50	12.85	16.22
F(000)	1276	2000	1800	2736
no. of obsd reflns	7159	10 370	9231	15 283
no. of params refnd	353	590	535	724
GOF	0.974	0.975	0.965	1.092
R_1	0.0742	0.0508	0.0496	0.0602
wR_2	0.2064	0.1252	0.1128	0.2253

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 **1**, **3**, **4**, and **5** are summarized in Table 5.

2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_4$H$_3$NH (L^1). 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 **L^1** in 73.8% yield (3.75 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.12 (d, J_{H-H} = 6.9 Hz, 12H, CHMe_2), 3.06 (hepta, J_{H-H} = 6.9 Hz, 2H, CHMe$_2$), 6.20 (m, 1H, 3-pyr), 6.49 (s, 1H, 4-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, CHMe_3), 28.35 (2C, CHMe$_3$), 110.31 (1C, 4-pyr), 117.14 (1C, 3-pyr), 123.65 (1C, 5-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-(2-Ph$_2$PC$_6$H$_4$N═CH)C$_4$H$_3$NH (L^2). To a dried MeOH solution (15 mL) of pyrrole-2-carboxyaldehyde (0.34 g, 3.6 mmol) were added 2-diphenylphosphinophenylamine (1.00 g, 3.6 mmol) and a catalytic amount of formic acid (0.25 mL) under stirring. The reaction mixture was stirred for 24 h at 40 °C. The viscous oil residues were isolated after driving off the solvent under reduced pressure. Recrystallization from ethyl ether yielded **L^2** as colorless crystals in 35% yield (0.45 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.12 (m, 1H, 3-pyr), 6.50 (s, 1H, 4-pyr), 6.67 (dd, 1H, J_{H-H} = 7.4 Hz, C_6H_4), 6.96 (s, 1H, 5-pyr), 7.02−7.06 (dd, 1H, J_{H-H} = 7.4 Hz, C_6H_4), 7.11(t, 1H, J_{H-H} = 7.4 Hz, C_6H_4), 7.14−7.19 (m, 4H, *o*-C_6H_5), 7.32−7.34 (m, 6H, *m*,*p*-C_6H_5), 7.40 (t, 1H, J_{H-H} = 7.4 Hz, C_6H_4), 7.97 (s, 1H, N═C−H), 11.35 ppm (s, 1H, N−H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 110.65 (1C, 4-pyr), 116.23 (1C, 3-pyr), 117.38 (1C, 5-pyr), 123.18 (1C, *ipso*-PC_6H_4), 125.91 (2C, *m*−PC_6H_4), 128.80 (6C, *m*,*p*-C_6H_5), 130.23 (1C, *p*-PC_6H_4), 132.07 (1C, *ipso*-pyr), 133.12 (1C, *o*-PC_6H_4), 134.40, 134.66 (6C, *o*,*ipso*-C_6H_5), 137.76 (1C, *ipso*-NC_6H_4), 148.67 ppm (1C, N═CH). IR (KBr pellets): ν 3241, 3070, 3049, 2896, 1620, 1575, 1560, 1478, 1463, 1433, 1418, 1339, 1311, 1264, 1198, 1159, 1128, 1093, 1062, 1033, 999, 970, 942, 880, 853, 816, 786, 741, 693, 602, 586, 521, 503, 492, 476, 435, 407 cm^{-1}. Anal. Calcd for $C_{23}H_{19}N_2P$ (%): C, 77.95; H, 5.40; N, 7.90. Found: C, 77.90; H, 5.07; N, 7.76.

