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Alkaline earth metal complexes stabilized by amidine and guanidine ligands: synthesis, structure and their catalytic activity towards polymerization of *rac*-lactide

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A series of amidine ligands RAm^{DIPP} (R is backbone substituent, R = 2-methylpyridine (HL^1), N,N,2-trimethylaniline (HL^2), N,N-dimethylpropan-1-amine (HL)[3]; DIPP (2,6-diisopropylphenyl) is N substituent) and a (*Z*)-1,1-diethyl-2,3-bis(2-methoxyphenyl)guanidine ligand (HL^4) have been synthesized. Reaction of HL^1-HL^4 with Ca[N(SiHMe$_2$)$_2$](THF) or Ca[N(SiMe$_3$)$_2$](THF)$_2$, respectively, afforded complexes **1**-**8** (**1**: [L^{1}Am^{DIPP}Ca(SiHMe$_2$)$_2$]$_2$, **2**: L^{1}Am^{DIPP}CaN(SiMe$_3$)$_2$·(THF)$_2$, **3**: L^{2}Am^{DIPP}CaN(SiHMe$_2$)$_2$·(THF)$_2$, **4**: L^{2}Am^{DIPP}CaN(SiMe$_3$)$_2$·(THF), **5**: L^{3}Am^{DIPP}CaN(SiHMe$_2$)$_2$·(THF)$_2$, **6**: L^{3}Am^{DIPP}CaN(SiMe$_3$)$_2$·(THF)$_2$, **7**: [L^{4}CaN(SiHMe$_2$)$_2$]$_2$, **8**: [L^{4}CaN(SiMe$_3$)$_2$]$_2$). All the complexes were well-defined by NMR spectrum analyses and the molecular structures of **3** and **5**-**8** were further determined by single crystal X-ray diffraction analyses. In combination with an excess of PhOH as the chain transfer agent, complexes **1**-**8** catalyzed immortal ring-opening polymerization of *rac*-lactide in a controlled manner and exhibited moderate catalytic activity at room temperature. The end-group fidelity of the resultant polymer was certified by NMR and MALDI-TOF mass spectra.

Introduction

Well-defined heteroleptic Ae complexes have displayed remarkable catalysis in "immortal" ring-opening polymerization (*i*ROP) of bio-resourced cyclic esters[1], hydroamination[2], terminal alkyne coupling[3], hydrogenation[4] and so on. However, compared with the well-established transition metal based chemistry, the alkaline-earth metal based chemistry is still an infant. The development was impeded by the fact that the heteroleptic complexes Ae-Nu (Nu = nucleophilic group) readily decompose during deleterious Schlenk-type equilibria to generate the poorly reactive and ill-defined homoleptic [{L$_n$X}$_2$Ae] (where {L$_n$X}$^-$ is a monoanionic ancillary ligand) and [(AeNu$_2$)$_n$] species.[5] This issue has been preliminarily addressed by employing sterically demanding multi-dentate ligands, such as tris(pyrazolyl)borates,[6] aminotrop(on)iminates,[7] *β*-diketiminates,[2b,8] bis- or tris-(imidazolin-2-ylidene-1-yl)borate[9] and phenolate[1a,10]. However, suitable {L$_n$X}$^-$ ancillary ligands being able to stabilize {L$_n$X}Ae-Nu are still very scarce.

The bidentate amidinate and guanidinate ligands have been used to stabilize various metal ions across the periodic table of elements, since they can be easily modified by attaching substituents of various steric and electronic properties.[11] In addition, these anionic ligands have a common characteristic that the negative charge is delocalized to reduce their nucleophilicity, which effectively shields the alkaline earth cations and increases stability of the resultant complexes by avoiding reorganization and Schlenk equilibrium *etc* side reactions.[5c,11a,b,12] Indeed, amidinate ligands RAmAr (R is backbone substituent, Ar is N substituent) have successfully stabilized calcium hydride complexes. In addition, a type of tridentate amidinate ligand featuring a coordinating side-arm of N substituent has been explored for calcium metal.[13] While as far as we known, the backbone substituent of amidinate ligands containing coordinating heteroatoms have not been investigated even for transition metals, which should provide a useful platform for "tailoring" new versatile ligand systems due to its potential to form cage coordination environment.

Herein, we synthesized some novel amidine and guanidine ligands bearing different substituent groups on the backbone (HL$^{1-4}$, **Scheme 1** and **Chart 1**) and through their reaction with homoleptic calcium amide, Ca[N(SiHMe$_2$)$_2$]$_2$(THF) and Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$, respectively, to prepare a series of heteroleptic calcium complexes **1**-**8**. The catalytic behavior of these complexes towards immortal ring-opening polymerization of *rac*-lactide with an excess of phenol as the chain transfer agent, for the first time, is presented.

Results and Discussion

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† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra of thiourea (**I**), HL^4 and complexes **1**-**8**, crystal structure of guanidine ligand **HL^4**, crystallographic data and structure refinement details for **HL^4** and complexes **3**, **5**-**8**, ROP of *rac*-LA catalyzed by calcium complexes **1**-**8**. CCDC reference numbers 1835586 (**3**), 1835587 (**5**), 1835588 (**6**), 1854590 (**7**), 1835589 (**8**), 1852436 (HL^4)]. See DOI: 10.1039/x0xx00000x

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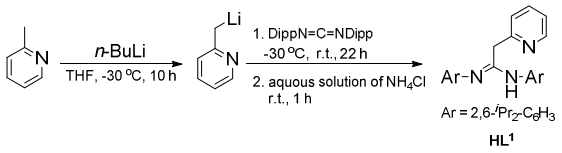
Synthesis of amidine and guanidine ligands (HL^{1-4})

In contrast to the classical route to synthesize N,N'-disubstituted amidines through imidoylchloride intermediates,[11a,14] the N,N'-disubstituted amidines with various backbone substitutents were prepared via reaction of N,N'-disubstituted carbodiimide with lithium alkyl species. Hence, HL^1 was synthesized through the following procedure (**Scheme 1**): 2-methylpyridine reacted with butyl lithium in THF to afford 2-pyridylmethyllithium. Then a THF solution of bis(2,6-diisopropylphenyl)carbodiimide was gradually transferred into the above mixture. After 22 h, an aqueous solution of ammonium chloride was added to terminate the reaction and HL^1 was isolated as white powder in 43%. The amino proton shows a broad resonance at 7.68 ppm in the ^{1}H NMR spectrum while a doublet at 3.63 ppm is assigned to the methylene protons.



Scheme 1 Syntheses of HL^1.

Following the similar procedure, HL^2 with a longer coordinating side arm (**Chart 1**) was prepared through employing N,N'-dimethyl-*o*-toluidine and bis(2,6-diisopropylphenyl)carbodiimide in a high yield (87%). The resonance belonged to methylene protons of HL^2 appears at 3.60 ppm comparable to that of HL^1. While the chemical shift of the amino proton exhibits at a relatively up field 6.84 ppm.

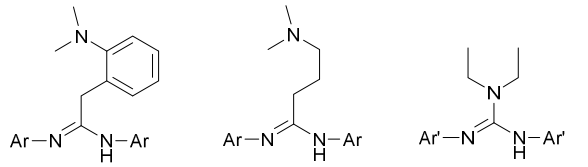
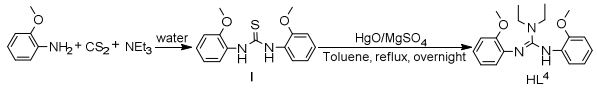


Chart 1 Structures of HL^2, HL^3 and HL^4.

