ORGANOMETALLICS

Preparation and Structure of Iminopyrrolyl and Amidopyrrolyl Complexes of Group 2 Metals

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Supporting Information

ABSTRACT: Reactions of *N*-aryliminopyrrolyl ligand **1a**, 2-(2,6-ⁱPr₂C₆H₃N=CH)-C₄H₃NH (Imp^{Dipp}-H), with dibenzylcalcium gave two types of pyrrolylcalcium complexes, bis(iminopyrrolyl)calcium (**2a**) and (amidopyrrolyl)calcium (**3a**), via alkane elimination and ligand alkylation reaction,



respectively. Preparation of a mono(iminopyrrolyl) complex, (iminopyrrolyl)Ca[N(SiMe_3)_2](THF)_2 (4a), was accomplished by the addition of 1 equiv of 1a to Ca[N(SiMe_3)_2]_2(THF)_2. A series of group 2 metal bis(iminopyrrolyl) complexes, $[(Imp^{Dipp})_2M(THF)_3]$ (M = Sr (5a), Ba, (6a)) and $[(Imp^{Me})_2Ca(THF)_2]$ (2b) (2-(4-MeC_6H_4N=CCH_3)-C_4H_3NH (Imp^{Me}-H)), was selectively prepared via amine elimination reactions, and their molecular structures were clarified by X-ray diffraction studies.

INTRODUCTION

Alkaline-earth metal compounds have attracted recent interest because of their catalytic applications to ring-opening polymer-ization of cyclic esters,^{1,2} polymerization of styrene and dienes,³ and hydroamination and hydrophosphination reactions of alkenes and alkynes.⁴ Determining the structure and reactivity of alkaline-earth metal species is an important step toward the design and development of efficient catalysts; however, full realization of the catalytic potential of these elements still requires substantial advances in understanding their basic coordination and organometallic chemistry. To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates, 2e,g,5 aminotrop(on)iminates, $^{6}\beta$ -diketiminates, 2f,7 and bis(imino)pyrroles,⁸ have been introduced to prepare welldefined alkaline-earth metal complexes. We and others are interested in synthetic studies of bidentate and tridentate iminopyrrolyl ligands for early transition metals,9 rare-earth metals,^{8,10} and main group elements.¹¹ Iminopyrrolyl ligands were introduced to the metal center through not only deprotonation reaction of the acidic pyrrolyl proton but also alkylation reaction of the imine moiety by using alkylmetal precursors.^{9d,i,10g} Roesky et al. recently reported the preparation of heavier alkaline-earth metal complexes of tridentate 2,5-bis(imino)pyrrolyl ligands, as efficient catalysts for intramolecular hydroamination reactions,⁸ and iminopyrrolyl complexes of magnesium through deprotonation reaction.¹¹ Few studies have explored the coordination behavior and chemical reactions of iminopyrrolyl complexes of alkaline-earth metals other than magnesium. Herein, we report the synthesis and characterization of heavier alkaline-earth metal complexes

supported by bidentate iminopyrrolyl ligands. Ligand alkylation and deprotonation reactions using $Ca(CH_2Ph)_2(THF)_{0.5}$ as the precursor led to the formation of (amidopyrrolyl)- and bis(iminopyrrolyl)calcium complexes. A mono(iminopyrrolyl) complex was prepared from $Ca[N(SiMe_3)_2]_2(THF)_2$ and 1 equiv of the *N*-aryliminopyrrolyl ligand. We also prepared bis(iminopyrrolyl) complexes of strontium and barium by the amine elimination reaction of $M[N(SiMe_3)_2]_2(THF)_3$ (M = Sr, Ba) with 2 equiv of the *N*-aryliminopyrrolyl ligand. Effects of ionic radii of the alkaline-earth metals on the coordination number of bis(iminopyrolyl)metal complexes were clarified by X-ray diffraction studies.