{[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)}$_2$ (1). To a toluene solution (5.0 mL) of Y(CH$_2$SiMe$_3$)$_3$-(THF)$_2$ (0.383 g, 0.775 mmol) was added dropwise equivalent **L^1** (0.197 g, 0.776 mmol in 2 mL of toluene) at room temperature. The mixture was then stirred for 24 h. Removal of the volatiles gave a deep yellowish, oily residue. The residue was dissolved with 3 mL of hexane and then cooled to −30 °C for 12 h to give yellow solids. The solids were washed carefully by a small amount of hexane (0.5 mL) and then dried in vacuum to afford complex **1** in 55% yield (0.257 g). Colorless single crystals for X-ray analysis grew from a mixture of toluene and hexane at −30 °C within a week. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.42 (m, 4H, Y−CH_2-SiMe$_3$), 0.32 (s, 18H, Y−CH$_2$SiMe_3), 0.51 (s, 18H, CH−CH$_2$-SiMe_3), 0.95 (m, 1H, CH−CH_2SiMe$_3$), 1.35 (br, 8H, THF), 1.38 (d, J_{H-H} = 8.0 Hz, 6H, CHMe_2), 1.41 (m, 2H, CH−CH_2SiMe$_3$), 1.45 (d, J_{H-H} = 8.0 Hz, 6H, CHMe_2), 1.63 (d, J_{H-H} = 8.0 Hz, 6H, CHMe_2), 1.70 (d, J_{H-H} = 8.0 Hz, 1H, CH−CH_2SiMe$_3$), 1.77 (d, J_{H-H} = 8.0 Hz, 6H, CHMe_2), 3.38 (br, 8H, THF), 4.30 (m, 4H, CHMe$_2$), 4.61 (m, 1H, CH−CH$_2$SiMe$_3$), 5.69 (d, J_{H-H} = 8.0 Hz, 1H, CH−CH$_2$SiMe$_3$), 6.25 (s, 2H, 4-pyr), 6.68 (s, 2H, 3-pyr), 7.16 (m, 6H, C_6H_3), 7.82 ppm (s, 2H, 5-pyr). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 1.62 (s, 6C, CH−CH$_2$SiMe_3), 5.36 (s, 6C, Y−CH$_2$SiMe_3), 25.61 (br, 4C, THF), 25.81, 25.96, 26.48, 27.38 (s, 8C, CHMe_2), 26.64, 26.90, 27.74, 28.33 (s, 4C, CHMe$_2$), 27.94 (s, 2C, CH−CH$_2$SiMe$_3$), 28.60 (s, 2C, Y−CH$_2$SiMe$_3$), 64.44, 64.82 (s, 2C, CH−CH$_2$SiMe$_3$), 70.13 (s, 4C, THF), 108.24 (s, 2C, 3-pyr), 114.30 (s, 2C, 4-pyr), 123.74 (s, 2C, 5-pyr), 124.75 (s, 4C, *m*-C_6H_3), 125.25 (s, 2C, *p*-C_6H_3), 148.69, 148.88 (s, 4C, *o*-C_6H_3), 150.00 (s, 2C, *ipso*-pyr), 158.61 ppm (s, 2C, *ipso*-C_6H_3). IR (KBr pellets): ν 2960, 2869, 1579, 1460, 1424, 1382, 1362, 1321, 1297, 1248, 1232, 1191, 1106, 1036, 1016, 861, 804, 780, 742, 712, 619 cm^{-1}. Anal. Calcd for $C_{61}H_{94}N_4O_2Si_4Y_2$ (%): C, 60.77; H, 7.86; N, 9.29. Found: C, 60.22; H, 7.23; N, 9.50.

[2-(2,6-^{i}Pr$_2$C$_6$H$_3$N═CH)C$_4$H$_3$N]$_2$Y(CH$_2$SiMe$_3$)(THF) (2). Following a procedure similar to that described for the preparation of **1**, treatment of a toluene solution (5.0 mL) of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.283 g, 0.572 mmol) with 2 equiv of **L^1** (0.294 g, 1.148 mmol in 2 mL of toluene) afforded complex **2** (0.355 g, 82.3%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.52 (s, 2H, CH_2SiMe$_3$), 0.18 (s,

9H, CH_2SiMe_3), 1.12 (s, 6H, $CHMe_2$), 1.14 (s, 6H, $CHMe_2$), 1.20 (s, 12H, $CHMe_2$), 1.34 (s, 4H, THF), 3.14 (br, 4H, $CHMe_2$), 3.81 (s, 4H, THF), 6.54 (s, 2H, 3-pyr), 6.92 (s, 2H, 4-pyr), 7.06 (s, 2H, 5-pyr), 7.16 (b, 6H, *m,p*-C_6H_3), 7.82 ppm (s, 2H, N=C−*H*). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.80 (3C, $SiMe_3$), 23.17 (1C, $CHMe_2$), 23.60 (2C, $CHMe_2$), 25.98 (2C, $CHMe_2$), 26.32 (1C, $CHMe_2$), 26.64 (2C, THF), 26.64 (2C, $CHMe_2$), 28.76 (1C, $CHMe_2$), 29.04 (2C, $CHMe_2$), 29.32 (1C, $CHMe_2$), 34.63 (d, J_{Y-C} = 39.3 Hz, 1C, CH_2SiMe_3), 71.37 (2C, THF), 113.73 (4C, 3,4-pyr), 123.23 (2C, 5-pyr), 124.21 (4C, *m*-C_6H_3), 126.76 (2C, *p*-C_6H_3), 137.40 (2C, *ipso*-pyr), 138.83 (2C, *o*-C_6H_3), 142.36 (2C, *o*-C_6H_3), 148.27 (2C, *ipso*-C_6H_3), 164.48 ppm (2C, N=*C*H). IR (KBr pellets): ν 2961, 2868, 1627, 1577, 1443, 1392, 1301, 1171, 1036, 981, 861, 747 cm^{-1}. Anal. Calcd for $C_{42}H_{61}N_4OSiY$ (%): C, 66.82; H, 8.14; N, 7.42. Found: C, 66.57; H, 8.25; N, 7.24.

