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Monomeric, Dimeric, and Trimeric Calcium Compounds Containing Substituted Pyrrolyl and Ketiminate Ligands: Synthesis and Structural Characterization

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A series of monomeric, dimeric, and trimeric calcium compounds containing substituted pyrrolyl or ketiminate ligands were synthesized, and characterized by NMR spectroscopy and single crystal X-ray diffractometry. The reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 equiv of $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ in toluene generates the dimeric complex, $[Ca\{N(SiMe_3)\}[\mu-\eta^1:\eta^5\text{-}\{C_4H_3N(2\text{-}CH_2NEt_2)\}]]_2$ (**1**) in which two substituted pyrrolyl ligands bind two Ca centers in a η^1 and η^5 fashion. The reaction between $Ca[N(SiMe_3)_2]_2(THF)_2$ and 2 equiv of $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ in THF yields a monomeric calcium compound $Ca[C_4H_3N(2\text{-}CH_2NEt_2)]_2(THF)_2$ (**2**) that exhibits a facial octahedral geometry on the central Ca atom. Similarly, the reactions of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 and 2 equiv of OCMeCHCMeNHAr (Ar = 2,6-diisopropylphenyl) generate $[Ca(OCMeCHCMeNAr)\{N(SiMe_3)_2\}]_2$ (**3**) and $[Ca(\mu\text{-}OCMeCHCMeNAr)(OCMeCHCMeNAr)]_2$ (**4**), respectively. In **3**, the Ca atom possesses a distorted tetrahedral geometry where as in **4**, a square plane is developed by the two calcium atoms with the bridging participation of two oxygen atoms from two ketiminate ligands. The in situ reaction of OCMeCHCMeNHAr, $Ca[N(SiMe_3)_2]_2(THF)_2$, and isopropyl alcohol results in a trimeric calcium alkoxide compound $Ca_3(\mu\text{-}OCMeCHCMeNAr)_2(OCMeCHCMeNAr)(\mu_3\text{-}O\text{-}^iPr)_2(\mu_2\text{-}O\text{-}^iPr)$ (**5**). Compounds **1**, **2**, and **5** showed good catalytic activity in the ring-opening polymerization of ε-caprolactone and L-lactide.

Introduction

Green chemistry[1] and material science[2] are among the two most important research avenues considering current perspectives in modern chemistry. Environmentally friendly[3] polyesters[4] such as poly(caprolactone) and polylactide are used widely in various applications because of their biocompatible properties. For example, polylactide, a highly versatile biodegradable aliphatic polyester, can be obtained from lactide through ring-opening polymerization in the presence of catalysts.[5] It can be easily produced commercially, in a high molecular weight form through ring-opening lactide polymerization using most widely a stannous octanoate, [tin(II) bis-2-ethylhexanoic acid],[6] catalyst. The development of new human-friendly metal catalysts for lactide ring-opening polymerization is a growing interest for biomedical and pharmaceutical applications. Various discrete metal

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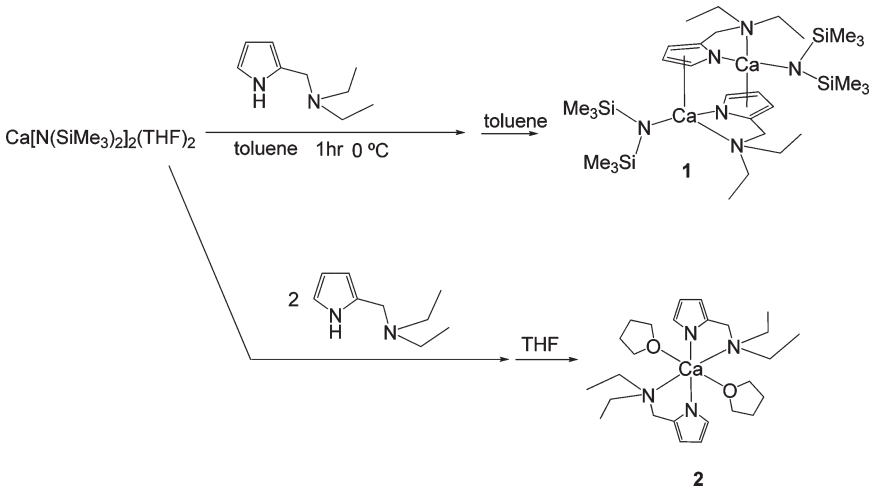
Scheme 1



complexes have been introduced in lactide polymerization and these include the metals Ca,[7] Zn,[8] Mg,[9] and Fe[10] which are considered as human-friendly metals, and their complexes have been employed in lactide and other ring-opening polymerizations. Bidentate β-diketiminate ligands were used to access a number of Zn(II) and Mg(II) complexes, several of which demonstrated excellent LA polymerization behavior.[11] In this connection, we have forwarded our interest to the investigation of the activity in the ring-opening polymerization of lactones and lactides[12] and focus our strategy on the use of calcium because of its high biocompatible characteristics and itself, is a kinetically labile ion.[13] By using a 1:1 ligand combination of β-diketone and functionalized alcohol around the metal center, Otway and co-workers reported some calcium derivatives,[14] using the ligand, 'tmhd' (where tmhd = 2,2,6,6,-tetramethyl-3,5-heptanedione). In continuation to use this ligand, Mingos and his group, reported some calcium complexes,[15] $[Ca_3(tmhd)_6)]$ and $[Ca_2(tmhd)_4(EtOH)_2]$, having a wide range of coordination modes. Employment of the recent availability of the bis[bis(trimethylsilyl)]amides in transamination schemes resulted in the preparation of several organometallic derivatives of calcium.[16] However, the chemistry of alkaline earth metal amides has been limited to the bis[bis(trimethylsilyl)]amides, as summarized in a recent review article.[17] In the presence of donors, such as tetrahydrofuran (THF), the amido derivatives display monomeric species with two amides and two THF donors bound to the metal centers.[18] In a continuation of the use of THF donors, Vargas et al. have reported one novel calcium derivative,[19] $Ca[NDiip(SiMe_3)]_2(THF)_2$ along with other alkaline earth metal arylsilylamides.