Employing the above procedure to synthesize HL^3 with flexible side arm N,N-(dimethylamino)propyl (**Chart 1**), encountered a problem that reaction of butyl lithium with N,N-(dimethylamino)propyl chloride can't generate the expected lithium salt. Hence, instead of lithium salt, a Grignard reagent (N,N-(dimethylamino)propyl)magnesium chloride was used to react with bis(2,6-diisopropylphenyl)carbodiimide to afford HL^3 as light yellow powder in a medium yield (67%). The resonance of amino proton within HL^3 shows at a much higher field (5.29 ppm) as compared to those of HL^1 and HL^2. Meanwhile, the methylene protons gives a triplet at 2.28 ppm shifting upfield due to the absence of electron withdrawing effect of the phenyl group.

To introduce an additional coordination atom, we chose 2-methyloxy aniline to synthesize N,N'-bis(2-methoxyphenyl)methanediimine according to the literature procedure.[15] However, for the first step (**Scheme 2**), reaction of CS_2 with 2-methyloxy aniline and triethylamine in water always gave the corresponding thiourea (**I**) contaminated by the same amount of triethylamine evidenced by the ^{1}H NMR spectrum analysis, since the integral intensity ratio of resonances at 3.05 ppm, 1.35 ppm and 3.77 ppm assigned to methylene and methyl protons of triethylamine and methyl protons of methoxy group, respectively, is 2:3:2 (**Fig. S1**). Treatment of the above product with mercuric oxide and magnesium sulfate in refluxing toluene solution afforded a pale yellow solid. In the ^{1}H NMR spectrum, resonances at 3.40 ppm and 1.21 ppm belonged to methylene and methyl protons of triethylamine appear again. To our surprise, the integration intensity ratio of them to the singlet at 3.67 ppm assigned to methyl protons of methoxy group is 5:3, suggesting that there are only two ethyl groups (**Fig. S2**). X-ray diffraction analysis indicated that the afforded product is a guanidine compound, HL^4 (**Chart 1**, **Fig. S3**). It exists exclusively in the Z_{anti} configuration. There is unequivocal difference of ca. 0.118 Å in the lengths of the C-N and the C=N bonds, which is a typical bond distances of guanidine ligands.[5c,16] The reason for the generation of HL^4 is unclear since employing 2,6-diisopropyl aniline as the reagent, the corresponding carbodiimide was exclusively isolated even in the presence of triethylamine.



Scheme 2 Syntheses of HL^4.

Synthesis and characterization of complexes 1-8

Following the remarkable work reported by Anwander that the Si-H···Ln agostic interaction facilitates to stabilize the complexes based on rare-earth elements,[17] Yann[10e,18] has implemented $N(SiHMe_2)_2^-$ amido groups to prepare $Ae[N(SiHMe_2)_2]_2(THF)_n$ (Ae = Ca, n = 1; Sr, n = ⅔; Ba, n = 0)[10e] and has shown that Ae···H secondary interactions are very effective for the stabilization of electrophilic Ae^{2+} species. Thus we initially attempted to prepare heteroleptic compounds by treatment of $Ca[N(SiHMe_2)_2]_2(THF)$ with an equimolar amount of HL^1 through amine elimination reaction. A white precipitate formed slowly upon stirring at room temperature, which was collected by filtration after the suspension being stirred overnight. In the ^{1}H NMR spectrum recorded in C_6D_6 at room temperature, the Si-H resonance at δ 5.17 is noticeably deshielded as compared to that in the free amine ($NH(SiHMe_2)_2$: δ 4.70 ppm). The absence of resonances at 3.75 and 1.35 ppm indicates that there is no coordination of THF molecule. Hence, the *ortho* proton of pyridyl group exhibits a signal at 8.20 ppm downfield shifting than that in the neutral ligand (8.17 ppm), suggesting that the pyridyl group may coordinate to the calcium center.[19] The methyl protons of isopropyl groups show two doublets at 1.28 and 1.23 ppm, meaning the two asymmetric phenyl groups. The above characterization precluded the possibility of complex **1** being monomeric structure. Hence, we speculated that complex **1** is a dimer with a center Ca_2N_2 planar core where the two metal centers are bridged by $N_{pyridyl}$ atoms (**Scheme 3**), leading to the poor solubility of **1**. While reaction of HL^1 with $Ca[N(SiMe_3)_2]_2(THF)_2$ afforded complex **2** with good solubility even in hexane. ^{1}H NMR spectrum analysis indicated that there exists two coordinating THF

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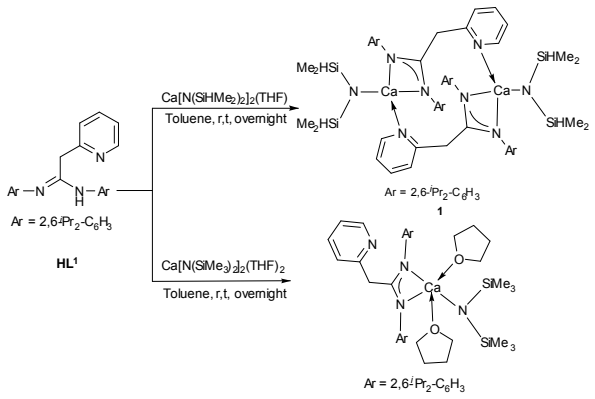
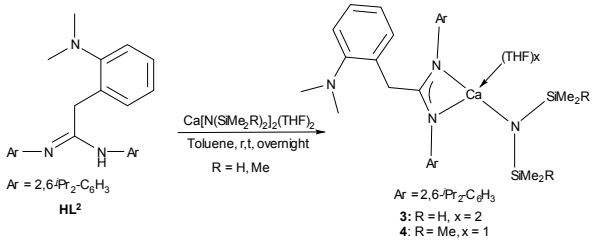
molecules. The *ortho* proton of pyridyl group exhibits an upfield shift at 6.09 ppm, suggesting the absence of pyridyl coordination to the metal center, which corresponds to a monomeric species of complex **2**.



Scheme 3 Syntheses of complexes **1** and **2**.

HL[2] with a longer coordinating side arm reacted with $Ca[N(SiHMe_2)_2]_2(THF)$ to afford a stable monomeric complex **3** confirmed by X-ray diffraction analysis (**Fig. 1**). The calcium center is capped by the bidentate NCN ligand in a η^3-coordination fashion, two THF molecules and one amide group. Compound **3** also presents an evident case of stabilization by Ca···H–Si agostic interaction, as demonstrated by the asymmetry in the Ca–$N(SiHMe_2)_2$ fragment, which is reflected by the discrepancy between the large Ca1-N4-Si2 and much more acute Ca1-N4-Si1 angles (130.94 ° and 101.19 °), corresponding to a much shorter Ca1-Si1 distance (3.151 Å) with respect to Ca1-Si2 (3.679 Å). Furthermore, the co-planar Ca1, N4, Si1 and H1A atoms also attest the agostic Ca1···H1-Si1 interaction[1a]. The $^1J_{(Si,H)}$ coupling constant of 163.3 Hz is further indicative of weak agostic Ca···H–Si interaction, which is in accordance with previous report for alkaline earth metal complexes[1a]. While treatment of HL[2] with the bulky $Ca[N(SiMe_3)_2]_2(THF)_2$ generated complex **4** that contains only one THF molecule, since the integration intensity ratio of resonances at 3.89 ppm and 1.97 ppm assigned to CH_2 and $N(CH_3)_2$, respectively, is 1:3. The chemical shift (1.97 ppm) of methyl protons of $N(CH_3)_2$ is nearly the same with that found in complex **3**, suggesting that N atom of $N(CH_3)_2$ doesn't coordinate to the calcium center.