[2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_2$Y(NH-C$_6$H$_3$-^{i}Pr$_2$-2,6)(THF) (3). Reaction of complex **2** (0.306 g, 0.405 mmol) and 2,6-diisopropylaniline (0.0071 g, 0.400 mmol) in toluene (7 mL) at room temperature took place immediately upon addition. The reaction mixture was kept stirring for 6 h. The volatiles were removed under reduced pressure to leave a brown residue, which was dissolved with hexane (3 mL) and then cooled to −30 °C. After 12 h, crystalline solids precipitated on the bottom of the flask. The solids were separated by filtration and washed with a small amount of hexane (3 × 0.5 mL) and then dried in vacuum to afford yellow crystals of **3** (0.274 g, 80.3%). Recrystallization from toluene at −30 °C for a couple of days gave crystals suitable for X-ray analysis. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.79−1.39 (m, 36H, $CHMe_2$), 1.20 (br, 4H, THF), 2.63−2.71 (m, 2H, $CHMe_2$), 2.72−2.79 (m, 2H, $CHMe_2$), 3.13−3.17 (m, 1H, $CHMe_2$), 3.50−3.53 (m, 1H, $CHMe_2$), 3.73, 3.98 (br, 4H, THF), 4.78 (s, 1H, N*H*), 6.40 (s, 1H, 3-pyr), 6.65 (s, 1H, 3-pyr), 6.78 (s, 1H, 4-pyr), 6.80 (d, J_{H-H} = 3.2 Hz, 1H, 4-pyr), 6.89 (d, J_{H-H} = 7.6 Hz, 1H, 5-pyr), 7.05 (d, J_{H-H} = 3.6 Hz, 1H, 5-pyr), 7.10−7.32 (m, 9H, *m, p*-C_6H_3), 7.66 (s, 1H, C*H*=N), 7.88 (s, 1H, C*H*=N). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 22.54, 23.05, 23.30, 23.60, 23.89, 24.17, 24.51, 25.50, 26.61, 26.90, 27.20, 27.61 (12C, $CHMe_2$), 28.27 (1C, $CHMe_2$), 28.62 (2C, $CHMe_2$), 29.03, 29.60, 33.37 (3C, $CHMe_2$), 25.94 (2C, THF), 72.83 (2C, THF), 113.33, 113.64 (2C, 3-pyr), 116.04, 119.39 (2C, 4-pyr), 122.81, 123.02 (2C, 5-pyr), 123.36, 124.38 (2C, *p*-NC_6H_4), 123.57, 124.79 (4C, *m*-NC_6H_4), 126.87 (3C, *m,p*-NHC_6H_4), 132.75, 133.02, 134.82, 137.79, 140.81, 142.14 (6C, *o*-C_6H_4), 137.07, 140.34 (2C, *ipso*-pyr), 148.12, 148.77 (2C, *ipso*-NC_6H_4), 152.60 (1C, *ipso*-NHC_6H_4), 164.12, 164.94 ppm (2C, *C*H=N). IR (KBr pellets): ν 3678, 3231, 3064, 2962, 2868, 1627, 1596, 1578, 1461, 1391, 1340, 1302, 1257, 1171, 1091, 1035, 981, 883, 782, 746 cm^{-1}. Anal. Calcd for $C_{57}H_{76}N_5OY$ (%): C, 73.13; H, 8.18; N, 7.48. Found: C, 73.37; H, 8.29; N, 7.58.