In a continuation of our previous studies[20] on the lactide polymerization, herein we report the synthesis and characterization of a series of novel calcium complexes, $[Ca\{N(SiMe_3)\}-[\mu-\eta^1:\eta^5-\{C_4H_3N(2-CH_2NEt_2)\}]]_2$ (**1**), $Ca[C_4H_3N(2-CH_2-NEt_2)]_2(THF)_2$ (**2**), $[Ca(OCMeCHCMeNAr)\{N(SiMe_3)_2\}]_2$ (**3**), $[Ca(\mu\text{-}OCMeCHCMeNAr)(OCMeCHCMeNAr)]_2$ (**4**), $Ca_3(\mu\text{-}OCMeCHCMeNAr)_2(OCMeCHCMeNAr)(\mu_3\text{-}O\text{-}^iPr)_2-(\mu_2\text{-}O\text{-}^iPr)$ (**5**), and their catalytic activities toward ε-caprolactone and L-lactide. To the best of our knowledge, all the calcium compounds derived from either substituted pyrrolyl or ketiminate ligands are very rare and still remain less explored.

Results and Discussion

Synthesis and Characterization. The syntheses of calcium compounds containing substituted pyrrolyl and ketiminate ligands are summarized in Scheme 1 and 2,

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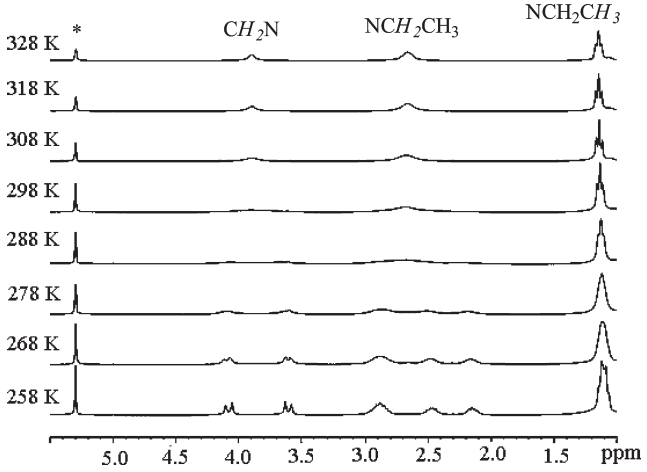
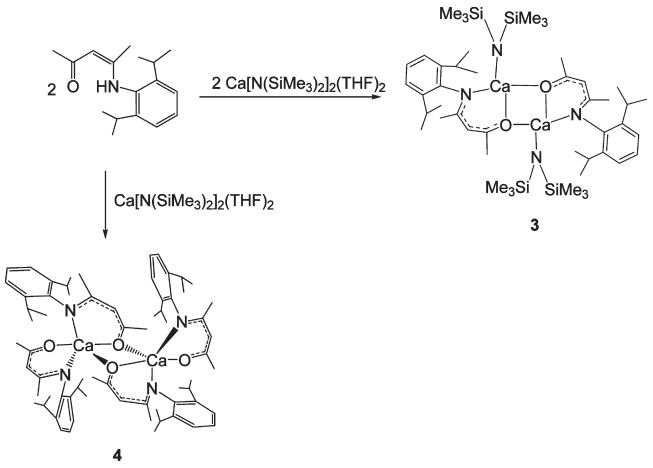


Figure 1. Variable-temperature ^{1}H NMR spectra of compound **1** using 300 MHz NMR.

Scheme 2



respectively. The reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 equiv $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ in toluene gives the dimeric compound, $[Ca\{N(SiMe_3)_2\}[\mu-\eta^1:\eta^5\text{-}\{C_4H_3N(2\text{-}CH_2NEt_2)\}]]_2$ (**1**) in 31% yield. The variable-temperature ^{1}H NMR spectra of **1** in CD_2Cl_2 are shown in Figure 1. At room temperature, compound **1** exhibits broad resonances for the NEt_2 and the CH_2 of the pyrrolyl side chain. However, when the temperature is lowered to 258 K, the broad CH_2 resonance of the ethyl group separates into three multiplets with 2:1:1 ratio, and the broad CH_2 resonance of the pyrrolyl side arm splits into two doublets, which indicates the slow limit of the flipping of the Ca−N−C−C−N five-membered ring and the rotation of N−Et bond. The pyrrole rings of **1** bind to calcium centers in η^1 and η^5 manner simultaneously, and their ^{1}H NMR spectra show resonances at δ 6.39, 6.49, and 6.91, signifying downfield shifts comparable to the free ligand of $[C_4H_3NH(2\text{-}CH_2NEt_2)]$, which are at δ 6.07, 6.16, and 6.73 in $CDCl_3$. This phenomena can also be seen in the literature that describes the CH resonances of $[Ca(pyr^*)_2(THF)]$ [pyr* = pyrrolyl] indicating the π-bonded pyrrolyl ligands.[21] Compound **1** is not very thermally stable in THF which decomposes within a couple of days forming $Ca[N(SiMe_3)_2]_2(THF)_2$ and **2** (vide infra), based on the ^{1}H NMR spectroscopic data.

When 2 equiv of $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ reacted with $Ca[N(SiMe_3)_2]_2(THF)_2$ in THF, a monomeric calcium compound $Ca[C_4H_3N(2\text{-}CH_2NEt_2)]_2(THF)_2$ (**2**) was obtained in 62.5% yield. Compound **2** shows good solubility in benzene-d_6. A similar compound $[Ca(2\text{-DMAMP})_2(THF)_2]$, [where 2-DMAMP = 2-(dimethylaminomethyl)-pyrrole] reported by Vargas and Ruhlandt-Senge[22] has limitations related to the solubility in common organic solvents. Presumably, the longer side arm of NEt_2 increases the van der Waals forces between the molecule and the solvents. The six-coordinate compound **2** showed broad and complicated ^{1}H NMR signals at room temperature. However, when the solvent temperature was raised to 344 K, the ^{1}H NMR spectrum showed two THF resonances at δ 1.47 and 3.58 and ethyl group resonances at δ 0.79 and 2.54.

