# Zinc and enolato-magnesium complexes based on bi-, tri- and tetradentate aminophenolate ligands†

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***Received (in Montpellier, France) 24th July 2008, Accepted 29th August 2008***
***First published as an Advance Article on the web 14th October 2008***
**DOI: 10.1039/b812754a**



The coordination chemistry of a series of potentially tetra-, tri- and bi-dentate aminophenol pro-ligands ([L$^1$]H–[L$^5$]H) with magnesium and zinc derivatives has been studied. Reactions of the pro-ligands [L$^1$]H, [L$^2$]H and [L$^3$]H with one equiv. of $ZnEt_2$ or $Zn(N(SiMe_3)_2)_2$ in toluene at room temperature afford cleanly, *via* ethane or amine elimination, the ethyl- and amido-zinc complexes **1–4**. Complexes [L$^4$]ZnEt (**5**) and [L$^4$]$Zn(N(SiMe_3)_2)_2$ (**6**) derived from the tridentate pro-ligand [L$^4$]H were prepared in 84% and 76% yields, following similar alkane and amine elimination protocols, respectively. The 1 : 1 reactions of bidentate pro-ligand [L$^5$]H with $ZnEt_2$ or $Zn(N(SiMe_3)_2)_2$ in toluene using different reaction protocols systematically yielded mixtures of the bis(ligand) complex [L$^5$]$_2$Zn (**7**) and the corresponding ethyl-$\{[L^5]ZnEt\}_n$ (**8**; $n$ = 1 or 2) or amido- $\{[L^5]Zn(N(SiMe_3)_2)\}_n$ complexes (**9**; $n$ = 1 or 2). The synthesis of magnesium-enolate complexes **10** and **11** was carried out in a one-pot, two-step procedure by first reacting pro-ligands [L$^1$]H and [L$^4$]H with one equiv. of Mg($n$,$s$Bu)$_2$ to generate the corresponding $\{[L^n]Mg(n,sBu)\}_n$ species, which were further reacted with one equiv. of 2,4,6-$Me_3C_6H_2COMe$. All complexes have been characterized by multinuclear NMR, elemental analysis, and by single-crystal X-ray diffraction studies for five-coordinate magnesium complex **10**, and four-coordinate Zn complexes **3–7**. Preliminary studies indicate that magnesium species **10** and **11** as well as zinc complexes **1** and **5** are not active initiators for the polymerization of methyl methacrylate, even in combination with one equiv. of Li[OC(=$CH_2$)(2,4,6-$Me_3C_6H_2$)], while zinc complexes **2**, **4** and **6** are effective initiators for the ring-opening polymerization of ε-caprolactone and *rac*-lactide at 20 °C.

## Introduction

The coordination chemistry of aminophenolate ligands has been intensively studied in recent years. Of particular interest are ligands of general type **A**, of which relevant examples disclosed in the literature are shown in Chart 1. According to the number and nature of extra donor arms, such monoanionic compounds can accommodate a broad range of coordination geometries as bidentate, tridentate or tetradentate ligands for various oxophilic metals and some of the resulting complexes can be used as efficient (pre)catalysts in a variety of processes. Early reports on tripodal [L$_2$NO]$^-$ ligands were focused on the coordination chemistry of Cu(II),[1] Zn(II),[2,3] Cu(I),[4,5] and Ni(II).[6] Triaminophenolate ligands have been shown to adopt bidentate (Al(III)), tridentate (Mg(II), Ca(II), Zn(II)) and tetradentate (K(I), Cr(III), Fe(II), Co(II)) binding modes.[7] Phenolate ligands functionalized with triazacyclononanes have been reported as well for the coordination of a variety of early transition metals (Sc(III), Y(III), Ti(IV), V(III), Cr(III)) and related group 13 metals (Al(III), In(III), Ga(III), Tl(III)).[8] Very recently Lappert and coll. introduced piperazinylphenolate ligands onto Zn(II) centers and showed they behave as bidentate chelates.[9] Other recent applications involve the coordination of tripodal [L$_2$NO]$^-$ ligands onto group 3 and 4 metals, essentially for olefin and polar monomers polymerization purposes.[10–12] Mononuclear[13a] and dinuclear[13b] zinc complexes supported by bulky tridendate diamino-phenolate ligands have been prepared and the former mononuclear complexes have been shown to polymerize lactide with good control and at a rate faster than any other Zn-containing system reported previously. Also, bidentate aminophenolate ligands have been used for preparing low-coordinate complexes of group 13 metals (Al(III), Ga(III))[14] and magnesium complexes,[15] which are useful for ring-opening polymerization catalysis.