Scheme 4 Syntheses of complexes **3** and **4**.

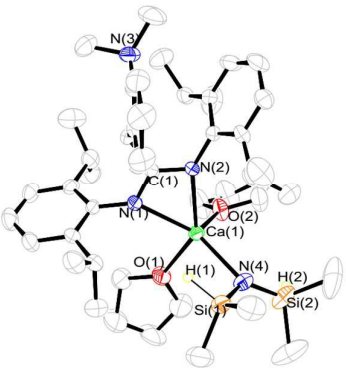
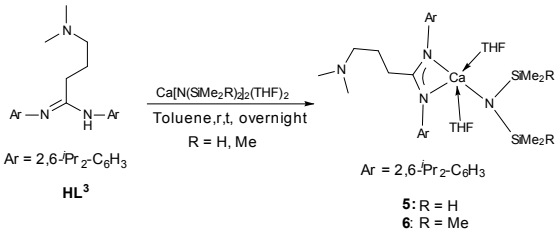
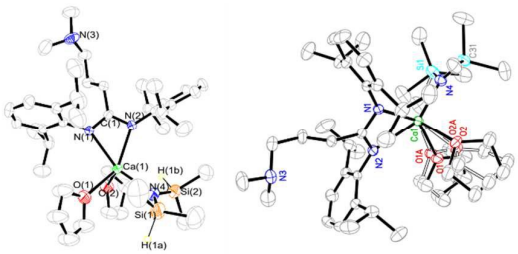


Fig. 1 Crystal structure of complex **3**. Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms except Si-H are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for complex **3**: Ca1-N1 2.417, Ca1-N2 2.426, Ca1-O1 2.388, Ca1-O2 2.375, Ca1-N4 2.358, Ca1-H1 2.608, Ca1-Si1 3.151, Ca1-Si2 3.679, Ca1-N4-Si1 101.19, Ca1-N4-Si2 130.94

HL[3] with a flexible coordination arm reacted with $Ca[N(SiHMe_2)_2]_2(THF)$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ to give the corresponding complexes **5** and **6**, both possess the similar monomeric structure determined by X-ray analyses (**Fig. 2**). While the $^1J_{(Si,H)}$ coupling constant of 147.4 Hz in **5** falls in the range indicative of moderate agostic Ca···H–Si interactions (140-160 Hz) observed in lanthanide complexes[20]. An amino moiety, a coordinating *N,N*-bidentate ligand, and two solvated THF molecules, generate a distorted square pyramid environment around the calcium center. The ligand adopts a η^3-coordination fashion around the center metal, while the N3 atom still doesn't coordinate to the central metal, which might be attributed to the steric hindrance of the isopropyl in phenyl ring.



Scheme 5 Syntheses of complexes **5** and **6.**



Complex 5 **Complex 6**

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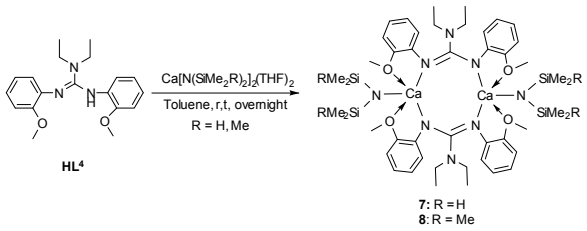
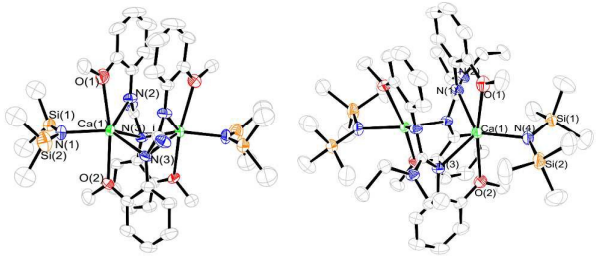
Fig. 2 Crystal structures of complexes **5** and **6**. Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms except Si-H are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for complex **5**: Ca1-N1 2.434, Ca1-N2 2.397, Ca1-O1 2.371, Ca1-O2 2.389, Ca1-N4 2.326, Ca1-H1b 2.971, Ca1-Si2 3.212, Ca1-Si1 3.564, Ca1-N4-Si2 105.68, Ca1-N4-Si1 125.63; complex **6**: Ca1-N2 2.454, Ca1-N1 2.405, Ca1-O1 2.406, Ca1-O2 2.389, Ca1-N4 2.332, Ca1-Si1 3.506, Ca1-Si2 3.394, Ca1-N4-Si1 114.33, Ca1-N4-Si2 120.92

When employing the guanidine compound HL[4] as the ligand scaffold, the corresponding heteroleptic calcium complexes **7** and **8** are C_2-symmetric dimers (**Fig. 3**). A NCN unit bridges two metal centers via two separated N atoms. These two NCN planes locate in *trans* configuration and are almost perpendicular to Ca1-Ca1' axial. Each calcium center sits in one distorted trigonal bipyramid geometry with two O atoms in the axial direction and three N atoms in the equatorial plane. Thus each guanidinate ligand acts as a κ^1-O: κ^1-N/κ^1-N: κ^1-O tetradentate mode. This kind of coordination mode is rare in alkaline earth metal complexes. The averaging bond length between calcium and N atoms of NCN units in complex **7** (2.3875 Å) is slightly shorter than those found in amidinate ligated complexes **3** (2.4215Å) and **5** (2.4155 Å). While the Ca1-N4 (2.437 Å) and Ca-O (2.5880 Å) bond distances are much longer compared to those within **3** (Ca1-N4: 2.358 Å, Ca-O: 2.3815 Å) and **5** (Ca1-N4: 2.326 Å, Ca-O: 2.3800 Å). The above trend is also observed between **8** and **6**.



Scheme 6 Syntheses of complexes **7** and **8.**



Complex 7 **Complex 8**

Fig. 3 Molecular structures of complexes **7** (left) and **8** (right). Thermal ellipsoids are drawn at the 35% probability level. All hydrogen atoms and the ethyl group of NEt_2 for **7** are omitted for clarity. All hydrogen atoms for **8** are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for complex **7**: Ca1-N3i 2.377, Ca1-N2 2.398, Ca1-O2 2.629, Ca1-O1 2.547, Ca1-N1 2.437, Ca1-Si2 3.208, Ca1-Si1 3.504, Ca1-N1-Si2 105.79, Ca1-N1-Si1 121.81; complex **8**: Ca1-N3 2.437, Ca1-N1 2.403, Ca1-O2 2.544, Ca1-O1 2.637, Ca1-N4 2.360, Ca1-Si1 3.527, Ca1-Si2 3.447, Ca1-N4-Si1 120.45, Ca1-N4-Si2 116.07

Ring-opening polymerization of *rac*-LA initiated by calcium complexes 1-8

The highly efficient strategy of preparing biodegradable and biocompatible polylactide (PLA) from the bio-resourced lactic acid (LA) has been established recently named "immortal ring-opening polymerization",[21] which overcomes the vital drawback of low catalytic efficiency for the conventional coordination polymerization and provides PLA in a highly efficient mode of "one metal-active species multiple polymer chains" with very low metal residue.[22] Meanwhile, the molecular weight and the molecular weight distribution of the resultant polymer are precisely controlled according to the feed of the chain transfer agent. Noteworthy is that the polymer chain ends are automatically functionalized by the transfer agent. To date, the most suitable and widely investigated chain transfer agents (CTAs) are small molecular alcohols or polymeric alcohols.[23] No reports have been related to a phenol as a CTA because its acidity is much stronger than the alcohols, which might abstract the ligand from the central metal. However, many antimicrobial agents contain phenolic hydroxyl group rather than alcoholic hydroxyl group, like chromene and its derivatives, which have been used for antimicrobial[24], antioxidant[25], anticancer[26], anthelmintic[27], congnitive functions enhanced[28] and anti-inflammatory[29]. Therefore, investigation of phenol as the chain transfer agent of *i*ROP is very attractive.