Similarly, the reactions of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 and 2 equiv of OCMeCHCMeNHAr, where Ar = 2,6-diisopropylphenyl, in toluene gave $[Ca(OCMeCHCMeNAr)\{N(SiMe_3)_2\}]_2$ (**3**) and $[Ca(\mu\text{-}OCMeCHCMeNAr)(OCMeCHCMeNAr)]_2$ (**4**), respectively, in good yield. The dimeric ketiminate calcium amide compound **3** showed one set of ketiminate resonances with a characteristic methine proton at δ 5.03 and one $N(SiMe_3)_2$ resonance at δ 0.26 at room temperature. In contrast to **3**, compound **4** exhibited very complicated ^{1}H NMR spectra. Even though repeating fractional recrystallizations were performed to purify compound **4**, the same ^{1}H NMR spectra were obtained. Five methine proton resonances were observed in the range of δ 4.73−4.88, which indicates the presence of five different types of ketiminate bonding modes in the calcium compound. Therefore, limited information concerning the structures in solution could be obtained. Presumably, the dimeric bis(ketiminate)calcium compound **4** dissociates at a certain level to form a monomeric structure because of the larger steric effect of the bulky ketiminate ligands. Similar phenomena were also observed concerning the lactide polymerization on calcium complexes what Chisholm et al. described before using β-diiminato and bulky tris-pyrazolylborates.[23]

Interestingly, the reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ with 1 equiv of OCMeCHCMeNHAr in toluene and the subsequent addition of 1 equiv of isopropyl alcohol generated an asymmetrical trinuclear calcium cluster $Ca_3(\mu\text{-}OCMeCHCMeNAr)_2(OCMeCHCMeNAr)(\mu_3\text{-}O\text{-}^i\text{Pr})_2(\mu_2\text{-}O\text{-}^i\text{Pr})$ (**5**). Compound **5** contains three calcium centers and two different modes of ketiminate ligands, which can be observed from the ^{1}H NMR spectra of **5** showing two singlets at δ 5.18 and 5.10 in a 1:2 ratio. Again, two types of isopropoxide ligands exist in the molecule, and two multiplets at δ 4.45 and 3.50 for the isopropyl methine protons are observed.

Molecular Structures of 1−5. To further characterize the molecular structures of these compounds, compounds **1**−**5** were determined by single crystal X-ray diffractometry. The crystallographic data are summarized in

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Table 1. Summary of Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**·toluene	**4**·toluene	**5**
formula	$C_{30}H_{66}Ca_2N_6Si_4$	$C_{26}H_{46}CaN_4O_2$	$C_{26.5}H_{45.5}CaN_2OSi_2$	$C_{82}H_{112}Ca_2N_4O_4$	$C_{60}H_{93}Ca_3N_3O_6$
fw	703.41	486.75	504.41	1297.92	1072.61
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$
a, Å	9.8626(6)	8.7173(3)	11.8253(9)	11.5199(8)	10.8503(16)
b, Å	17.5189(10)	14.7092(5)	17.5332(13)	12.8966(9)	24.432(4)
c, Å	12.1437(7)	10.4000(3)	15.4155(12)	14.4381(10)	24.362(4)
α, deg	90	90	90	100.6850(10)	90
β, deg	92.749(2)	92.366(2)	107.253(2)	107.6900(10)	102.430(4)
γ, deg	90	90	90	103.7830(10)	90
V, Å^3	2095.8(2)	1332.40(8)	3052.4(4)	1906.2(2)	6307.1(16)
Z	2	2	2	1	4
d_c, Mg/m^3	1.115	1.213	1.099	1.131	1.130
μ, mm^{-1}	0.413	0.264	0.303	0.199	0.309
$F(000)$	768	532	1100	704	2328
cryst size	0.24 × 0.19 × 0.17	0.15 × 0.13 × 0.12	0.25 × 0.22 × 0.13	0.16 × 0.10 × 0.08	0.17 × 0.13 × 0.11
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
no. of rflns collected	31116	10416	45537	30271	84698
ind rflns	5045 (R_{int} = 0.0472)	3220 (R_{int} = 0.0336)	7361 (R_{int} = 0.0449)	9846 (R_{int} = 0.0420)	13093 (R_{int} = 0.2049)
data/restraints/params	5045/0/198	3220/0/153	7361/0/310	9846/2/467	13093/0/675
goodness-of-fit on F^2	1.0267	1.053	1.050	1.053	1.001
R_1, wR_2 ($I > 2\sigma(I)$)	0.0338, 0.0858	0.0397, 0.1012	0.0363, 0.0909	0.0441, 0.1017	0.0566, 0.1045
R_1, wR_2 (all data)	0.0543, 0.0910	0.0593, 0.1101	0.0544, 0.0990	0.0784, 0.1140	0.1607, 0.1370
largest diff peak, hole (e/Å^3)	0.283, −0.293	0.567, −0.227	0.432, −0.225	0.275, −0.227	0.353, −0.285

Table 1, and selected bond lengths and angles are listed in Table 2. The molecular structures of **1**−**5** are shown in Figures 2−6. Compound **1** has a dimeric structure with the substituted pyrrolyl [$C_4H_3N(2\text{-}CH_2NEt_2)$] bound with two calcium centers simultaneously in a η^1 and η^5 modes. Although pyrrolyl ligands can coordinate to metals in a η^1 or η^5 manner,[21,24] only a few limited examples of pyrrolyl ligands bound to two metal centers with η^1:η^5 modes have been characterized structurally,[25] and this is the first example of a η^1:η^5 pyrrolyl coordination to two calcium centers. In compound **1**, a substituted pyrrolyl ligand, [$C_4H_3N(2\text{-}CH_2NEt_2)$], binds to a calcium center through the nitrogen atoms of the pyrrole ring and the NEt_2 fragment, forms a five-membered ring of Ca-[η^1-{$C_4H_3N(2\text{-}CH_2NEt_2)$}]. Two Ca[$\eta^1$-{$C_4H_3N(2\text{-}CH_2NEt_2)$}] fragments are interlocked through η^5-pyrrole rings to the other calcium atom, and the bond length from calcium to the centroid of the pyrrole ring is about 2.511 Å. The bond length of Ca to the nitrogen of the η^1 pyrrolyl ring is 2.4242(13) Å. Both the results are similar to the reported Ca−η^5-pyrrole ring bond lengths, which are about 2.581 Å and the Ca−η^1-pyrrole ring bond lengths, which are about 2.467 Å.[26]

Compound **2** exhibits a facial octahedron with the chelation of four N-donor atoms generated from a pair of each unit of the pyrrolyl ligand, $C_4H_3N(2\text{-}CH_2NEt_2)$, and monodentate orientation of two O-donor atoms from two THF molecules. The coordination geometry is somewhat different from a regular octahedron since the angles involving the atoms in *trans* positions are perfectly 180° whereas those involving the *cis* atoms slightly differ from 90°. Concerning the behavior of different bonding modes, the NEt_2 fragment forms two five-membered rings with bite angles of 75.27(4)°. The two THF molecules and the two pyrrole rings are both occupying at *trans* positions. The structure is relatively similar to the structure of [$Ca(2\text{-}DMAMP)_2(THF)_2$] reported by Vargas and Ruhlandt-Senge.[22] However, the bond lengths of calcium to the coordinated atoms of **2** are all slightly longer (ca. 0.011 to 0.054 Å) than the corresponding bond lengths of [$Ca(2\text{-}DMAMP)_2(THF)_2$] presumably because of the larger steric effect of the diethylamino fragments of compound **2**.