Y[2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_3$ (4). To a toluene solution (3.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.192 g, 0.386 mmol) was added dropwise 3 equiv of **L^1** (0.295 g, 1.160 mmol in 2 mL of toluene) under stirring. The mixture was reacted for 24 h at room temperature, then the volatiles were removed under reduced pressure. The residue was dissolved with 3 mL of hexane. The hexane solution was cooled to −30 °C and kept at this temperature overnight to afford white solids deposited on the bottom of the flask. The solids were collected by filtration and then dried under reduced pressure to generate **4** as a white powder (0.263 g, 80.2%). Colorless crystals for X-ray analysis grew from the mixture of toluene and hexane at −30 °C within several days. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.68 (d, J_{H-H} = 6.8 Hz, 9H, $CHMe_2$), 0.96, 0.97, 0.99, 1.01, 1.02 (m, 27H, $CHMe_2$), 2.52 (hepta, J_{H-H} = 6.8 Hz, 3H, $CHMe_2$), 2.91 (hepta, J_{H-H} = 6.8 Hz, 3H, $CHMe_2$), 6.46, 6.47 (dd, J_{H-H} = 3.6 Hz, 3H, 4-pyr), 6.91 (d, J_{H-H} = 3.6 Hz, 3H, 3-pyr), 6.96 (s, 3H, 5-pyr), 7.05 (m, 3H, *p*-C_6H_3), 7.13 (m, 6H, *m*-C_6H_3), 7.69 ppm (s, 3H, N=CH). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 23.18, 23.69, 26.33, 26.69 (12C, $CHMe_2$), 28.75, 29.31 (6C, $CHMe_2$), 114.24 (3C, 4-pyr), 123.96 (3C, 3-pyr), 124.21 (3C, 5-pyr), 124.71 (3C, *m*-C_6H_3), 126.82 (3C, *p*-C_6H_3), 137.08 (3C, *ipso*-pyr), 140.80 (3C, *m*-C_6H_3), 142.14 (3C, *o*-C_6H_3), 143.55 (3C, *o*-C_6H_3), 147.66 (3C, *ipso*-C_6H_3), 164.83 ppm (3C, N=*C*H). IR (KBr): ν 3585, 2964, 2867, 1627, 1595, 1573, 1490, 1389, 1291, 1170, 1035, 981, 749 cm^{-1}. Anal. Calcd for $C_{51}H_{63}N_6Y$ (%): C, 72.15; H, 7.48; N, 9.90. Found: C, 71.68; H, 7.22; N, 10.35.

[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) (5). To a stirred solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.206 g, 0.416 mmol) in 4.0 mL of toluene was added dropwise **L^2** (0.147 g, 0.414 mmol) in 2 mL of toluene. After stirring for 12 h at room temperature, the solvent was stripped off and 3 mL of hexane was added. The mixture was then cooled to −30 °C and kept at this temperature overnight to afford reddish-yellow solids, which were washed with a small amount of hexane to remove impurities and then dried in vacuum to afford **5** as a yellow powder in 40.5% yield (0.11 g). Suitable yellow crystals for X-ray analysis grew from a mixture of toluene/hexane at −30 °C in a week. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −1.07 (dd, J_{Y-C-H} = 12.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H, Y−C*H*$_2$SiMe$_3$), −0.60 (dd, J_{Y-C-H} = 12.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H, Y−C*H*$_2$SiMe$_3$), −0.25 (dd, J_{Y-C-H} = 12.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H, Y−C*H*$_2$SiMe$_3$), −0.17 (dd, J_{Y-C-H} = 12.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H, Y−C*H*$_2$SiMe$_3$), 0.20 (s, 9H, CH−CH$_2$Si*Me*$_3$), 0.27 (m, 1H, CH−C*H*$_2$SiMe$_3$), 0.43 (s, 9H, Y−CH$_2$Si*Me*$_3$), 0.47 (s, 9H, CH−CH$_2$Si*Me*$_3$), 0.61 (s, 9H, Y−CH$_2$Si*Me*$_3$), 0.77 (m, 1H, CH−C*H*$_2$SiMe$_3$), 1.09 (br, 4H, THF), 1.67 (m, 2H, CH−C*H*$_2$SiMe$_3$), 3.53 (br, 4H, THF), 5.11 (d, J_{H-H} = 8.0 Hz, 1H, C*H*−CH$_2$SiMe$_3$), 5.65 (d, J_{H-H} = 8.0 Hz, 1H, C*H*−CH$_2$SiMe$_3$), 6.35 (s, 1H, 4-pyr), 6.55 (t, J_{H-H} = 7.2 Hz, 1H, *m*-PC$_6$H$_4$), 6.62 (t, J_{H-H} = 7.2 Hz, 1H, *m*-PC$_6$H$_4$), 6.67 (s, 1H, 3-pyr), 6.70 (d, J_{H-H} = 7.2 Hz, 1H, *o*-PC$_6$H$_4$), 6.76 (s, 1H, 4-pyr), 6.81 (m, 1H, *o*-PPh$_2$), 6.83 (s, 1H, 5-pyr), 6.98 (t, J_{H-H} = 8.0 Hz, 2H, *m*-PPh$_2$), 7.04−7.18 (m, 1H, 3-pyr, 1H, 4-pyr, 11H, PPh$_2$), 7.22 (t, J_{H-H} = 7.6 Hz, 4H, *p*-PPh$_2$), 7.30 (m, 1H, *o*-PC$_6$H$_4$), 7.39 (t, J_{H-H} = 8.0 Hz, 2H, *m*-PPh$_2$), 7.44−7.49 (m, 2H, *m*-NC$_6$H$_4$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 0.87, 1.14 (s, 6C, CH−CH$_2$Si*Me*$_3$), 4.94, 5.14 (s, 6C, Y−CH$_2$-Si*Me*$_3$), 25.41 (br, 2C, THF), 26.09 (s, 1C, CH−*C*H$_2$SiMe$_3$), 28.42 (d, J_{Y-C} = 41.1 Hz, 1C, Y−*C*H$_2$SiMe$_3$), 29.39 (d, J_{Y-C} = 40.3 Hz, 1C, Y−*C*H$_2$SiMe$_3$), 31.08 (s, 1C, CH−*C*H$_2$SiMe$_3$), 56.43, 58.07 (s, 2C, *C*H−CH$_2$SiMe$_3$), 70.77 (br, 2C, THF), 110.78, 111.37 (s, 2C, 3-pyr), 114.19 (d, J = 6.0 Hz, 2C, *o*-NC$_6$H$_4$), 115.13 (d, J = 6.0 Hz, 2C, *m*-PC$_6$H$_4$), 116.82, 117.15 (s, 2C, 4-pyr), 122.96, 124.49 (s, 2C, *ipso*-PC$_6$H$_4$), 128.97−129.96 (m, 14C, *p*-PC$_6$H$_4$, *m,p*-C$_6$H$_5$), 133.77−135.35 (m, 14C, *o*-PC$_6$H$_4$, *o,ipso*-C$_6$H$_5$), 130.63, 130.83 (s, 2C, 5-pyr), 134.46, 134.90 (s, 2C, *ipso*-pyr), 151.70 ppm (d, J = 32 Hz, 2C, *ipso*-NC$_6$H$_4$). IR (KBr pellets): ν 3054, 2950, 2891, 1575, 1480, 1450, 1434, 1285, 1248, 1166, 1129, 1095, 1034, 861, 786, 743, 695 cm^{-1}. Anal. Calcd for $C_{66}H_{88}N_4OP_2Si_4Y_2$ (%): C, 60.72; H, 6.79; N, 4.29. Found: C, 60.37; H, 6.65; N, 4.30.