RESULTS AND DISCUSSION

We have continuously studied the complexation reaction of imine-based ligands to alkylmetal precursors;¹² for example, when tetrabenzylzirconium was treated with iminopyrrolyl ligands, an alkyl migration reaction was observed.⁹¹ We thus used Ca(CH₂Ph)₂(THF)_{0.5} as an entry for preparing heavier alkaline-earth metal complexes with iminopyrrolyl ligands. Treatment of Ca(CH₂Ph)₂(THF)_{0.5} with 1 equiv of bulky iminopyrrolyl ligand **1a** resulted in the formation of two types of calcium complexes, mononuclear bis(iminopyrrolyl)calcium complex **2a** and dinuclear (amidopyrrolyl)calcium complex **3a**. By monitoring the complexation reaction in the ¹H NMR spectrum, we observed the resonances corresponding to the complexes **2a** and **3a** in a 1:1.6 ratio; a toluene elimination reaction smoothly proceeded to afford **2a**, while a benzyl

Received: December 5, 2011 Published: March 14, 2012

migration to the imine moiety of the ligand gave 3a (eq 1). Aiming at preparing (amidopyrrolyl)calcium complex 3a in a



selective manner, we conducted a slow addition of ligand 1a to the solution of $Ca(CH_2Ph)_2(THF)_{0.5}$ at low temperature; however, both complexes 2a and 3a were formed in all runs examined. Finally, complex 3a was isolated by washing with pentane and THF followed by crystallization and was fully characterized by ¹H and ¹³C NMR spectroscopy. Noteworthy was that three correlating resonances in THF- d_{8} , determined by the ¹H, ¹H-COSY spectrum, were observed at δ 2.31, 2.81, and 4.13, assignable to the PhCH₂CH moiety in the benzylated ligand backbone. Three broad signals for the dissymmetric pyrrolyl moiety appeared at δ 6.5, 5.5, and 4.8, and the signals were observed in a higher magnetic field than those of 2a due to the η^5 -coordination of the pyrrolyl ring to the calcium atom. Similar intramolecular alkylation of iminopyrrolyl ligands by alkylmetal precursors of group 3 and 4 metals was noted previously.^{9i,10g} The connectivity and nuclearity of **3a** as shown in eq 1 are supported by an X-ray diffraction study, the quality of which is unfortunately too low for publication. Some examples of the μ - η^1 : η^5 -coordination mode of the pyrrolyl ring bridging two metal centers have been reported to date.^{10g,13,14}

In contrast to the alkane elimination reaction, amine elimination reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 equiv of 1a resulted in the formation of mono(iminopyrrolyl)calcium complex 4a, and a ligand amination reaction was not observed in this case (Scheme 1). In the ¹H NMR spectrum of 4a, a singlet resonance due to the bis(trimethylsilyl)amido group was observed at δ 0.23. On the other hand, addition of 2 equiv of 1a to $Ca[N(SiMe_3)_2]_2(THF)_2$ resulted in the selective formation of bis(iminopyrrolyl)calcium complex 2a. In the ¹H NMR spectrum of 2a, one singlet resonance assignable to the imine moiety was observed at δ 7.90, indicating a symmetric structure in solution. The molecular structures of 2a and 4a were clarified by X-ray diffraction studies (both complexes depicted in Figure 1), and bond distances and angles are listed in Table 1. The calcium center of 2a adopts a six-coordinated distorted octahedral geometry surrounded by two chelating iminopyrrolyl ligands and two cis-arranged THF molecules. The bond distances of Ca-N^{pyr} (Ca-N1, 2.422(2) Å; Ca-N3, 2.393(2) Å) are shorter than those of Ca-N^{imine} (Ca-N2, 2.526(2) Å; Ca-N4, 2.534(2) Å). The bond lengths of Ca-O (Ca-O1, 2.389(2) Å; Ca-O2, 2.411(2) Å) are in the range of normal Ca-O bonds.¹⁵ The pyrrolyl nitrogen atoms are oriented mutually *cis* with an N1-Ca-N3 angle of 100.18(8)°, and the imine nitrogen atoms occupy the trans positions (N2-Ca-N4, $177.91(7)^{\circ}$). The calcium complex 4a has a five-coordinated



Figure 1. Molecular structures of complexes (a) 2a and (b) 4a with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1. Bond D	Distances (Å) and A	angles (deg) of
(Iminopyrrolyl)c	calcium Complexes	2a and 4a

	2	a	
Ca-N1	2.422(2)	Ca-N2	2.526(2)
Ca-N3	2.393(2)	Ca-N4	2.534(2)
Ca-O1	2.389(2)	Ca-O2	2.411(2)
N1-Ca-N2	72.38(7)	N1-Ca-N3	100.18(8)
N2-Ca-N4	177.91(7)	O1-Ca-O2	89.29(7)
	4	a	
Ca-N1	2.388(2)	Ca-N2	2.467(2)
Ca-N3	2.312(2)	Ca-O1	2.3890(18)
Ca-O2	2.4040(18)		
N1-Ca-N2	72.93(7)	N1-Ca-N3	147.59(8)
N2-Ca-N3	139.48(7)	O1-Ca-O2	170.88(7)
Ca-N3-Si1	117.05(11)	Ca-N3-Si2	111.31(11)

distorted trigonal-bipyramidal geometry with one iminopyrrolyl ligand, one bis(trimethylsilyl)amido ligand, and two THF located at the axial position. The bond distances of Ca $-N^{amido}$ (2.312(2) Å) are shorter than that of Ca $-N^{pyr}$ (2.388(2) Å) due to the effective donation of the nitrogen lone pair to the Lewis acidic metal center.