The molecular structure of **3** consists of a toluene molecule and a dimeric calcium molecule. The coordination geometry of the calcium atom can be described as a distorted tetrahedron, in which the ketiminate ligand coordinates to one calcium atom with its nitrogen atom and bridges to two calcium atoms with its oxygen atom and vice versa. The two calcium atoms and two oxygen atoms form the diamond-shaped plane Ca(1)−O(1)−Ca(1A)−O(1A) with the angle of O(1A)−Ca(1)−N(1) and Ca(1)−O(1)−Ca(1A) at 74.11(4)° and 105.88(4)°, respectively. In comparison to a similar monodiketiminate calcium compound (BDI)Ca[$N(SiMe_3)_2$](THF) reported by Chisholm,[7b] the monoketiminate calcium compound **3** forms a dimeric structure presumably because of the smaller steric effect of the ketiminate while the larger steric effect of diketminate only forms a monomeric (BDI)Ca[$N(SiMe_3)_2$](THF).

The crystal of **4** contains one dimeric unit of calcium as well as one toluene molecule in the unit cell diagram where one of the toluene carbon atoms is disordered and divided into two parts with the ratio of 43% and 57%. The molecular structure of **4** can be described as edge-sharing

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**–**5**

		1	
Ca(1)-N(1A)	2.4245(13)	Ca(1)−N(2)	2.5825(13)
Ca(1)−N(3)	2.2863(12)	Ca(1)−N(1)	2.7612(12)
Ca(1)−C(1)	2.7685(15)	Ca(1)−C(2)	2.7978(16)
Ca(1)−C(3)	2.7839(16)	Ca(1)−C(4)	2.7600(16)
N(2)−Ca(1)−N(1A)	70.35(4)	N(3)−Ca(1)−N(1A)	118.24(4)
N(2)−Ca(1)−N(3)	115.64(4)		
		2	
Ca(1)−N(1)	2.3976(12)	Ca(1)−N(2A)	2.5769(12)
Ca(1)−O(1)	2.3959(10)		
N(2)−Ca(1)−N(2A)	180.00(5)	O(1)−Ca(1)−O(1A)	180.00(4)
N(1)−Ca(1)−N(1A)	180.00(5)	N(1)−Ca(1)−N(2A)	75.27(4)
		3	
Ca(1)−N(1)	2.4257(12)	Ca(1)−O(1)	2.2981(10)
Ca(1)−N(2)	2.2915(13)	Ca(1)−O(1A)	2.3025(10)
N(1)−Ca(1)−O(1)	78.62(4)	O(1)−Ca(1)−O(1A)	74.11(4)
O(1)−Ca(1)−N(2)	143.75(4)	O(1A)−Ca(1)−N(1)	128.72(4)
O(1A)−Ca(1)−N(2)	112.30(4)	N(2)−Ca(1)−N(1)	115.37(4)
		4	
Ca(1)−O(1)	2.2035(11)	Ca(1)−N(2)	2.4918(12)
Ca(1)−N(1)	2.4303(13)	Ca(1)−O(2)	2.3115(10)
Ca(1)−O(2A)	2.3441(11)		
O(1)−Ca(1)−O(2)	156.98(4)	N(1)−Ca(1)−N(2)	111.52(4)
N(1)−Ca(1)−O(2A)	114.89(4)	O(2A)−Ca(1)−N(2)	133.59(4)
O(2)−Ca(1)−N(2)	78.80(4)	Ca(1)−O(2)−Ca(1A)	105.07(4)
		5	
Ca(1)−O(1)	2.215(2)	Ca(1)−N(1)	2.487(3)
Ca(1)−O(2)	2.396(2)	Ca(1)−O(3)	2.435(2)
Ca(1)−O(4)	2.414(2)	Ca(1)−O(5)	2.337(2)
Ca(2)−O(2)	2.339(2)	Ca(2)−O(4)	2.306(2)
Ca(2)−O(5)	2.326(2)	Ca(2)−O(6)	2.297(2)
Ca(2)−N(2)	2.414(3)	Ca(3)−O(3)	2.345(2)
Ca(3)−O(4)	2.303(2)	Ca(3)−O(5)	2.330(2)
Ca(3)−O(6)	2.285(2)	Ca(3)−N(3)	2.427(3)
O(1)−Ca(1)−O(5)	173.58(8)	O(4)−Ca(1)−N(1)	176.81(8)
O(2)−Ca(1)−O(3)	144.85(8)	O(3)−Ca(1)−O(5)	77.75(7)
O(1)−Ca(1)−N(1)	77.64(8)	Ca(1)−O(3)−Ca(3)	88.70(8)
Ca(1)−O(4)−Ca(3)	90.23(7)	Ca(1)−O(5)−Ca(2)	91.82(8)
Ca(1)−O(2)−Ca(2)	90.04(8)	Ca(1)−O(4)−Ca(2)	90.39(8)
O(2)−Ca(2)−O(6)	153.07(8)	N(2)−Ca(2)−O(4)	130.17(9)
N(2)−Ca(2)−O(5)	140.12(9)	Ca(2)−O(6)−Ca(3)	87.71(8)
Ca(2)−O(4)−Ca(3)	87.06(8)	Ca(2)−O(5)−Ca(3)	85.94(7)
N(2)−Ca(2)−O(2)	76.25(8)	O(3)−Ca(3)−O(6)	154.74(89)
N(3)−Ca(3)−O(3)	77.21(8)	N(3)−Ca(3)−O(4)	126.95(9)
N(3)−Ca(3)−O(5)	145.29(8)	O(4)−Ca(3)−O(5)	71.93(8)

bis(trigonal bipyramidal), in which the two oxygen atoms from two ketiminate ligands act as bridging atoms together with two calcium atoms to form a square plane. A schematic drawing is shown in Scheme 4. Two oxygen atoms each from the ketiminate ligands occupy the axial positions with the bond angles of O(1)−Ca(1)−O(2) at 156.98(4)°. The bond length of calcium atom to the terminal oxygen atom (2.2035(11) Å) is about 0.11 Å relatively shorter than that of calcium to the bridging oxygen atom (2.3115(10) Å). The bond lengths of calcium to nitrogen atoms of the two ketiminate ligands are relatively similar (2.4303(13) and 2.4918(12) Å). In comparing with similar bis(diketiminate)calcium compound, $(BDI)_2Ca$,[7b] unlike the ketiminate calcium compound **4** which forms a dimeric structure, the bulkier diketiminate ligand is sufficiently demanding to prevent dimerization and forms a monomeric geometry of the calcium atom.