In the presence of 5 equiv. of phenol, the ability of heteroleptic complexes **1-8** to promote the ring-opening polymerization of *rac*-LA was examined (**Table 1**, entries 1-8). All the binary catalytic systems exhibited moderate catalytic activities by giving polylactides with relative narrow molecular weight distributions (M_w/M_n = 1.27-1.50). The observed molecular weights are in good agreement with the calculated ones, attesting of efficient chain transfer between the growing and resting (macro)alcohols, as expected for effective *i*ROP processes (**Table 1**, entries 1-8). On contrary, the homoleptic calcium complexes $Ca[N(SiHMe_2)_2]_2(THF)$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ yielded PLAs with significantly broader molecular weight distributions (M_w/M_n = 1.98-2.05) (**Table 1**, entries 9 and 10), suggesting that the ligand wasn't abstracted from the metal center by the phenol. Independently of the nature of the ancillary ligand, slower rates were observed with $N(SiMe_3)_2^-$ bound to the metal center than with $N(SiMe_2H)_2^-$. That was unexpected for the immortal ROP of *rac*-LA performed in the presence of an excess of transfer agent (PhOH) since following rapid protonolysis of the Ca–Nu and/or the initial monomer insertion, all active species have the same identity. The influence of the chain transfer agent was then probed by using complex **2** (**Table 1**, entries 11-14). Under the same monomer-to-Ca ratio (500:1), the molecular weight of the resultant PLA decreased from 3.15×10^4 Da to 0.33×10^4 Da with increasing the chain transfer agent loading from 1 to 20 equiv. relative to $[Ca]_0$, consistent with the calculated one. While keeping the CAT-to-Ca ratio at a constant, the molecular weight distributions of the afforded PLA became broader and the discrepancies between calculated and observed molecular weights became larger with increasing the *rac*-lactide loading from 200 to 1000 equiv. relative to $[Ca]_0$ (**Table 1**, entries 15 and 16). This might be due to the serious transesterification. The PLA afforded under

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low monomer loading (**Table 1**, entry 16) was used to analyze the end-group fidelity that is crucial to evaluate the efficiency of a catalyst system for the *i*ROP of cyclic esters. The polymer sample was characterized by ^{1}H NMR spectroscopy (**Fig. 4**). The polymer chains are capped by the hydroxyl group at one end evidenced by giving the resonance at 2.70 ppm and *Ph*O from chain transfer agent PhOH at the other end by giving the multiplets at 7.38 and 7.08 ppm assignable, which is a typical feature of a polymer obtained by coordination-insertion mechanism. This result was further corroborated by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (**Fig. 5**). The MALDI-TOF mass spectrum consists of one series of molecular ion peaks, which presumably correspond to the linear PLA with PhO-/-OH as the chain ends. The MALDI-TOF mass spectrum also shows that the oligomers with a molecular weight interval of 72.06 arising from the intermolecular transesterification.

Table 1 ROP of *rac*-LA catalyzed by calcium complexes **1**-**8**/PhOH.[a]

entry	cat.	$[M]_0/[cat]_0/[CTA]_0$	Conv.[b] (%)	$M_{n,calcd}$[c] (10^4)	$M_{n,exp}$[d] (10^4)	M_w/M_n[d]
1	**1**	500/1/5	79	1.14	1.30	1.47
2	**2**	500/1/5	62	0.89	0.98	1.27
3	**3**	500/1/5	92	1.32	1.51	1.36
4	**4**	500/1/5	68	1.06	0.98	1.42
5	**5**	500/1/5	87	1.25	1.38	1.50
6	**6**	500/1/5	73	1.05	0.97	1.39
7[e]	**7**	500/1/5	89	1.28	1.62	1.43
8[e]	**8**	500/1/5	82	1.18	1.26	1.31
9[f]	**A**	500/1/5	79	1.14	0.97	1.98
10[g]	**B**	500/1/5	74	1.07	0.92	2.05
11	**2**	500/1/1	46	3.31	3.15	1.32
12	**2**	500/1/2	62	2.23	2.31	1.33
13	**2**	500/1/10	60	0.43	0.60	1.35
14	**2**	500/1/20	57	0.21	0.33	1.34
15	**2**	1000/1/10	51	0.74	1.05	1.48
16	**2**	200/1/10	89	0.26	0.28	1.17

[a] Cat.: 10 μmol, $[M]_0$: 1.0 M, Solvent: THF, Temperature: 25 °C, Time: 12 h. [b] Determined by ^{1}H NMR spectrum. [c] $M_{n,calcd} = [M]_0/[CTA]_0 \times 144.13 \times$ conv. (%). [d] Determined by GPC against polystyrene standard, M_n using a correcting factor for polylactides (0.58). [e] cat.: 5 μmol. [f] A = $Ca[N(SiHMe_2)_2]_2(THF)$. [g] B = $Ca[N(SiMe_3)_2]_2(THF)_2$.

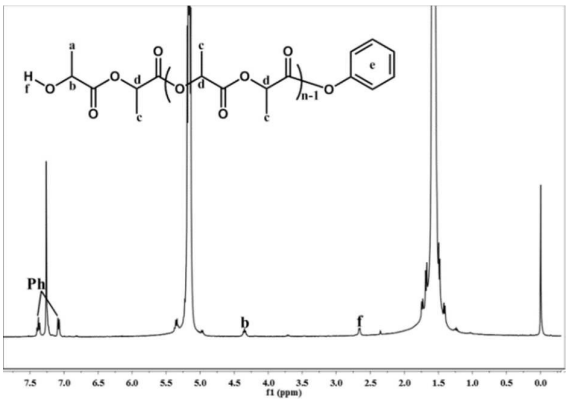

Fig. 4 ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of a low molecular weight ($M_{n,GPC}$ = 2 800 g·mol^{-1}, M_w/M_n = 1.17) prepared with the binary catalyst **2**/PhOH (**Table 1**, entry 16).

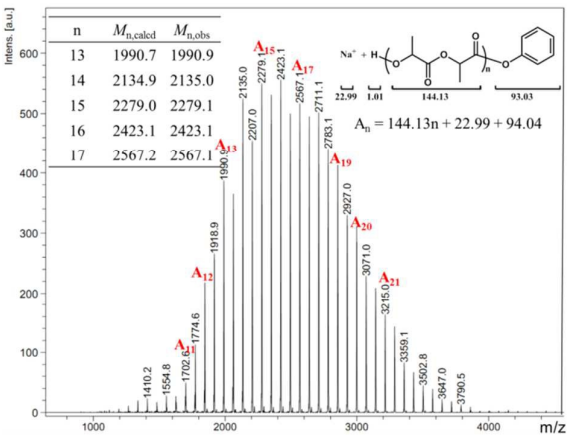

Fig. 5 MALDI-TOF mass spectrum (Na^+) of a PLA sample ($M_{n,GPC}$ = 2 800 g·mol^{-1}, M_w/M_n = 1.17) prepared with the binary catalyst **2**/PhOH ($[LA]_0/[\mathbf{2}]_0/[PhOH]_0$ = 200/1/10) (A_n = 144.13n + 22.99 + 94.04, where n is the degree of polymerization, M_{Na} = 22.99 g·mol^{-1}, M_{LA} = 144.13 g·mol^{-1} and M_{PhOH} = 94.04 g·mol^{-1}).