With the selective formation of calcium complexes 2a and 4a in hand, we carried out the preparation of bis(iminopyrrolyl) complexes of strontium (5a) and barium (6a) via an amine

Scheme 1. Preparation of Mono- and Bis(iminopyrrolyl) calcium Complexes



elimination method as outlined in eq 2. Treatment of $M[N(SiMe_3)_2]_2(THF)_3$ (M = Sr, Ba) with 2 equiv of



iminopyrrolyl ligand 1a in toluene at 90 °C gave bis(iminopyrrolyl) complexes 5a and 6a in 89% and 92% yield, respectively. The ¹H NMR spectra of both complexes revealed one set of resonances corresponding to the iminopyrrolyl ligands, but no signal due to the bis(trimethylsilyl)amido groups attached to the metal center was observed, suggesting the complete elimination of 2 equiv of HN(SiMe₃)₂. Notably, the corresponding mono(iminopyrrolyl) complex, (Imp^{Dipp})Ba[N- $(SiMe_3)_2$, was not detected in the ¹H NMR spectrum, probably due to the increased basicity of the bis(trimethylsilyl)amido group bound to the barium atom after introducing one iminopyrrolyl ligand and facial approach of a second iminopyrrolyl ligand to the larger central metal compared with the calcium atom. Both complexes 5a and 6a were characterized spectroscopically as well as by combustion analysis. Furthermore, we prepared magnesium complex 7a, (Imp^{Dipp}),Mg-(THF), via an alkane elimination reaction of $Mg(CH_2Ph)_2$ with 2 equiv of 1a (eq 2), according to the synthetic route of bis(iminopyrrolyl)magnesium complexes reported by Roesky et al.¹¹ In contrast to the reaction in eq 1, we did not detect any ligand-alkylated product from the reaction mixture.

The molecular structures of bis(iminopyrrolyl) complexes 5a-7a were determined by single-crystal X-ray diffraction studies and are depicted in Figure 2. Selected bond distances and angles of 5a-7a are summarized in Table 2. The metal centers of strontium complex 5a and barium complex 6a are coordinated by two chelating iminopyrrolyl ligands and three THF molecules, adopting a seven-coordinated distorted pentagonal bipyramidal geometry. Two nitrogen atoms of the imine group are located at the axial site (N2–Sr–N2*, $178.20(9)^{\circ}$; N2–Ba–N2*, $178.27(19)^{\circ}$), while two pyrrolyl nitrogen atoms and three THF molecules occupy the equatorial sites. The bond distances of M–N^{pyr} (Sr–N1, 2.651(2) Å; Ba–N1, 2.821(5) Å) are almost the same as those of M–N^{imine}

(Sr–N2, 2.6691(19) Å; Ba–N2, 2.823(4) Å). The elongation of the metal–nitrogen covalent bond is probably due to steric crowding of the equatorial plane.^{7a,c,8,16}

In contrast to the heavier group 2 metal complexes, magnesium complex 7a has a five-coordinated distorted square-pyramidal geometry surrounded by two iminopyrrolyl ligands at the basal plane of the square pyramid and one THF located at the axial position. The magnesium atom is located 0.526 Å above the basal plane containing the N1, N2, N3, and N4 atoms. The low coordination number of 7a is ascribed to the smaller ionic radius of the magnesium atom and the bulkiness of the 2,6-diisopropylphenyl group, which occupies the opposite side of the THF molecule.

When the less bulky iminopyrrolyl ligand **1b** was introduced to the smaller group 2 metals, i.e., calcium and magnesium, by the amine or alkane elimination procedures (eq 3), we obtained



bis(iminopyrrolyl) complexes 2b and 7b, both of which contained 2 equiv of THF, as confirmed by their ¹H NMR spectra.