This report describes the synthesis and structural characterization of a series of new amido- and alkyl-zinc and

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† Crystallographic data for complexes **3–7** and **10**. CCDC reference numbers 672301–672306. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b812754a

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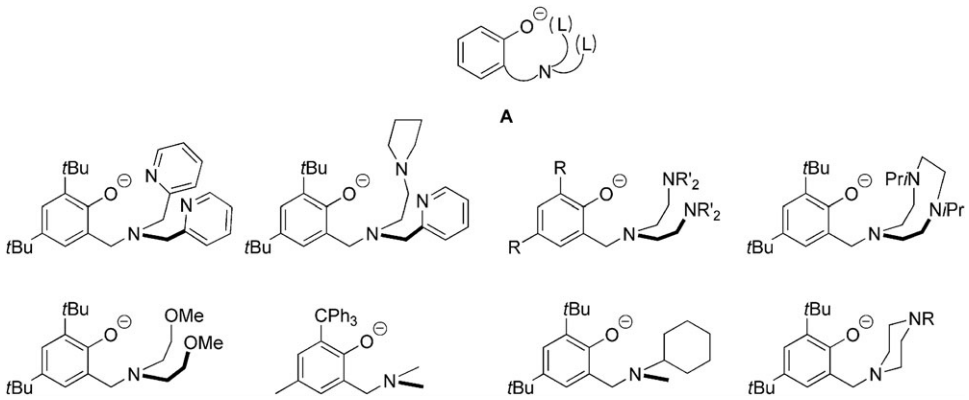


**Chart 1** Examples of aminophenolate-type ligands useful in coordination chemistry and catalysis.

enolato-magnesium complexes with such aminophenolate ligands. The denticity of the latter has been varied from 4- to 2-coordinate ligands in order to evaluate the stabilization of the metal center. The presence of non-bound donor arms, which could readily exchange in solution with bound arms, may be an important factor in this respect, with possible important implications for catalytic applications. Preliminary investigations of the reactivity of some of the prepared complexes toward polar monomers are also reported.

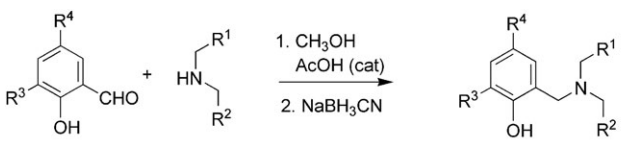
## Results and discussion

### Synthesis of aminophenol pro-ligands

The aminophenol pro-ligands used in this study were prepared in a straightforward manner, by reductive amination, following a one-pot, two-step procedure similar to that reported for known bis(pyridylmethyl) derivative [$L^1$]H (Scheme 1).[16] The new compounds [$L^2$]H, [$L^3$]H, [$L^4$]H and [$L^5$]H were prepared in 74%, 40%, 38% and 46% overall yields (not optimized), starting from bis(picolyl)amine, *N*,*N*-bis[2-(3,5-dimethyl-1-pyrazole)ethyl]-amine, *N*-benzyl-*N*-(2-methyl-pyridine)amine, and commercially available *N*,*N*-bis(benzyl)amine, respectively. The ligand precursors were obtained as colorless or yellowish powders, and their identity was confirmed by NMR and high-resolution mass spectrometry. Such ligand architecture allows steric and electronic variations on both the phenol and the pyridine or pyrazole donor fragments.