A molecular structure of **5** is shown in Figure 6(a). The molecular structure of **5** consists of three calcium atoms,

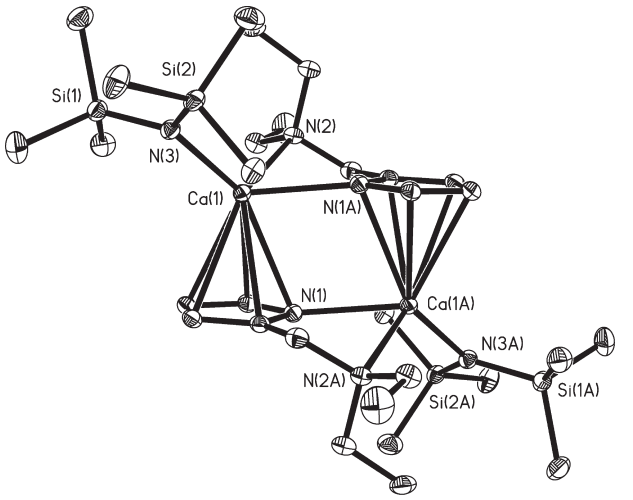


Figure 2. Molecular structure of **1**. Thermal ellipsoids were drawn at 30% probability and hydrogen atoms are omitted for clarity.

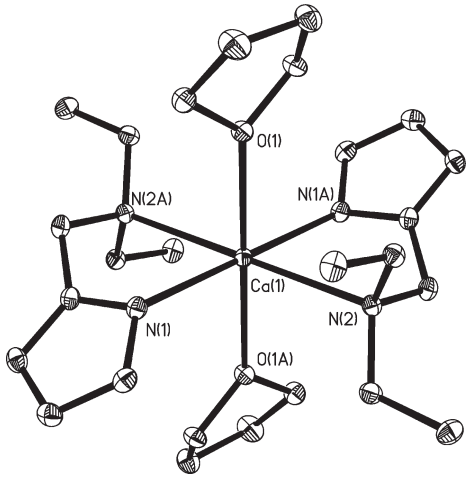


Figure 3. Molecular structure of **2**. Thermal ellipsoids were drawn at 30% probability and hydrogen atoms are omitted for clarity.

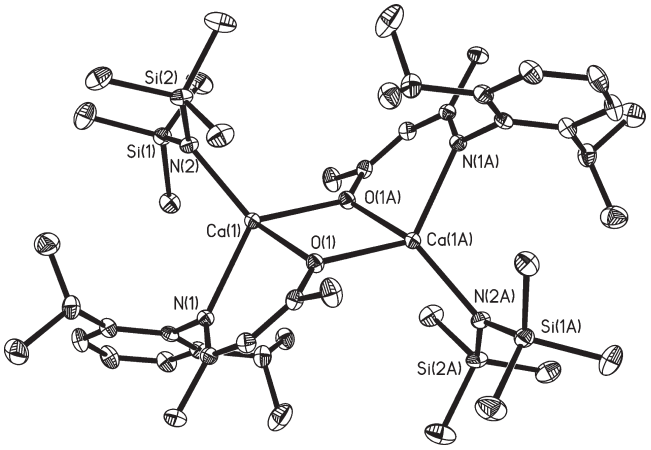


Figure 4. Molecular structure of **3**. Thermal ellipsoids were drawn at 30% probability and hydrogen atoms are omitted for clarity.

three isoproxide fragments, and three ketiminate ligands. The core structure of **5** is shown in Figure 6(b). The three calcium atoms of **5** form a trigonal plane with two isoproxide fragments capped in a μ_3-O mode on each

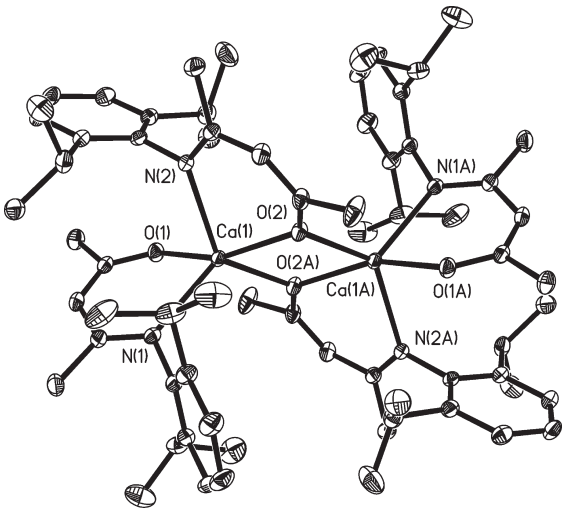


Figure 5. Molecular structure of **4**. Thermal ellipsoids were drawn at 30% probability and hydrogen atoms are omitted for clarity.

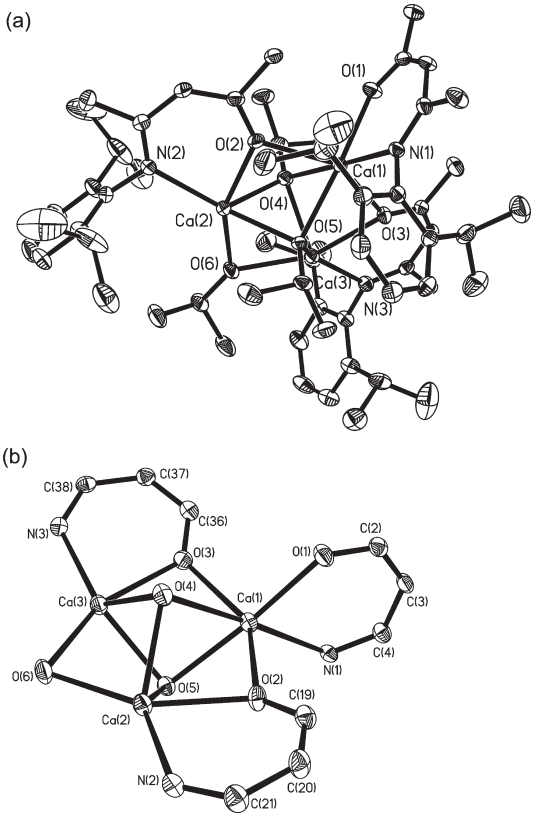
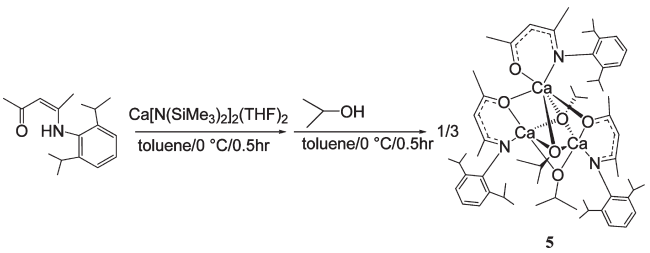