The molecular structures of **2b** and **7b** were also clarified by X-ray diffraction studies to reveal that both complexes are isostructural. Figure 3 shows the structure of **2b**, while the structure of **7b** is shown in the Supporting Information. Selected geometries of **2b** and **7b** are listed in Table 3. The metal center has a six-coordinated octahedral geometry with two pyrrolyl nitrogen atoms, imine nitrogen atoms, and two oxygen atoms *trans* to each other. In contrast to **2a**, the two chelating iminopyrrolyl moieties of **2b** are coplanar due to the less bulky aromatic substituent on the imine nitrogen atom. The different bulkiness of the iminopyrrolyl ligand in **1a** and **1b** affected the coordination number of the magnesium complexes **7a** and **7b**; the second THF coordinates to the metal center at the position *trans* to the other THF molecule.

With the same series of group 2 metal bis(iminopyrrolyl) complexes in hand, we preliminarily studied their catalytic performance for ring-opening polymerization of ε -caprolactone.¹⁷ Bis(iminopyrrolyl)calcium complexes **2a** or **2b** showed low catalytic activity (less than 20% yield), whereas quantitative conversions of the monomers were observed for amidocalcium complexes **3a** and **4a**. In contrast to the polymerization reaction by amidocalcium complexes **3a** and **4a**, the reaction mixture of bis(iminopyrrolyl)strontium and -barium complex **5a** or **6a** and ε -caprolactone (100 equiv) became highly viscous in 3 min with the consumption of all the monomers. GPC measurements of the poly(ε -caprolactone)s revealed the formation of very high molecular weight polymers ($M_n = 1.0 \times 10^5$ for **5a**; $M_n = 1.8 \times 10^5$ for **6a**), probably due to the low initiation efficiency of the heavier alkaline-earth metal catalysts.

Article



Figure 2. Molecular structures of bis(iminopyrrolyl) complexes of group 2 metals with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. (a) $(Imp^{Dipp})_2Sr(THF)_3$ (5a), (b) $(Imp^{Dipp})_2Ba(THF)_3$ (6a), and (c) $(Imp^{Dipp})_2Mg(THF)$ (7a).

Table 2. Bond Distances and Angles of Group 2 Metal Bis(iminopyrrolyl) Complexes 5a-7a

	5a	6a	7a
M-N1	2.651(2)	2.821(5)	2.122(2)
M-N2	2.6691(19)	2.823(4)	2.142(2)
M-01	2.647(2)	2.746(5)	2.0265(19)
M-O2	2.624(3)	2.773(4)	
N1-M-N2	66.38(6)	62.44(12)	79.46(8)
N1-M-N1*	151.62(10)	152.3(2)	$162.57(9)^a$
N2-M-N2*	178.20(9)	178.27(19)	$140.04(9)^{b}$
O1-M-O2	143.87(4)	143.25(9)	
^a N1–Mg–N3. ^b N	12-Mg-N4.		

SUMMARY

We selectively prepared mono- and bis(iminopyrrolyl)calcium complexes **2a** and **4a** by the reaction of Ca[N-(SiMe₃)₂]₂(THF)₂ with 1 or 2 equiv of iminopyrrolyl ligand **1a**. When Ca(CH₂Ph)₂(THF)_{0.5} was used as a starting material, alkane elimination and ligand alkylation reactions of iminopyrrolyl ligand **1a** gave **2a** and **3a**. Characterization of **3a**, formed via imine alkylation reaction of **1a**, revealed the dimeric structure through μ - η ¹: η ⁵-pyrrolyl coordination of the ligand. Bis-(iminopyrrolyl) complexes of strontium and barium were prepared by the amine elimination reaction using M[N(SiMe₃)₂]₂-(THF)₃ (M = Sr, Ba). The heavier group 2 metal complexes of strontium (**5a**) and barium (**6a**) had a seven-coordinated



Figure 3. Molecular structure of $(Imp^{Me})_2Ca(THF)_2$ (2b) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

pentagonal-bipyramidal geometry, and the metal- N^{pyr} bonds were relatively longer than the other amidometal complexes of barium and strontium. Bis(iminopyrrolyl)complexes of strontium (5a) and barium (6a) were highly active for the ringopening polymerization of ε -caprolactone, affording high molecular weight poly(ε -caprolactone)s compared to the polymers produced by calcium and magnesium complexes.