### Synthesis and structure of zinc complexes

Reactions of the pro-ligands [$L^1$]H, [$L^2$]H and [$L^3$]H with one equiv. of $ZnEt_2$ or $Zn(N(SiMe_3)_2)_2$ in toluene at room temperature afford cleanly, *via* ethane or amine elimination, the ethyl- and amido-zinc complexes **1–4** (Scheme 2). These compounds were isolated in good yields (65–87%) as colorless or pale yellow solids, which are readily soluble in hydrocarbon (benzene, toluene, pentane, hexanes) and chlorinated ($CH_2Cl_2$) solvents. In our hands, [$L^1$]ZnEt (**1**), which was previously reported as unstable over hours,[2a] could be stored for weeks in the glovebox at −30 °C without significant decomposition. Compound **1** and the three other new complexes [$L^2$]Zn($N(SiMe_3)_2$) (**2**), [$L^3$]ZnEt (**3**) and [$L^3$]Zn($N(SiMe_3)_2$) (**4**) were authenticated by elemental analyses and $^1$H and $^{13}$C NMR spectroscopy. The $^1$H and $^{13}$C NMR spectra of complexes **1**, **2** and **3** in $C_6D_6$ at room temperature show each one set of resonances for equivalent (on the NMR timescale) 2-pyridylmethyl and (3,5-dimethyl-1-pyrazolyl)ethyl groups, respectively. Variable-temperature NMR spectroscopy of complex **3** in toluene-$d_8$ revealed decoalescence of the resonances upon lowering the temperature, eventually resulting in the observation of individual resonances for four *methyl*-pyrazolyl and two $NCH_2CH_2$-pyrazolyl groups at −80 °C. As further supported by the solid state structure of **3** (*vide infra*), these observations are consistent with only one of the pyrazolyl groups coordinated onto the metal center and fast exchange of the coordinated and free pyrazolyl groups on the NMR timescale at relatively high temperature. The same situation, that is a coordinated pyridyl group and a free pyridyl group, can be envisioned for complexes **1** and **2**. Alternatively, we cannot rule out that both pyridyl groups are coordinated to the zinc center in **1** and **2**, either in a symmetric or dissymmetric fashion; the latter situation was observed in zinc complexes supported by aminophenolate ligands bearing 2-methoxyethyl arms, in

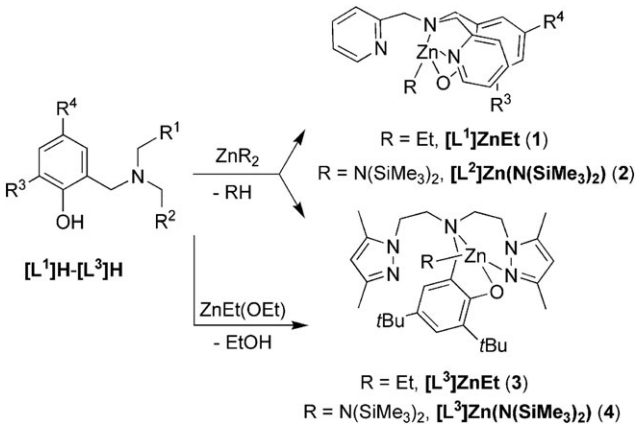


**[$L^1$]H**: $R^1 = R^2$ = 2-pyridyl, $R^3 = R^4$ = *t*Bu
**[$L^2$]H**: $R^1 = R^2$ = 2-pyridyl, $R^3$ = Me, $R^4$ = Cl
**[$L^3$]H**: $R^1 = R^2$ = 2-(3,5-dimethyl-1-pyrazolyl)methyl, $R^3 = R^4$ = *t*Bu
**[$L^4$]H**: $R^1$ = 2-pyridyl, $R^2$ = phenyl, $R^3 = R^4$ = *t*Bu
**[$L^5$]H**: $R^1 = R^2$ = phenyl, $R^3 = R^4$ = *t*Bu

**Scheme 1** Synthesis of aminophenol pro-ligands [$L^n$]H.






**Scheme 2** Preparation of zinc aminophenolate complexes **1–4**.

which one methoxy arm is tightly coordinated and the other one is weakly coordinated onto the metal center.[3] On the other hand, the $^{1}H$ and $^{13}C$ NMR spectra for complex **4** in $C_6D_6$ at room temperature show four *methyl*-pyrazolyl and two $NCH_2CH_2$-pyrazolyl groups. This also indicates that, in this complex, one of the pyrazolyl groups is coordinated to the metal center while the second one is free (or more weakly coordinated), but that these two groups do not exchange rapidly on the NMR timescale under these conditions. Apparently, the different bulkiness of the ethyl and bis-(trimethylsilylamido) groups may account for this different fluxional behavior.