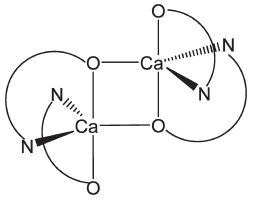
Figure 6. (a) Molecular structure of **5**. Thermal ellipsoids were drawn at 30% probability and hydrogen atoms are omitted for clarity. (b) The core structure of compound **5** contains three Ca atoms, backbones of the four ketiminate ligands, and the oxygen atoms of the three isoproxide fragments.

side of the calcium trigonal plane and one isoproxide bridged in a μ_2-O mode to one edge, Ca(2) and Ca(3), of the trigonal plane. The bond lengths of oxygen atoms of the face bonded isopropoxide to the calcium atoms, Ca-(μ_3-O), ranged from 2.30 to 2.42 Å, which are longer than the bond lengths of the oxygen atom of the bridged isopropoxide to the calcium atom, Ca−(μ_2-O), ranged from 2.29 to 2.30 Å. These results are consistent with the

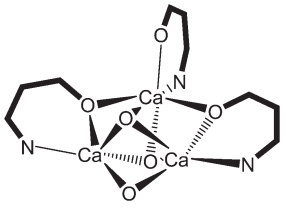
Scheme 3



Scheme 4. Edge Sharing Bis(Trigonal Bipyramidal)



Scheme 5



reported data.[27] The other two edges of the calcium trigonal plane are bridged with two oxygen atoms of two ketiminate ligands where their nitrogen atoms bind terminally to Ca(2) and Ca(3), respectively. The geometries surrounding Ca(2) and Ca(3) are both described as distorted trigonal bipyramidal with their axial angles of O(6)−Ca(2)−O(2) and O(6)−Ca(3)−O(3) at 153.07(8)° and 154.74(8)°, respectively. However, the environment of Ca(1) is different from those of Ca(2) and Ca(3), having its six coordination and forming a distorted octahedral geometry where the axes of O(5)−Ca(1)−O(1) and N(1)−Ca(1)−O(4) at 173.58(8)° and 176.81(8)° are close to linearity and the distorted axis O(5)−Ca(1)−O(1) is only at 144.85(8)°. A schematic drawing of the core structure of **5** is shown in Scheme 5 where the three Ca−Ca distances are about 3.34 Å.

Polymerization of ε-Caprolactone and L-Lactides. Compounds **1**−**5** have been attempted as catalysts for the ring-opening polymerization of ε-caprolactone and L-lactide. The results are presented in Table 3. Compound **3** has a low melting point which is not easy to handle at room temperature and therefore was not used as catalyst in these reactions. Compound **4** shows no activity toward ε-caprolactone and L-lactide in CH_2Cl_2 or THF even at 40 °C for 2 h. Since compound **2** shows a good activity (entry 2) toward ring-opening polymerization of ε-caprolactone with very high conversion, the pyrrolyl fragments in compounds **1** and **2** would be considered as

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Table 3. Polymerization of ε-Caprolactone (CPL) and L-Lactide (LA) Using Compounds **1**, **2**, and **5** as Initiators (I)

entry	[cat]	monomer	rxn temp/ time(m)	solvent	conversion (%)	activity[a]	$Mn_{,theor}$[b]	$Mn_{,cor}$[c]	PDI	f (%)[d]
1	**1**	CPL	40/5	CH_2Cl_2	91	124500	10387	36700	1.53	28
2	**2**	CPL	25/1	CH_2Cl_2	93	636100	10615	32000	1.53	33
3	**2**	CPL	25/2	THF	84	287300	9588	19500	1.64	49
4	**5**	CPL	25/5	THF	99	135400	11300	13000	1.43	87
5	**1**	LA	40/120	CH_2Cl_2	98	7100	14125	9900	1.35	143
6[e]	**1**	LA	40/60	CH_2Cl_2	96	13800	13836	17300	1.49	80
7	**2**	LA	25/20	CH_2Cl_2	95	41000	13692	11000	1.22	124
8	**2**	LA	25/40	THF	81	17500	11675	7200	1.23	162
9	**5**	LA	25/30	CH_2Cl_2	84	24200	12107	12000	1.14	101
10	**5**	LA	25/180	THF	83	4000	11963	5200	1.15	232

[a] $g_{pol}mol_{cat}^{-1}\cdot h^{-1}$. [b] $Mn_{,theor} = ([CPL]_0/[Ca]_0) \times 114.14 \times$ conversion (%) for CPL; $Mn_{,theor} = ([LA]_0/[Ca]_0) \times 144.13 \times$ conversion (%). [c] $Mn_{,cor} = 0.259\ Mn_{,GPC\text{-}St}^{1.073}$ for CPL[f]; $Mn_{,cor} = 0.58\ Mn_{,GPC\text{-}St}$ for LA[g]. [d] Initiator efficiency = $Mn_{,theor}/Mn_{,cor}$. [e] Isopropyl alcohol was added. [f] P. Dubois, P., I. Barakat, R. Jerome, P. Teyssie *Macromolecules*, **1993**, *26*, 4407. [g] J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun*. **1997**, *18*, 325.

nonspectrator ligands. The reaction initiated by compound **1**, which is a dimeric species, is slower, and therefore elevation of temperature is necessary during the polymerization (entry 1). Compounds **1** and **2** show low initiator efficiency (28 and 33%, respectively), and bring about PCL with fair PDI (polydispersity) value (= 1.51) in CH_2Cl_2 as solvent. However, while the polymerization reaction is initiated by compound **2** in THF, the initiator efficiency increases to 49% and the PDI of the resulting polymer also increases to 1.64 as well, presumably because of an unknown process resulting from the variation of coordination mode of THF to compound **2**. Compound **5** exhibits very good activity and high initiator efficiency (89%) toward ε-caprolactone polymerization. The PDI of the resulting polymer is fairly narrow (1.43). Because of inactivity of compound **4**, in compound **5** the ketiminate parts would be stationary spectrator ligands and the isopropoxide motifs would participate in the polymerization reaction.