Table 3. Bond Distances	(Å)) and Angles	(deg)) of 2b	and 7b
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	2	Ь	
Ca-N1	2.398(4)	Ca-N2	2.448(3)
Ca-O1	2.349(4)	N1-Ca-N2	110.01(14)
N1-Ca-O1	88.38(14)	N2-Ca-O1	91.59(13)
7b			
Mg-N1	2.1241(11)	Mg-N2	2.1950(13)
Mg-O1	2.1483(13)	N1-Mg-N2	102.44(5)
N1-Mg-O1	89.70(4)	N2-Mg-O1	89.69(5)

EXPERIMENTAL SECTION

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or an argon-filled glovebox. Tetrahydrofuran, pentane, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon and then distilled over CaH₂ prior to storing in the glovebox. Benzene- d_6 was dried over Na/K alloy and stored in the glovebox. ¹H NMR (300 MHz, 400 MHz) and ¹³C NMR (75 MHz, 100 MHz) spectra were measured on a Varian-Unity-INOVA-300 and a Bruker AVANCEIII-400 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer at the Faculty of Engineering Science, Osaka University. Iminopyrrolyl ligands,^{9e} [M{N(SiMe₃)₂}₂(THF)_n] (M = Sr, n = 3; Ba, n = 3; Ca, n = 2),¹⁸ $[Ca(CH_2Ph)_2(THF)_{0.5}]$,^{15a} and $[Mg(CH_2Ph)_2]^{19}$ were prepared according to the literature procedures. Gel permeation chromatographic analysis was carried out at 40 °C by using a Shimadzu LC-10A liquid chromatograph system and a RID 10A refractive index detector, equipped with a Shodex KF-806 L column, which was calibrated versus commercially available polystyrene standards (Showa Denko).

Synthesis of (Amidopyrrolyl)calcium Complex 3a. [Ca- $(CH_2Ph)_2(THF)_{0.5}$] (300 mg, 1.16 mmol) and $[Imp^{Dipp}-H]$ (294 mg, 1.16 mmol) were placed in a Schlenk flask, and THF (12 mL) was added. The reaction mixture was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure. The remaining solid was washed with THF/pentane (v/v = 1/2) and then dried in vacuo to give white solids of 3a (45% yield, 273 mg, 0.259 mmol). 3a was recrystallized from THF/pentane (v/v = 1/1) at -35 °C as block-shaped colorless crystals: mp 133-134 °C (dec); ¹H NMR (400 MHz, -60 °C, THF- d_8) δ 6.75–6.95 (m, 10H, m-ⁱPr₂C₆H₃, m- and p-Ph), 6.40–6.57 (m, 8H, p-Pr₂C₆H₃, o-Ph, and pyr), 5.5 (br, 2H, pyr), 4.8 (br, 2H, pyr), 4.56 (m, 2H, CH(CH₃)₂), 4.09-4.17 (m, 2H, N-CHCH₂Ph), 3.67 (m, 2H, CH(CH₃)₂), 3.55-3.65 (m, 16H, THF), 2.76-2.86 (m, 2H, N-CHCH₂Ph), 2.25-2.36 (m, 2H, N-CHCH₂Ph), 1.72–1.84 (m, 16H, THF), 1.26 (d, ${}^{3}J$ = 6.0 Hz, 6H, $CH(CH_3)_2$, 1.13 (d, ³J = 6.4 Hz, 6H, $CH(CH_3)_2$), 1.08 (d, ³J = 6.4 Hz, 6H, CH(CH₃)₂), 0.88 (d, ${}^{3}J$ = 6.0 Hz, 6H, CH(CH₃)₂); ${}^{13}C{}^{1}H$ NMR (100 MHz, -60 °C, THF- d_8) δ 159.8 (*ipso-i*Pr₂C₆H₃), 146.5 (o-ⁱPr₂C₆H₃), 145.5 (pyr), 144.9 (o-ⁱPr₂C₆H₃), 144.8 (ipso-Ph), 130.8 (o-Ph), 127.0 (m-ⁱPr₂C₆H₃), 124.0 (m-Ph), 122.9 (p-Ph), 122.5 (pyr), 117.1 (p-ⁱPr₂C₆H₃), 104.8 (pyr), 104.4 (pyr), 72.7 (N-CH), 68.2 (THF), 50.3 (CH₂Ph), 27.6 (CH(CH₃)₂), 26.7 (CH(CH₃)₂), 26.5 $(CH(CH_3)_2)$, 26.3, (THF), 26.3, $(CH(CH_3)_2)$, 26.0 $(CH(CH_3)_2)$. Resonances for both carbon atoms of m-^{*i*}Pr₂C₆H₃ appeared at δ 127.0. A signal of one methyl carbon was overlapped with the resonance of THF. Anal. Calcd for C₆₄H₈₈Ca₂N₄O₄: C 72.68, H 8.39, N 5.30. Found: C 72.25, H 8.54, N 5.32