Conclusions

A series of novel amidine ligands RAm^{DIPP} (HL^{1-3}) and a guanidine ligand (HL^4) have been prepared and characterized. A large family of heteroleptic silylamido alkaline earth metal complexes **1**-**8** supported by these novel amidinate ligands and the guanidinate ligand have been developed. The solvation and aggregation of the afforded complexes were related to the flexibility of the substituent. Reaction of HL^1 bearing rigid substituent (R = 2-methylpyridine) with $Ca[N(SiHMe_2)_2]_2(THF)$ afforded an unsolvated dimer. While, treatment of HL^2 and HL^3 containing flexible substituents (R = N,N,2-trimethylaniline or N,N-dimethylpropan-1-amine) with $Ca[N(SiMe_2X)_2]_2(THF)_2$ (X = H, Me), respectively, gave THF-solvated monomeric complexes. The guanidinate calcium complexes **7** and **8** are

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dimers bearing a rare κ^1-O:κ^1-N/κ^1-N:κ^1-O ligand coordination mode, which is ascribed to the small steric hindrance. The successful isolation of these complexes provides a new avenue for the synthetic organometallic chemists to design stable alkaline earth metal complexes. These complexes exhibit moderate activities and an immortal manner toward the ROP of *rac*-lactide in the presence of PhOH as the chain transfer agent, for the first time. This provides a convenient approach to binding functional phenolic hydroxyl group to the biocompatible polymers.

Conflicts of interest

There are no conflicts to declare.

Experiment section

Materials

All operations were carried out under a dry nitrogen atmosphere using Schlenk techniques or in a nitrogen gas filled MBraun glovebox. Solvents were reagent grade, dried by standard methods and distilled under nitrogen prior to use. Toluene was purified using an SPS Braun system. THF was dried by distillation over sodium with benzophenone as indicator under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. Phenol was purchased from Aldrich and dried over by calcium hydride prior to distillation. Calcium iodide was purchased from Aldrich and stored in a glovebox. $Ca[N(SiHMe_2)_2]_2(THF)$ or $Ca[N(SiMe_3)_2]_2(THF)_2$ can be prepared via salt metathesis involving treatment of the metal halides with alkali metal amide,[30] which is prepared by adopting the metathetical procedure for the synthesis of $Ba[N(SiMe_3)_2]_2(THF)_2$. *rac*-LA was recrystallized with dry ethyl acetate three times. Glassware and flasks using in the polymerization were dried in an oven at 115 ^oC overnight and exposed to a vacuum-nitrogen cycle three times.

Techniques

Calcium complexes for NMR measurements were prepared in NMR tubes and sealed with paraffin film in the glovebox. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 (FT, 400 MHz for ^1H, 100 MHz for ^{13}C) spectrometer. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC).The MALDI-TOF mass spectrum was obtained with a Bruker Daltonic MicroFlex LT at the National Analytic Research Center of the Changchun Institute of Applied Chemistry (CIAC). The number-molecular weight (M_n) and weight distribution (PDI) of the polymers were measured using a TOSOH HLC 8220 GPC instrument at 40 ^oC with THF as eluent with a flow rate of 0.35 mL min^{-1}. Note that the values were relative to polystyrene standards.

X-ray Crystallographic Study

Crystal for X-ray analysis was obtained as described in the following preparations. The crystal was manipulated in a glovebox. A suitable single crystal of complexes was sealed in a thin-walled glass capillary, and the data collection was performed at -88.5 ^oC on a Bruker SMART APEX diffractometer with a CCD area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection for single crystal of HL^4 ligand was performed at 23 ^oC on a Bruker SMART APEX diffractometer with a CCD area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit-cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. All calculations were carried out using the SHELXL-2014/7 program. The molecular structure was resolved by using the ORTEP program. The cif and checkcif files of complexes are given as ESI.

A typical procedure for polymerization of *rac*-LA

A typical polymerization procedure (**Table 1**, entry 1) can be described as follows. Polymerizations of *rac*-LA were carried out in a 25 mL flask under a nitrogen atmosphere. A 3 mL flask was charged with a solution of complex **1** and phenol as chain transfer agent (CTA), prepared previously by addition of CTA to complex **1** in 2 mL of THF. Next, the solution was added to a stirred solution of *rac*-LA in THF at 25 ^oC. The polymerization was stirred for 12 h and then quenched by adding several drops acidified ethanol. Then polymers were precipitated with abundant ethanol, collected, and dried at 45 ^oC under a vacuum to a constant weight.

Synthesis of pro-ligands and representative complexes

Synthesis of N,N'-bis(2,6-diisopropylphenyl)-2-(2-methylpyridyl)acetimidamide (HL^1). The DippN=C=NDipp was synthesized according to a previous report.[15] Under a nitrogen atmosphere, ^{n}BuLi (0.206 mmol) was added dropwise to a stirred solution of 2-methylpyridine (0.206 mmol) in THF at -30 ^oC. During addition, the color of the solution changed to red from colorless. The mixture was stirred 10h. Then DippN=C=NDipp was added to above solution and reacted for 2 h at -30 ^oC and 22h at room temperature, then quenched with NH_4Cl aqueous solution. The insoluble white solid was removed by filtration, and the filtrate was extracted with CH_2Cl_2 twice, collected the organic phase, and dried with anhydrous $MgSO_4$ overnight. Removing the solvent under reduced pressure and recrystallization with hexane gave a white powder (yield: 43 %). ^1H NMR ($CDCl_3$, 400 MHz, 25 ^oC): δ 8.57 (d, 1H, C_5H_4N), 7.68 (brs, 1H, N*H*), 7.63 (t, 1H, Ar-*H*), 7.22 (m, 2H, Ar-*H*), 7.16 (m, 2H, Ar-*H*), 7.05 (d, 2H, Ar-*H*), 6.99 (m, 2H, Ar-*H*), 3.63 (d, 2H, CH_2), 3.14 (sept, 2H, $CH(CH_3)_2$), 2.97 (sept, 2H, $CH(CH_3)_2$), 1.30-1.21 (m, 5H, $CH(CH_3)_2$), 1.18 (d, 7H, $CH(CH_3)_2$), 1.09 (d, 5H, $CH(CH_3)_2$), 1.01 (d, 7H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 ^oC): δ 156.61 (s, N*C*N), 152.68 (s,

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C_5H_4N), 149.31 (s, *Ar*), 146.92 (s, *Ar*), 145.93 (s, *Ar*), 139.30 (s, *Ar*), 137.12 (s, *Ar*), 134.55 (s, *Ar*), 127.44 (s, *Ar*), 124.18 (s, *Ar*), 123.05 (s, *Ar*), 122.72 (s, *Ar*), 122.32 (s, *Ar*), 122.04 (s, *Ar*), 38.33 (s, CH_2), 28.77 (s, $CH(CH_3)_2$), 27.93 (s, $CH(CH_3)_2$), 23.89 (s, $CH(CH_3)_2$), 23.47 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{31}H_{41}N_3$: C, 81.71; H, 9.07; N, 9.22. Found: C, 81.63; H, 8.99; N, 9.24.