Compounds **1**, **2**, and **5** also demonstrate good activity toward ring-opening polymerization of L-lactide with very high conversion. Unlike the poly(caprolactone), the polymerization rates of L-lactide by these complexes proceeded much slower than those of poly(caprolactone) with the reaction time ranging from 20 to 180 min as the conversion higher than 80% (entry 5−10). The initiator efficiency of these complexes is high (80−232%). The polymerization of L-lactide initiated by compounds **1**, **2**, and **5** in CH_2Cl_2 results in narrow PDI values (1.14−1.35) of polylactide. Similar to the results of poly(caprolactone), the order of the PDI value of the resulting polymers by these complexes is compound **1** > compound **2** > compound **5**. The trend might be attributed to the dimeric feature of compound **1** and the difference of the reaction activity between substituted pyrrolyl and isopropoxide motifs. Addition of isopropyl alcohol into the polymerization reaction initiated by **1** increases the reaction rate, decreases the initiator efficiency, and slightly broaden the PDI value of the resulting polymer. While THF was employed as solvent, the initiator efficiency of compounds **1** and **2** increases; however, the PDI values of PCL remain almost the same.

It is worthy to note that compound **5** catalyzed the ring-opening polymerization of L-lactide in CH_2Cl_2 with very high reactivity and also generated low PDI value of polylactide.

Experimental Section

General Procedure. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or glovebox. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature or at specific temperatures. Chemical shifts for ^1H and ^{13}C spectra were recorded in parts per million relative to the residual protons of $CDCl_3$ (δ 7.24, 77.0), CD_2Cl_2 (δ 5.30, 54.2), toluene-d_8 (2.30, 21.3), and C_6D_6 (δ 7.15, 128.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center of the NCHU. $Ca[N(SiMe_3)_2]_2(THF)_2$,[28] $[C_4H_3NH(2\text{-}CH_2NEt_2)]$,[29] and OCMeCHCMeNHAr[9] were prepared in a similar procedure as reported in the literature.

$[Ca\{N(SiMe_3)_2\}[\mu\text{-}\eta^1\text{:}\eta^5\text{-}\{C_4H_3N(2\text{-}CH_2NEt_2)\}]]_2$ (1). A 50 mL Schlenk flask charged with $Ca[N(SiMe_3)_2]_2(THF)_2$ (0.50 g, 0.99 mmol) and toluene (15 mL) was added a $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ (0.15 g, 1.00 mmol)/ toluene (10 mL) solution dropwise at 0 °C. The mixture was further stirred for 1 h, and the volatiles were removed under vacuum. The residue was recrystallized from a toluene solution at −20 °C for a couple of days to yield 0.108 g of final product. (31% yield). ^1H NMR (CD_2Cl_2, 258K): δ −0.061. (s, 36H, SiMe_3), 1.08 (t, 6H, NCH_2CH_3), 1.12 (t, 6H, NCH_2CH_3), 2.15 (m, 2H, NCH_2CH_3), 2.46 (m, 2H, NCH_2CH_3), 2.88 (m, 4H, NCH_2CH_3), 3.84 (dd, 4H, $-CH_2NEt_2$), 6.39 (s, 2H, pyrrolyl H), 6.49 (s, 2H, pyrrolyl H), 6.91 (s, 2H, pyrrolyl H). ^{13}C NMR (CD_2Cl_2, 258K): δ 4.7 (q, NSiMe_3), 7.6 (q, NCH_2CH_3), 11.1 (q, NCH_2CH_3), 44.5 (t, NCH_2CH_3), 46.5 (t, -CH_2NEt_2), 52.6 (t, -CH_2NEt_2), 109.1 (d, pyrrolyl *C*H), 111.2 (d, pyrrolyl *C*H), 127.7 (q, pyrrolyl *C*H), 136.8 (s, pyrrolyl C_{ipso}). This compound is very air sensitive and even after repeatedly performing the elemental analysis, no satisfactory data has been obtained.

$Ca[C_4H_3N(2\text{-}CH_2NEt_2)]_2(THF)_2$ (2). A 50 mL Schlenk flask charged with $Ca[N(SiMe_3)_2]_2(THF)_2$ (1.00 g, 1.98 mmol) and THF (15 mL) was added a $[C_4H_3NH(2\text{-}CH_2NEt_2)]$ (0.59 g, 3.90 mmol)/THF (10 mL) solution dropwise at 0 °C. The mixture was further stirred for 1 h, and the volatiles were removed under vacuum. The residue was recrystallized from a THF solution at −20 °C for a couple of days to yield 0.60 g of final product.

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(30) (a) Sheldrick, G. M. *SHELX97 − Programs for Crystal Structure Analysis: Structure Determination* (*SHELXS*); University of Göttingen: Göttingen, Germany, 1997;(b) Sheldrick, G. M. *SHELX97 − Programs for Crystal Structure Analysis: Refinement* (*SHELXL*); University of Göttingen, Göttingen, Germany, 1997.

(62.5% yield). ^{1}H NMR (C_6D_6, 344 K): δ 0.79 (s, 12H, NCH_2CH_3), 1.47 (t, 8H, THF), 2.54 (q, 8H, NCH_2CH_3), 3.58 (t, 8H, THF), 3.69 (s, 4H, $-CH_2NEt_2$), 6.25 (s, 2H, pyrrolyl H), 6.66 (s, 2H, pyrrolyl H), 7.05 (s, 2H, pyrrolyl H). ^{13}C NMR (C_6D_6, 344 K): δ 9.9 (q, NCH_2CH_3), 25.8 (t, THF), 45.7 (t, NCH_2CH_3), 53.1 (t, $-CH_2NEt_2$), 67.8 (t, THF), 107.7 (d, pyrrolyl *C*H), 109.8 (d, pyrrolyl *C*H), 128.3 (d, pyrrolyl *C*H), 135.5 (s, pyrrolyl C_{ipso}). This compound is very air sensitive and even after repeatedly performing the elemental analysis, no satisfactory data has been obtained.