Synthesis of [(Imp^{Dipp})Ca(N(SiMe₃)₂)(THF)₂] (4a). Toluene (20 mL) was added to a Schlenk flask containing solid [Ca{N- $(SiMe_3)_2$ }₂(THF)₂] (750 mg, 1.48 mmol) and [Imp^{Dipp}-H] (375 mg, 1.48 mmol) at room temperature, and then the reaction mixture was stirred for 12 h. All volatiles were removed under reduced pressure. The remaining solid was washed with pentane (5 mL) and then dried in vacuo to give white solids of 4a (597 mg, 67%). 4a was recrystallized from pentane and several drops of THF at -35 °C as block-shaped colorless crystals: mp 111–115 °C; ¹H NMR (400 MHz, 30 °C, C₆D₆) δ 7.88 (s, 1H, N=CH), 7.47 (s, 1H, pyr), 7.11–7.16

(m, 3H, Ar), 6.91–6.97 (m, 1H, pyr), 6.65–6.61 (m, 1H, pyr), 3.56– 3.66 (m, 8H, THF), 3.14 (sept, ${}^{3}J$ = 6.8 Hz, 2H, CH(CH₃)₂) 1.25– 1.31 (m, 8H, THF), 1.20 (d, ${}^{3}J$ = 6.8 Hz, 6H, CH(CH₃)₂), 1.11 (d, ${}^{3}J$ = 6.8 Hz, 6H, CH(CH₃)₂), 0.23 (s, 18 H, N(SiMe₃)₂); ${}^{13}C{}^{1}H{}$ NMR (100 MHz, 30 °C, C₆D₆) δ 162.2 (C=N), 149.2 (Ar), 140.9 (Ar), 137.3 (pyr), 136.6 (pyr), 125.3 (Ar), 123.6 (Ar), 122.7 (pyr), 112.3 (pyr), 69.7 (THF), 28.0 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.3 (THF), 23.4 (CH(CH₃)₂), 5.23 (N(SiMe₃)₂). Anal. Calcd for C₃₁H₅₅CaN₃O₂Si₂: C 62.26, H 9.27, N, 7.03. Found: C 62.22, H 9.36, N 7.16.

Synthesis of $[(Imp^{Dipp})_2Ba(THF)_3]$ (6a). $[Ba{N(SiMe_3)_2}_2(THF)_3]$ (200 mg, 0.30 mmol) and [Imp^{Dipp}-H] (170 mg, 0.67 mmol) were dissolved in toluene (5 mL). The reaction mixture was stirred for 12 h at 90 °C. The reaction mixture was then cooled to room temperature, and all volatiles were removed under reduced pressure. The remaining solid was washed with pentane (5 mL) and then dried in vacuo to give white solids, which were recrystallized from THF/pentane (v/v = 1/2) at -35 °C as block-shaped colorless crystals, 6a (261 mg, 92%): mp 145-151 °C (dec). Evacuation of the colorless crystals for a long time led to the formation of white powders, probably due to the loss of packing and coordinating THF molecules to form (Imp^{Dipp})₂Ba- $(THF)_{2}$. ¹H NMR (400 MHz, 30 °C, THF- d_{8}) δ 7.75 (s, 2H, N= CH), 7.08 (d, ${}^{3}J$ = 7.8 Hz, 4H, *m*-Ar), 7.00 (br, 2H, pyr), 6.98 (t, ${}^{3}J$ = 7.8 Hz, 2H, p-Ar), 6.54 (dd, ${}^{3}J$ = 3.3 Hz, ${}^{4}J$ = 1.2 Hz, 2H, pyr), 6.03 $(dd, {}^{3}J = 3.3 \text{ Hz and } {}^{3}J = 1.5 \text{ Hz}, 2H, pyr), 3.59-3.66 (br, 8H, THF),$ 3.18 (sept, ${}^{3}J = 6.9$ Hz, 4H, CH(CH₃)₂), 1.74–1.79 (m, 8H, THF), 1.12 (br, 24H, CH(CH₃)₂); ¹³C{¹H} NMR (100 MHz, 30 °C, THFd₈) δ 161.7 (C=N), 152.1 (ipso-Ar), 141.0 (o-Ar), 138.4 (pyr), 137.3 (pyr), 124.2 (p-Ar), 123.6 (m-Ar), 122.4 (pyr), 110.5 (pyr), 68.2 (THF), 28.8 (CH(CH₃)₂), 26.4 (THF), 26.1 (CH(CH₃)₂), 23.2 $(CH(CH_3)_2)$. Anal. Calcd for $C_{46}H_{66}BaN_4O_3$: C 64.21, H 7.73, N 6.51. Found: 63.82, H 7.56, N 6.31.