Synthesis of HL^2

HL^2 was synthesized using the similar method as HL^1 (yield: 87 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ^{o}C): δ 7.23 (m, 1H, Ar-*H*), 7.19 (d, 1H, Ar-*H*), 7.17 (d, 1H, Ar-*H*), 7.13 (d, 2H, Ar-*H*), 7.08 (d, 2H, Ar-*H*), 7.05-7.04 (m, 2H, Ar-*H*), 6.98 (m, 1H, Ar-*H*), 6.84 (brs, 1H, N*H*), 3.60 (d, 2H, CH_2), 3.21 (sept, 2H, $CH(CH_3)_2$), 3.10 (sept, 2H, $CH(CH_3)_2$), 2.73 (s, 6H, $N(CH_3)_2$), 1.33 (d, 8H, $CH(CH_3)_2$), 1.19 (d, 3H, $CH(CH_3)_2$), 1.15 (d, 3H, $CH(CH_3)_2$), 1.04 (d, 7H, $CH(CH_3)_2$), 1.00 (d, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): δ 155.01 (s, N*C*N), 152.83 (s, Ar), 146.95 (s, Ar), 146.38 (s, Ar), 139.17 (s, Ar), 134.51 (s, Ar), 131.80 (s, Ar), 128.40 (s, Ar), 127.47 (s, Ar), 124.38 (s, Ar), 123.50 (s, Ar), 123.18 – 122.91 (m, Ar), 122.74 (s, Ar), 122.22 (s, Ar), 120.26 (s, Ar), 45.30 (s, $N(CH_3)_2$), 33.70 (s, CH_2), 28.68 (s, $CH(CH_3)_2$), 28.02 (s, $CH(CH_3)_2$), 24.26 (s, $CH(CH_3)_2$), 23.36 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{34}H_{47}N_3$: C, 82.04; H, 9.52; N, 8.44. Found: C, 82.12; H, 9.41; N, 8.53.

Synthesis of HL^3

(3,3-(dimethylamino)propyl)magnesium chloride was synthesized according to a previous report.[31] The same method to obtain the light yellow powder of HL^3 (yield: 67 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ^{o}C): δ 7.24 (d, 1H, Ar-*H*), 7.14 (q, 4H, Ar-*H*), 7.03 (d, 1H, Ar-*H*), 5.29 (brs, 1H, N*H*), 3.15 (m, 4H, $CH(CH_3)_2$), 2.28 (t, 2H, CH_2), 2.16 (s, 6H, $N(CH_3)_2$), 2.05 (t, 2H, CH_2), 1.90 (quint, 2H, CH_2), 1.31 (d, 6H, $CH(CH_3)_2$), 1.27 (d, 6H, $CH(CH_3)_2$), 1.20 (d, 6H, $CH(CH_3)_2$), 1.01 (d, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): δ 154.91 (s, N*C*N), 147.19 (s, *Ar*), 144.22 (s, *Ar*), 139.14 (s, *Ar*), 133.38 (s, *Ar*), 128.27 (s, *Ar*), 123.66 (s, *Ar*), 123.10 (s, *Ar*), 122.94 (s, *Ar*), 59.54 (s, CH_2), 45.49 (s, $N(CH_3)_2$), 29.24 (s, CH_2), 28.48 (s, $CH(CH_3)_2$), 28.25 (s, $CH(CH_3)_2$), 25.09 (s, $CH(CH_3)_2$), 24.43 (s, $CH(CH_3)_2$), 24.13 (s, CH_2), 23.09 (s, $CH(CH_3)_2$), 22.43 (s, $CH(CH_3)_2$). Anal. Calcd for $C_{30}H_{47}N_3$: C, 80.12; H, 10.53; N, 9.34. Found: C, 80.21; H, 10.39; N, 9.27.

Synthesis of (*Z*)-1,1-diethyl-2,3-bis(2-methoxyphenyl)guanidine (HL^4).

*Synthesis of thiourea compound (**I**).* Carbon disulphide (50 mmol) was added dropwise to a stirred mixture of o-Anisidine (100 mmol) and NEt_3 (100 mmol) in 100 mL of water at room temperature. The reaction mixture was stirred for 1 h at room temperature and then heated to 90 ^{o}C for 14 h. After re-cooling the reaction mixture to room temperature, it was poured into 100 mL of CH_2Cl_2, following which the organic layer was separated and dried over $MgSO_4$. After filtration, the filtrate was concentrated and stored at -30 ^{o}C to afford a white powder under reduced pressure (yield: 81%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ^{o}C): δ 8.05 (brs, 2H, N*H*), 7.98-7.96 (d, 2H, Ar-*H*), 7.14 (t, 2H, Ar-*H*), 6.95 (t, 2H, Ar-*H*), 6.89-6.87 (d, 2H, Ar-*H*), 3.77 (s, 6H, OCH_3), 3.05 (q, 6H, CH_2CH_3), 1.35 ppm (t, 9H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): δ 178.13 (*C*=S), 151.11 (*Ar*), 126.30 (*Ar*), 123.84 (*Ar*), 120.21 (*Ar*), 55.52 (OCH_3), 45.68 ($N(CH_2CH_3)_3$), 8.42 ($N(CH_2CH_3)_3$). Anal. Calcd for $C_{21}H_{31}N_3O_2S$: C, 64.75; H, 8.02; N, 10.79. Found: C, 64.83; H, 8.17; N, 10.64.

Synthesis of HL^4. A mixture of the above thiourea compound (**I**) (10 mmol), HgO (20 mmol) and anhydrous $MgSO_4$ (24 mmol) in 250 mL of toluene was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered and the filtrate concentrated to dryness to afford a pale yellow solid (yield: 51%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ^{o}C): δ 7.19 (d, 1H, Ar-*H*), 7.04-6.96 (m, 1H, Ar-H), 6.82-6.79 (m, 4H, Ar-*H*), 6.77-6.75 (m, 2H, Ar-*H*), 6.01 (s, 1H, N*H*), 3.66 (s, 6H, OCH_3), 3.39 (q, 4H, CH_2CH_3), 1.21 (t, 6H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 ^{o}C): δ 150.46 (S, N*C*(N)N), 120.93 (brs, *Ar*), 110.82 (s, *Ar*), 55.49 (s, OCH_3), 42.36 (s, $N(CH_2CH_3)_2$), 13.13 (s, $N(CH_2CH_3)_2$). Anal. Calcd for $C_{19}H_{25}N_3O_2$: C, 69.70; H, 7.70; N, 12.83. Found: C, 69.89; H, 7.64; N, 12.71.

Synthesis of complex 1

Under a nitrogen atmosphere, to a stirred solution of $Ca[N(SiHMe_2)_2]_2(THF)$ (1.05 mmol) in 8 mL toluene was added the solution of ligand HL^1 (1 mmol) in 10 mL of toluene at room temperature. The reaction mixture was stirred at room temperature for overnight and was concentrated to approximately 1 mL, and was added several drops of hexane. The residue was cooled to -30 ^{o}C over several days to afford yellow powders (yield: 53%). ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 8.20 (d, 1H, C_5H_4N), 7.12 (m, 5H, Ar-*H*), 7.13 (d, 1H, Ar-*H*), 6.65 (t, 1H, C_5H_4N), 6.37 (t, 1H, C_5H_4N), 5.66 (d, 1H, C_5H_4N), 5.17 (s, $^1J_{Si,H}$ =147.5 Hz, 2H, Si*H*), 3.65 (s, 2H, CH_2), 3.57 (sept, 4H, $CH(CH_3)_2$), 1.28 (d, 12H, $CH(CH_3)_2$), 1.23 (d, 12H, $CH(CH_3)_2$), 0.17 (s, 10H, $SiHMe_2$), 0.11 ppm (s, 2H, $SiHMe_2$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 171.18 (s, N*C*N), 148.46 (s, *Ar*), 146.05 (s, *Ar*), 143.09.60 (s, *Ar*), 134.80 (s, *Ar*), 124.85 (s, *Ar*), 123.83 (s, *Ar*), 123.49 (s, *Ar*), 120.30 (s, *Ar*), 40.03 (s, NCN-CH_2), 28.49 (s, $CH(CH_3)_2$), 26.27 (s, $CH(CH_3)_2$), 23.52 (s, $CH(CH_3)_2$), 3.04 (s, $SiHMe_2$). Anal. Calcd for $C_{70}H_{108}Ca_2N_8Si_4$: C, 67.04; H, 8.68; N, 8.93. Found: C, 67.16; H, 8.73; N, 8.84.