[Ca(OCMeCHCMeNAr){N(SiMe$_3$)}]$_2$ (3). A 50 mL Schlenk flask charged with $Ca[N(SiMe_3)_2]_2(THF)_2$ (0.50 g, 0.99 mmol) and toluene (15 mL) was added a OCMeCHCMeNHAr (0.25 g, 0.96 mmol)/ toluene (10 mL) solution dropwise at 0 °C. The mixture was further stirred for 0.5 h, and the volatiles were removed under vacuum. The residue was recrystallized from a toluene solution at −20 °C for a couple of days to yield 0.25 g of final product. (57% yield). ^{1}H NMR (C_7D_8): δ 0.26 (s, 36H, $SiMe_3$), 1.34 (d, 12H, $CHMe_2$), 1.56 (s, 6H, C*Me*), 1.61 (d, 12H, $CHMe_2$), 2.21 (s, 6H, C*Me*), 3.04 (m, 4H, $CHMe_2$), 5.03 (s, 2H, CMeC*H*CMe), 7.14−7.31(s, 12H, Ph). ^{13}C NMR (C_7D_8): δ 6.3 (q, $SiMe_3$), 24.3 (q, *Me*), 25.2 (q, *Me*), 25.8 (q, *Me*), 29.6 (d, *C*HMe_2), 30.4 (q, *Me*), 101.7 (d, CMe*C*HCMe), 125.4 (d, Ph), 127.3 (d, Ph), 129.2 (d, Ph), 138.3 (s, Ph), 140.7 (s, Ph), 144.2 (s, Ph), 173.0 (s, *C*N), 174.8 (s, *C*O). $C_{46}H_{84}Ca_2N_4Si_4O_2$ (917.68) Calcd.: C 60.21, H 9.23, N 6.11 ; found: C 59.77, H 8.90, N 5.92.

[Ca(μ-OCMeCHCMeNAr)(OCMeCHCMeNAr)]$_2$ (4). A similar procedure as for syntheszing **3** was taken. $Ca[N(SiMe_3)_2]_2(THF)_2$ (0.50 g, 0.99 mmol) and OCMeCHCMeNHAr (0.5 g, 1.90 mmol) were used in the reaction. White crystals were obtained from a toluene solution (0.49 g, 85% yield). ^{1}H NMR (C_6D_6): δ 1.31−2.17 (m, 69H, CH_3), 2.98 (s, 3H, CH_3), 3.03−3.21 (m, 8H, $CHMe_2$), 4.73, 4.78,4.81, 4.84, 4.87 (m, 4H, MeCC*H*CMe), 7.00−7.21 (m, 12H, Ph). ^{13}C NMR (C_6D_6): δ 19.6−29.4 (CH_3, *C*HMe_2), 96.0−98.6 (MeC*C*HCMe), 101.1−147.4 (Ph), 166.8−195.9 (*C*N, *C*O). $C_{68}H_{96}Ca_2N_4O_4$ (1113.67) Calcd.: C 73.34, H 8.54, N 5.03 ; found: C 72.67, H 8.69, N 5.04.

Ca$_3$(μ-OCMeCHCMeNAr)$_2$(OCMeCHCMeNAr)(μ_3-O-^{i}Pr)$_2$(μ_2-O-^{i}Pr) (5). A 50 mL Schlenk flask charged with $Ca[N(SiMe_3)_2]_2(THF)_2$ (1.00 g, 1.90 mmol) and toluene (15 mL) was added a OCMeCHCMeNHAr (0.5 g, 1.90 mmol)/ toluene (10 mL) solution dropwise at 0 °C. The mixture was further stirred for 0.5 h at room temperature. The solution was then cooled to 0 °C, and a solution of isopropyl alcohol (0.147 mL, 1.90 mmol)/toluene (10 mL) was added dropwise and stirred for 0.5 h. The volatiles were removed under vacuum, and the residue was recrystallized from a toluene solution to yield 0.49 g of white crystals. (70% yield). ^{1}H NMR (C_6D_6): δ 1.00 (d, 6H, *Me*), 1.02 (d, 6H, *Me*), 1.12 (d, 6H, *Me*), 1.14 (d, 6H, *Me*), 1.22(d, 6H, *Me*), 1.29 (d, 9H, *Me*), 1.43 (d, 6H, *Me*), 1.48 (d, 9H, *Me*), 1.48 (s, 6H, C*Me*), 1.72 (s, 3H, C*Me*), 2.14 (s, 3H, C*Me*), 2.32 (s, 6H, C*Me*), 2.62 (m,1H, O*C*HMe_2), 2.85 (m, 2H, *CHMe*$_2$), 2.99 (m, 2H, *CH*Me_2), 3.50 (m, 3H, *CH*Me_2 + O*CH*Me_2), 4.45 (m, 1H, O*CH*Me_2), 5.00 (s, 2H, CMeC*H*CMe), 5.18 (s, 1H, CMeC*H*CMe), 6.99−7.19 (m, 9H, Ph). ^{13}C NMR (C_6D_6): δ 23.5, 24.0, 24.0, 24.2, 24.8, 25.0, 27.8, 28.1, 28.2, 28.3, 28.4, 28.5, 28.7, 62.4, 64.1, 64.2, 97.1, 97.5, 124.0, 124.1, 124.4, 125.3, 140.4, 140.8, 141.2, 144.6, 148.0, 169.9, 170.9, 180.5, 180.6. This compound is very air sensitive and even after repeatedly performing the elemental analysis, no satisfactory data has been obtained.

Polymerization. Polymerizations of ε-caprolactone and L-lactide were carried out in CH_2Cl_2 or THF solutions under a nitrogen-filled Schlenk line. Considering a typical synthetic method, initiator was first dissolved in 5 mL solvent, followed by the addition of caprolactone or lactide ([M]/[I] = 100); then it was stirred for a period of time to produce a gel- or solid-like polymer. The process continued until the mixture gradually quenched with acidified water (3% CH_3COOH), and the resulting solid was washed with hexane. It was dried to form a satisfactory yield.

Molecular weight of the polymers was determined on a gel permeation chromatography (GPC) instrument (Waters, RI 2414, pump 1515). M_n and M_w values were determined from calibration plots established with polystyrene standards.

Crystallographic Structural Determination of 1, 2, 3, 4, and 5. Crystal data collection, refinement parameter and bond lengths and angles are summarized in Tables 1 and 2, respectively. The crystals were mounted in capillaries and transferred to a goniostat and were collected at 150 K. Data were collected on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The structures of all complexes were determined by direct methods procedures in SHELXS,[30a] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[30b] For all the structures, the hydrogen atom positions were calculated, and they were constrained to idealized geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom.

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Supporting Information Available: Crystallographic data for compounds **1**−**5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.