Other heavier alkaline earth bis(iminopyrrolyl) complexes were prepared in similar manner to **6a**.

[(Imp^{Dipp})₂Ca(THF)₂] (2a). Colorless crystals were obtained in 90% yield: mp 132–138 °C (dec); ¹H NMR (300 MHz, 35 °C, C₆D₆) δ 7.90 (br, 2H, N=CH), 7.24 (br, 2H, *p*-Ar), 7.10 (br, 6H, *m*-Ar and pyr), 6.96–7.00 (m, 2H, pyr), 6.60 (br, 2H, pyr), 3.41 (br, 8H, THF), 3.22 (sept, ³J = 6.6 Hz, 4H, CH(CH₃)₂), 1.21 (br, 8H, THF), 1.16 (d, ³J = 6.6 Hz, 12H, CH(CH₃)₂), 1.08 (d, ³J = 6.6 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (75 MHz, 35 °C, C₆D₆) δ 162.5 (C=N), 150.0 (*ipso*-Ar), 141.1 (Ar), 137.6 (pyr), 137.4 (*p*-Ar), 124.9 (Ar), 123.6 (pyr), 121.9 (pyr), 112.0 (pyr), 68.8 (THF), 28.3 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 25.4 (THF), 23.2 (CH(CH₃)₂). Anal. Calcd for C₄₂H₅₈CaN₄O₂: C 73.00, H 8.46, N 8.10. Found: C 72.77, H 8.23, N 7.99.

[(Imp^{Me)}₂Ca(THF)₂] (2b). White crystals were obtained in 95% yield: mp 173–177 °C (dec); ¹H NMR (300 MHz, 35 °C, C_6D_6) δ 7.17–7.21 (m, 2H, pyr), 6.94–7.06 (m, 6H, Ar and pyr), 6.55–6.63 (m, 4H, Ar), 6.48–6.53 (m, 2H, pyr), 3.43–3.53 (m, 8H, THF), 2.15–2.17 (br s, 6H, CH₃), 2.03–2.06 (br s, 6H, CH₃), 1.25–1.35 (m, 8H, THF); ¹³C{¹H} NMR (75 MHz, 35 °C, C_6D_6) δ 167.4 (*C*=N), 148.2 (*ipso*-Ar), 139.2 (pyr), 136.8 (Ar), 133.6 (Ar), 129.8 (Ar), 123.7 (pyr), 116.4 (pyr), 111.7 (pyr), 68.4 (THF), 25.5 (THF), 21.0 (CH₃), 16.7 (CH₃). Anal. Calcd for C₃₄H₄₂CaN₄O₂: C 70.55, H 7.31, N 9.68. Found: C 70.21, H 7.11, N 9.39.

[(Imp^{Dipp})₂Sr(THF)₃] (5a). Colorless crystals were obtained in 89% yield: mp 142–146 °C (dec); ¹H NMR (300 MHz, 35 °C, C₆D₆) δ 7.91 (br, 2H, N=CH), 7.27 (br, 2H, p-Ar), 7.10 (br, 6H, *m*-Ar and pyr), 6.90 (br, 2H, pyr), 6.46 (br, 2H, pyr), 3.47 (br, 12H, THF), 3.11 (br, 4H, CH(CH₃)₂), 1.30 (br, 12H, THF), 1.08 (br, 24H, CH₃); ¹³C{¹H} NMR (75 MHz, 35 °C, C₆D₆) δ 162.1 (C=N), 149.8 (*ipso*-Ar), 140.7 (Ar), 138.0 (pyr), 137.6 (*p*-Ar), 124.9 (Ar), 123.6 (pyr), 122.3 (pyr), 112.2 (pyr), 68.3 (THF), 28.6 (CH(CH₃)₂), 25.6 (THF), 23.3 (CH(CH₃)₂). Anal. Calcd for C₄₆H₆₆N₄O₃Sr: C 68.15, H 8.20, N 6.91. Found: C 67.87, H 7.95, N 6.62.