The crystal structures of complexes **3** and **4** were determined by X-ray diffraction studies. Details of crystal and refinement data are reported in Table 1. Both complexes are monomeric in the solid state and feature a four-coordinated zinc center in a distorted tetrahedral geometry (Fig. 1 and 2). Consistent with the NMR observations in solution (*vide supra*), only one of the two pyrazolyl groups per molecule is coordinated, together with the bridging N and O atoms of the ligand, forming two six-membered metallacycles. Thus, though potentially tetradentate, the tripodal aminophenolate is actually tridentate.[7] The coordination sphere is completed by the alkyl or amido ligand. The Zn–O and Zn–N bond distances fall in normal ranges for similar complexes.[2] Significant differences between those two structures include a shorter Zn(1)–N(21) bond distance in **4** (2.121(2) Å) than in **3** (2.206(2) Å), likely reflecting the strong σ-donor effect of the amido group. The most acute angle among the two six-membered metallacycles is associated with the bite of the *N*,*N* chelate ring, although the difference is much more sensitive for **2** (86.86(7) *vs.* 95.01(6)°) than for **3** (93.50(7) *vs.* 95.71(6)°). Thus, rather unexpectedly, the bulkier $N(SiMe_3)_2$ group in **4** (as compared to ethyl in **3**) apparently does not induce a more acute bite angle of the *N*,*O* chelate ring, but a more opened bite angle of the *N*,*N* chelate ring. Both six-membered metallacycles in the two complexes adopt boat conformations, as observed in related tetrahedral trisaminophenolate zinc complexes.[2,7]

Attempts to prepare an ethoxide-zinc complex [$L^3$]ZnOEt (potentially useful for polymerization catalysis) from [$L^3$]H and ZnEt(OEt) did not afford the desired compound (Scheme 2). $^{1}H$ NMR monitoring of this reaction showed that only ethanol, and no ethane, elimination proceeded under these conditions (toluene, −78 °C to 20 °C) to form **3**, which could be isolated in pure form, though in modest yield (see Experimental section). Actually, the released ethanol slowly hydrolyzes the Zn–O(phenolate) bond of **3**, leading to free [$L^3$]H and Zn products that could not be identified. This competitive, undesired reaction was independently confirmed by the reactions of **3** with ethanol, benzyl alcohol or 2-propanol (1–5 equiv, toluene, 20 °C). Similarly, the reaction of **4** with 2-propanol appeared to be plagued by the release of free [$L^2$]H and, despite the fact that alcoholysis of the amido residue takes place as evidenced by the formation of $HN(SiMe_3)_2$ (identified by NMR), the desired zinc 2-propoxide complex could not be obtained in a pure form.

The new complexes [$L^4$]ZnEt (**5**) and [$L^4$]Zn($N(SiMe_3)_2$) (**6**) derived from the tridentate pro-ligand [$L^4$]H were prepared in 84% and 76% yields, following similar alkane and amine elimination protocols, respectively (Scheme 3). Those complexes are stable solids under inert atmosphere at room temperature, which feature the same solubility as above-mentioned for **1–4**. They were both characterized by $^{1}H$ and $^{13}C$ NMR solution spectroscopy and X-ray diffraction studies of single crystals grown from pentane solutions at 20 °C. Both the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of **5** and **6** in $C_6D_6$ or $CD_2Cl_2$ at room temperature contained a single set of sharp resonances, which could be assigned in details based on 2D $^{1}H$–$^{1}H$ COSY, and $^{1}H$–$^{13}C$ HMQC and HMBC experiments (see Experimental section), and which are consistent with the existence of a single species on the NMR timescale under these conditions. Complementary investigations in the case of **5** indicated that those NMR features were essentially unchanged in toluene-$d_8$ and $CD_2Cl_2$ down to −80 °C; in particular, no significant broadening of the signals was noticed at such low temperature. The above observations are consistent with the formation of a single diastereomer of **5** and **6**, because the relative configurations at the chiral bridging N atom and Zn center in these complexes are related.