Synthesis of complexes 2-7

Synthesis of $L^1Am^{DIPP}CaN(SiMe_3)_2{\cdot}(THF)_2$ (2). Following a similar procedure to that described for the preparation of complex **1**, complex **2** was isolated from the amine elimination reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ (1.05 mmol) and HL^1 (1 mmol) as a pale yellow powder (yield: 47%). ^{1}H NMR (C_6D_6, 500 MHz, 25 ^{o}C): δ

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7.23 (t, 2H, Ar-*H*), 7.17 (m, 3H, Ar-*H*), 7.14 (t, 2H, Ar-*H*), 6.62 (m, 1H, Ar-*H*), 6.09 (d, 1H, C_5H_4N), 5.83 (t, 1H, Ar-*H*), 4.90 (s, 1H, CH_2), 4.12 (s, 1H, CH_2), 3.61 (m, 8H, *THF*), 3.52-3.35 (m, 4H, $CH(CH_3)_2$), 1.33 (m, 8H, *THF*), 1.28 (d, 11H, $CH(CH_3)_2$), 1.05 (m, 13H, $CH(CH_3)_2$), 0.38 (d, 18H, $SiMe_3$). ^{13}C NMR (C_6D_6, 126 MHz, 25 ^{o}C): δ 160.37 (s, NCN), 157.93 (s, *Ar*), 147.65 (s, *Ar*), 145.43 (s, *Ar*), 142.22 (s, *Ar*), 144.44 (s, *Ar*), 135.67 (s, *Ar*), 134.11 (s, *Ar*), 124.63 (s, *Ar*), 124.39 (s, *Ar*), 123.96 (s, *Ar*), 121.61 (s, *Ar*), 109.06 (s, *Ar*), 75.94 (s, NCN-CH_2), 69.30 (s, *THF*), 28.47 (s, $CH(CH_3)_2$), 28.24 (s, $CH(CH_3)_2$), 25.32 (s, *THF*), 24.50 (s, $CH(CH_3)_2$), 5.64 (s, $SiMe_3$). Anal. Calcd for $C_{45}H_{74}CaN_4O_2Si_2$: C, 67.62; H, 9.33; N, 7.01. Found: C, 67.53; H, 9.47; N, 7.13.

Synthesis of $L^2Am^{DIPP}CaN(SiHMe_2)_2{\cdot}(THF)_2$ (3). Following a similar procedure to that described for the preparation of complex **1**, complex **3** was isolated from the amine elimination reaction of $Ca[N(SiHMe_2)_2]_2(THF)$ (1.05 mmol) and HL^2 (1 mmol) as a white solid (yield: 76%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane solution at -30 ◦C after several days. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 7.68 (d, 1H, Ar-*H*), 7.11 (m, 4H, Ar -*H*), 7.03 (dd, 3H, Ar-*H*), 6.95 (t, 1H, Ar-*H*), 6.66 (d, 1H, Ar-*H*), 5.11 (m, $^1J_{Si,H}$ =163.3 Hz, 2H, Si*H*), 3.82 (s, 2H, CH_2), 3.72 (sept, 4H, $CH(CH_3)_2$), 3.61 (m, 8H, *THF*), 1.93 (s, 6H, $N(CH_3)_2$), 1.33 (m, 32H, $CH(CH_3)_2$ + *THF*), 0.42 (d, 10H, $SiHMe_2$), 0.20 (d, 1H, $SiHMe_2$), 0.11 (d, 1H, $SiHMe_2$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 175.04 (s, NCN), 152.08 (s, *Ar*), 146.47 (s, *Ar*), 142.55 (s, *Ar*), 133.34 (s, *Ar*), 126.58 (s, *Ar*), 125.70 (s, *Ar*), 123.95 (s, *Ar*), 123.55 (s, *Ar*), 122.90 (s, *Ar*), 119.99 (s, *Ar*), 69.01 (s, *THF*), 44.43 (s, NMe_2), 28.41 (s, NCN-CH_2), 26.44 (s, $CH(CH_3)_2$), 25.28 (d, *THF*), 23.92 (s, $CH(CH_3)_2$), 5.29 (s, $SiHMe_2$). Anal. Calcd for $C_{46}H_{68}CaN_4O_2Si_2$: C, 68.61; H, 8.51; N, 6.96. Found: C, 68.53; H, 8.57; N, 7.04.

*Synthesis of $L^2Am^{DIPP}CaN(SiMe_3)_2{\cdot}(THF)$ (**4**).* Following a similar procedure to that described for the preparation of complex **1**, complex **4** was isolated from the amine elimination reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ (1.05 mmol) and HL^2 (1 mmol) as a pale white solid (yield: 68%). ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 7.51-7.48 (m, 1H, Ar-*H*), 7.24 (brs, 1H, Ar-*H*), 7.18 (d, 1H, Ar-*H*), 7.13 (s, 1H, Ar-*H*), 7.16 (s, 2H, Ar-*H*) 7.11(d, 1H, Ar-*H*), 7.03 (m, 2H, Ar-*H*), 6.73-6.70 (m, 1H, Ar-*H*), 3.89 (m, 4H, *THF*), 3.85 (s, 2H, CH_2), 3.63 (sept, 4H, $CH(CH_3)_2$), 1.97 (s, 6H, $N(CH_3)_2$), 1.38 (q, 28H, $CH(CH_3)_2$ + *THF*), 0.28 (s, 18H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 175.05 (s, NCN), 146.64 (s, *Ar*), 142.43 (s, *Ar*), 133.33 (s, *Ar*), 126.58 (s, *Ar*), 123.54 (s, *Ar*), 122.91 (s, *Ar*), 119.99 (s, *Ar*), 68.99 (s, *THF*), 44.35 (s, NMe_2), 28.41 (s, NCN-CH_2), 26.43 (s, $CH(CH_3)_2$), 25.26 (d, *THF*), 23.89 (s, $CH(CH_3)_2$), 5.27 ppm (s, $SiMe_3$). Anal. Calcd for $C_{44}H_{72}CaN_4OSi_2$: C, 68.69; H, 9.43; N, 7.28. Found: C, 68.73; H, 9.37; N, 7.23.