Polymerization of D,L-Lactide. A typical procedure for polymerization of D,L-LA was performed in a 25 mL round-bottom flask in a glovebox. To a stirred solution of D,L-LA (0.572 g, 3.97 mmol) in 3.0 mL of THF was added a THF solution (1.0 mL) of complex **2** (0.010 g, 0.0132 mmol, [LA]/[Cat] = 300:1). The reaction mixture was stirred for 1 h at room temperature and then was terminated by 1.0 mL of a mixture of HCl/CH_3OH/$CHCl_3$ (1:100:600 v/v). The viscous solution was quenched by ethanol (1:6 v/v) to give white solids, which were filtered, washed with ethanol, and then dried at 40 °C for 24 h in vacuo to give PLA (0.534 g, 93.3%). The molecular weight and the molecular weight distribution of the resulting polymer were determined by GPC. The tacticity of the PLA was calculated according to the methine region homonuclear decoupling ^{1}H NMR spectrum.

Conclusion

We have demonstrated a synthetic pathway for preparing a series of pyrrolide-stabilized yttrium mono- or bis-alkyl and

homoleptic complexes by treatment of rare earth metal tris(alkyl)s with neutral pyrrolide compounds. The amido derivative was isolated by amination of the corresponding alkyl complex with aniline. The protonolysis reaction along with intra- or intermolecular alkylation of the C═N bond of the ligands was observed in the process. The molecular structures and the coordination mode of the ligand are strongly dependent on ligand frameworks and reaction conditions. Complexes **1** and **5** represent rare examples of rare earth metal alkyl complexes stabilized by pyrrolide species in η^5-coordination mode, indicating that the pyrrolyl ring is an alternative to heterocyclopentadiene under certain conditions. All complexes except **4** are highly efficient initiators for controllable polymerization of D,L-LA to afford atactic polylactide with high molecular weight and narrow molecular weight distribution.

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Supporting Information Available: CIF files and crystallographic data for **1**, **3**, **4**, and **5** including atomic coordinates, full bond distances and bond angles, and anisotropic thermal parameters, as well as GPC curves of the PLA samples are available free of charge via the Internet at http://pubs.acs.org.

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