Synthesis of $[(Imp^{Me})_2Mg(THF)_2]$ (7b). $Mg(CH_2Ph)_2$ (103 mg, 0.50 mmol) and $[Imp^{Me}-H]$ (198 mg, 1.0 mmol) were dissolved in toluene (5 mL). The reaction mixture was stirred for 12 h at 90 °C. After cooling the reaction mixture to room temperature, all volatiles were removed under reduced pressure. The remaining solid was

washed with pentane (5 mL) and dried in vacuo to give white solids, which were crystallized from THF/pentane (v/v = 1/2) at -35 °C. Block-shaped colorless crystals of 7b were obtained (250 mg, 88%): mp 147–153 °C (dec); ¹H NMR (400 MHz, 30 °C, C₆D₆) δ 7.01–7.08 (m, 6H, Ar and pyr), 6.73–6.78 (m, 4H, Ar), 6.46–6.52 (m, 4H, pyr), 3.47–3.39 (m, 8H, THF), 2.18 (s, 6H, CH₃), 2.02 (s, 6H, CH₃), 1.23–1.30 (m, 8H, THF); ¹³C{¹H} NMR (75 MHz, 35 °C, C₆D₆) δ 167.5 (*C*=N), 148.2 (*ipso*-Ar), 139.2 (pyr), 136.7 (*p*-Ar), 133.5 (*m*-Ar), 129.7 (*o*-Ar), 123.7 (pyr), 116.3 (pyr), 111.7 (pyr), 68.3 (THF), 25.5 (THF), 20.9 (CH₃), 16.4 (CH₃). Anal. Calcd for C₃₄H₄₂MgN₄O₂: C 72.53, H 7.52, N 9.95. Found: C 72.27, H 7.41, N 9.72.

Similar to the synthesis of 7b, colorless crystals of 7a were obtained in 93% yield: mp 197–201 °C (dec); ¹H NMR (300 MHz, 35 °C, C₆D₆) δ 7.77 (d, ⁴J = 1.1 Hz, 2H, N=CH), 7.10–7.30 (m, 6H, Ar), 6.80 (dd, ³J = 3.5 Hz, ⁴J = 1.0 Hz, 2H, pyr), 6.32 (dd, ³J = 3.5 Hz, ⁴J = 1.7 Hz, 2H, pyr), 6.22–6.24 (m, 2H, pyr), 3.35 (br, 4H, THF), 3.17 (br, 4H, CH(CH₃)₂), 1.18 (m, 24H, CH(CH₃)₂), 1.10 (br, 4H, THF); 1³C{¹H} NMR (75 MHz, 35 °C, C₆D₆) δ 161.6 (C=N), 147.1 (*ipso*-Ar), 137.5 (*p*-Ar), 137.3 (pyr), 128.8 (*o*-Ar), 125.6 (*m*-Ar), 123.7 (pyr), 119.3 (pyr), 113.0 (pyr), 69.5 (THF), 28.8 (CH(CH₃)₂), 25.3 (THF), 25.2 (CH(CH₃)₂), 22.7 (CH(CH₃)₂). Anal. Calcd for C₃₈H₅₀MgN₄O, C 75.67, H 8.35, N 9.29. Found: C 75.44, H 8.15, N 8.92.

X-ray Crystallographic Analyses. Single crystals of 2a, 2b, 5a-7a, and 7b were grown from a solution of THF/pentane under argon atmosphere at a temperature of -35 °C. 4a was recrystallized from pentane and several drops of THF at -35 °C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) or 120(2) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector or a Rigaku Mercury CCD area detector with graphite-monochromated Mo K α (0.71075 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S2. The structure remnent parameters are methods (SIR92 or SIR2004)²⁰ and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.²¹ Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $\left[\sum w(F_o^2 - F_c^2)^2\right] (w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]),$ where $P = (Max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 and wR2 were $(\sum ||F_o| - |F_c||) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules.

ASSOCIATED CONTENT

S Supporting Information

Molecular structure of 7b, polymerization of ε -caprolactone catalyzed by bis(iminopyrrolyl) complexes of group 2 metals, and the ¹H NMR spectrum of the representative poly(ε -caprolactone), and CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the JSPS Fellowship to T.K.P. H.K. and K.Y. thank the Global COE (Center of Excellence) Program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University. K.Y. expresses his special thanks for the financial support provided by the JSPS Research Fellowships for Young Scientists. We acknowledge Dr. Kuntal

Pal for his contribution to X-ray analyses of the alkaline-earth metal complexes. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), Japan.

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