The solid-state structures of **5** and **6** have been determined by X-ray diffraction studies. The unit cells of **5** and **6** contain respectively three and two independent molecules, but both these sets of molecules have very similar overall geometry, bond distances and angles. The molecular structures of **5** and **6** are monomeric and feature a four-coordinated zinc center in a distorted tetrahedral geometry (Fig. 3 and 4). Details of crystal and refinement data are reported in Table 1. First, it is worth noting that the same relative configurations at the N and Zn atoms are observed in **5** and **6**. The Zn–O and Zn–N bond distances fall in normal ranges for similar complexes,[2,7] and compare well in particular with those found in **3** and **4** (and the bond angles as well). The angles at the metal involving the aminophenolate ligand are in the range 79.1(2)–118.9(3)°. The most acute is in both complexes logically associated with the bite of the five-membered *N*,*N* chelate ring, the extra methylene in the six-membered *N*,*O*-chelate ring allowing this latter chelate to adopt a less strained coordination geometry. As in complexes **3** and **4**, the six-membered metallacycles in **5** and **6** adopt boat conformations. The five-membered ring in **5** has a twisted conformation with the N(21) atom lying 0.56 Å out of the N(11)–Zn(1)–$C_2$ plane, while in **6** the atoms of the five-membered ring are coplanar to within *ca.* 0.14 Å.

**Table 1** Summary of crystal and refinement data for complexes **3**, **4**, **5**, **6**, **7** and **10**

| | **3** | **4** | **5** | **6** | **7** | **10** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{31}H_{49}N_5OZn$ | $C_{35}H_{62}N_6OSi_2Zn$ | $C_{30}H_{40}N_2OZn$ | $C_{34}H_{53}N_3OSi_2Zn$ | $C_{58}H_{72}N_2O_2Zn$ | $C_{38}H_{47}MgN_3O_2$ |
| Formula weight | 573.12 | 704.46 | 510.01 | 641.34 | 894.55 | 602.10 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Orthorhombic | Triclinic | Monoclinic |
| Space group | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ | $Pca2_1$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 31.6107(11) | 11.7495(4) | 13.9651(2) | 15.2406(8) | 10.646(2) | 10.4793(6) |
| $b$/Å | 11.2967(3) | 14.5448(5) | 17.5917(2) | 10.5921(6) | 14.508(3) | 22.4925(13) |
| $c$/Å | 17.4711(6) | 14.7216(5) | 21.1494(3) | 48.038(3) | 16.750(4) | 15.5746(9) |
| $\alpha$/° | 90 | 62.3027(17) | 76.8990(10) | 90 | 85.050(10) | 90 |
| $\beta$/° | 96.688(2) | 88.2672(17) | 79.3830(10) | 90 | 75.882(10) | 108.702(4) |
| $\gamma$/° | 90 | 67.8521(17) | 67.2880(10) | 90 | 80.339(10) | 90 |
| $V$/Å$^3$ | 6196.4(3) | 2030.70(13) | 4641.00(11) | 7754.8(8) | 2470.6(9) | 3477.2(3) |
| $Z$ | 8 | 2 | 6 | 8 | 2 | 4 |
| $D_c$/Mg m$^{-3}$ | 1.229 | 1.152 | 1.095 | 1.099 | 1.203 | 1.15 |
| $\mu$/mm$^{-1}$ | 0.823 | 0.696 | 0.815 | 0.722 | 0.540 | 0.087 |
| $F(000)$ | 2464 | 760 | 1632 | 2752 | 960 | 1296 |
| Crystal size/mm | 0.15 × 0.17 × 0.25 | 0.08 × 0.14 × 0.32 | 0.03 × 0.20 × 0.30 | 0.06 × 0.35 × 0.40 | 0.04 × 0.15 × 0.35 | 0.03 × 0.20 × 0.22 |
| $\theta$ range/° | 2.55 to 27.59 | 3.03 to 27.48 | 2.26 to 26.65 | 2.96 to 27.47 | 2.52 to 26.44 | 2.74 to 27.69 |
| Limiting indices | $-40 \le h \le 38$, $-14 \le k \le 10$, $-22 \le l \le 22$ | $-17 \le h \le 17$, $-22 \le k \le 21$, $-26 \le l \le 26$ | $-17 \le h \le 17$, $-22 \le k \le 21$, $-26 \le l \le 26$ | $-11 \le h \le 13$, $-19 \le k \le 19$, $-62 \le l \le 61$ | $-13 \le h \le 13$, $-18 \le k \le 18$, $-21 \le l \le 21$ | $-13 \le h \le 11$, $-29 \le k \le 29$, $-14 \le l \le 20$ |
| Refl. collected | 28 903 | 19 863 | 62 706 | 67 188 | 33 514 | 35 729 |
| Refl. unique [$I > 2\sigma(I)$] | 7145 (5024) | 9258 (7219) | 18 987 (10056) | 17 364 (13933) | 11 241 (8736) | 8082 (4998) |
| Data/restraints/param. | 7145/0/343 | 9258/0/406 | 18 987/0/919 | 17 364/1/745 | 11 241/0/640 | 8082/0/403 |
| Goodness-of-fit on $F^2$ | 1.035 | 1.008 | 1.064 | 1.179 | 1.012 | 1.012 |
| $R_1$ [$I > 2\sigma(I)$] (all data) | 0.0414 (0.0686) | 0.0410 (0.0583) | 0.0913 (0.1534) | 0.0843 (0.1008) | 0.0391 (0.0582) | 0.0542 (0.1053) |
| $wR_2$ [$I > 2\sigma(I)$] (all data) | 0.1072 (0.1196) | 0.0970 (0.1059) | 0.2698 (0.2910) | 0.2289 (0.2364) | 0.0831 (0.0914) | 0.1196 (0.1402) |
| Largest diff./e Å$^{-3}$ | 0.415 and −0.502 | 0.445 and −0.311 | 2.243 and −1.35 | 0.869 and −1.213 | 0.300 and −0.415 | 0.385 and −0.345 |