*Synthesis of $L^3Am^{DIPP}CaN(SiHMe_2)_2{\cdot}(THF)_2$ (**5**).* Following a similar procedure to that described for the preparation of complex **1**, complex **5** was isolated from the amine elimination reaction of $Ca[N(SiHMe_2)_2]_2(THF)$ (1.05 mmol) and HL^3 (1 mmol) as a white solid (yield: 74%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane solution at -30 ◦C after several days. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 7.14 (brs, 4H, Ar-*H*), 7.11-7.08 (m, 2H, Ar-*H*), 5.12 (brs, $^1J_{Si,H}$ =147.4 Hz, 2H, Si*H*), 3.52 (sept, 4H, $CH(CH_3)_2$), 2.23 (m, 2H, CH_2), 1.64 (s, 6H, $N(CH_3)_2$), 1.58 (t, 2H, CH_2), 1.38 (d, 12H, $CH(CH_3)_2$), 1.27 (d, 14H, $CH(CH_3)_2$ + CH_2), 0.15 ppm (s, 12H, $SiHMe_2$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 177.26 (s, NCN), 175.80 (s, *Ar*), 147.05 (s, *Ar*), 146.58 (s, *Ar*), 142.39 (s, *Ar*), 123.67 (s, *Ar*), 123.53 (s, *Ar*), 123.31 (s, *Ar*), 123.04 (s, *Ar*), 68.84 (s, *THF*), 45.06 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 28.31 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 25.83 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 25.51 (s, Ar-$CH(CH_3)_2$), 25.38 (s, *THF*), 24.16 (s, Ar-$CH(CH_3)_2$), 24.11 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 5.03 ppm (s, $SiHMe_2$). Anal. Calcd for $C_{42}H_{76}CaN_4O_2Si_2$: C, 65.83; H, 10.13; N, 7.31. Found: C, 65.91; H, 10.08; N, 7.26.

*Synthesis of $L^3Am^{DIPP}CaN(SiMe_3)_2{\cdot}(THF)_2$ (**6**).* Following a similar procedure to that described for the preparation of complex **1**, complex **6** was isolated from the amine elimination reaction of $Ca[N(SiMe_3)_2]_2(THF)_2$ (1.05 mmol) and HL^3 (1 mmol) as a pale white solid (yield: 71%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane solution at -30 ◦C after several days. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 7.18 (d, 1H, Ar-*H*), 7.16-7.15 (m, 3H, Ar-*H*), 7.11-7.07 (m, 2H, Ar-*H*), 3.66 (m, 6H, *THF*), 3.49 (sept, 4H, $CH(CH_3)_2$), 2.22-2.18 (m, 2H, CH_2), 1.66 (s, 6H, $N(CH_3)_2$), 1.61 (m, 2H, CH_2), 1.39 (d, 12H, $CH(CH_3)_2$), 1.30 (m, 20H, $CH(CH_3)_2$ + CH_2 + *THF*), 0.19 ppm (s, 18H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 176.86 (s, NCN), 145.87 (s, *Ar*), 142.39 (s, *Ar*), 142.22 (s, *Ar*), 123.66 (s, *Ar*), 123.58 (s, *Ar*), 123.51 (s, *Ar*), 69.40 (s, *THF*), 59.98 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 45.11 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 28.55 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 25.80 (s, *THF*), 25.18 (s, Ar-$CH(CH_3)_2$), 23.63 (s, NCN-$CH_2CH_2CH_2N(CH_3)_2$), 5.47 (s, $SiMe_3$). Anal. Calcd for $C_{44}H_{80}CaN_4O_2Si_2$: C, 66.61; H, 10.16; N, 7.06. Found: C, 66.67; H, 10.11; N, 7.13.

*Synthesis of $[L^4CaN(SiHMe_2)_2]_2$ (**7**).* Following a similar procedure to that described for the preparation of complex **1**, complex **7** was isolated from the amine elimination reaction of $Ca[N(SiHMe_2)_2]_2(THF)$ (1.05 mmol) and HL^4 (1 mmol) as a white solid (yield: 48%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane solution at -30 ◦C after several days. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 7.04 (d, 2H, Ar-H), 6.82 (t, 2H, Ar-*H*), 6.62 (t, 2H, Ar-*H*), 6.19 (d, 2H, Ar-*H*), 5.18 (m, $^1J_{Si,H}$ =167.9 Hz, 1H, Si*H*), 5.06 (m, 1H, Si*H*), 3.48 (s, 2H, OCH_3), 3.34 (s, 4H, OCH_3), 3.11 (sept, 1H, CH_2CH_3), 2.85 (sept, 3H, CH_2CH_3), 0.89 (t, 4H, CH_2CH_3), 0.65 (t, 2H, CH_2CH_3), 0.46 (d, 4H, $SiHMe_2$), 0.40 (brs, 4H, $SiHMe_2$), 0.20 ppm (brs, 4H, $SiHMe_2$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 164.54 (s, NCN), 159.01 (s, Ar), 151.60 (s, Ar), 151.31 (s, Ar), 139.68 (s, Ar), 139.57 (s, Ar), 138.21 (s, Ar), 122.94 (s, Ar), 121.85 (s, Ar), 121.32 (s, Ar), 121.02 (s, Ar), 120.21 (s, Ar), 118.63 (s, Ar), 110.44 (s, Ar), 110.08 (s, Ar), 56.15 (s, OCH_3), 55.74 (s, OCH_3), 42.11 (s, $N(CH_2CH_3)_3$), 12.11 (s, $N(CH_2CH_3)_3$), 4.93 (s, $SiHMe_2$),

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4.66 (s, SiH*Me*$_2$), 4.22 (s, SiH*Me*$_2$). Anal. Calcd for $C_{46}H_{76}Ca_2N_8O_4Si_4$: C, 55.38; H, 7.68; N, 11.23. Found: C, 55.41; H, 7.64; N, 11.13.

*Synthesis of [L^{4}CaN(SiMe$_3$)$_2$]$_2$ (**8**).* Following a similar procedure to that described for the preparation of complex **1**, complex **8** was isolated from the amine elimination reaction of Ca[N(SiMe$_3$)$_2$]$_2$(THF) (1.05 mmol) and HL^4 (1 mmol) as a white solid (yield: 53%). Single crystals suitable for X-ray analysis were obtained from a toluene/hexane solution at -30 ◦C after several days. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C): δ 6.95 (d, 2H, Ar-*H*), 6.83 (t, 2H, Ar-*H*), 6.60 (t, 2H, Ar-*H*), 6.17 (d, 2H, Ar-*H*), 3.37 (s, 6H, OC*H*$_3$), 3.09 (m, 2H, N(C*H*$_2$CH$_3$)$_3$), 2.97 (m, 2H, N(C*H*$_2$CH$_3$)$_3$), 0.84 (t, 6H, N(CH$_2$C*H*$_3$)$_3$), 0.26 ppm (s, 18H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 100 MHz, 25 ^{o}C): δ 176.04 (s, N*C*N), 153.01 (s, Ar), 144.92 (s, Ar), 142.29 (s, Ar), 123.58 (s, Ar), 123.43 (s, Ar), 120.17 (s, Ar), 69.66 (s, -O*C*H$_3$), 44.28 (s, N(*C*H$_2$CH$_3$)$_3$), 23.25 (s, N(CH$_2$*C*H$_3$)$_3$), 5.42 ppm (s, Si*Me*$_3$). Anal. Calcd for $C_{64}H_{84}Ca_2N_8O_4Si_4$: C, 62.91; H, 6.93; N, 9.17. Found: C, 62.87; H, 6.84; N, 9.23.

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Alkaline earth metal complexes stabilized by amidine and guanidine ligands: synthesis, structure and their catalytic activity towards polymerization of rac-lactide

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Amidine ligands with coordination backbone substitutes were synthesized, for the first time, and useful to stabilize heteroleptic calcium complexes. The rigidity of the substitutes has an influence on the solvation and aggregation of the corresponding calcium complexes. Delightedly, in the presence of PhOH as chain transfer agent, the afforded complexes could unprecedentedly catalyze "immortal" ring-opening polymerization of lactide.