The 1 : 1 reactions of bidentate pro-ligand [L$^5$]H with $ZnEt_2$ or $Zn(N(SiMe_3)_2)_2$ in toluene using a variety of protocols (reaction temperature, introduction order) systematically yielded mixtures of the bis(ligand) complex [L$^5$]$_2$Zn (**7**) and the corresponding ethyl- {[L$^5$]ZnEt}$_n$ (**8**; $n$ = 1 or 2) or amido- {[L$^5$]Zn(N(SiMe$_3$)$_2$)}$_n$ complexes (**9**; $n$ = 1 or 2) (Scheme 4). These mixtures never contained more than 80% of the desired complexes and could not be efficiently separated by recrystallization; only small amounts of **7**, which proved to be suitable for X-ray diffraction studies (*vide infra*), were isolated from some batches. Formation of **8** appeared to be somewhat favored by using excess of $ZnEt_2$ (5 equiv.), but all attempts to purify the desired complex from these mixtures also failed. Therefore, we could not probe whether homoleptic bis(ligand) complex **7** is a redistribution/disproportionation product of thermodynamically unstable heteroleptic complexes **7** or **8** (as observed by Lappert *et al.*),[9] or rather results from a kinetically fast consecutive reaction of **8** or **9** with [L$^5$]H.

Expectedly, the solid-state structure of **7** features a monomeric molecule with the Zn center in a distorted tetrahedral geometry coordinated by the four heteroatoms of the two aminophenolate ligands (Fig. 5). The complex is far from being centrosymmetric, with quite differentiated O–Zn–N angles within the two metallacycles (94.39(6) and 99.11(5)°). Also, one six-membered ring has a twisted envelop conformation with the N(11) atom lying *ca.* 0.79 Å out of the Zn(1)–O(51)–C(73)–C(72)–C(71) plane, while the second six-membered ring has a boat conformation with the O(1) and C(31) atoms lying *ca.* +0.38 and +0.65 Å out of the C(23)–C(22)–Zn(1)–N(1) plane. The Zn–O and Zn–N distances in **7** are slightly smaller than those observed in complexes **3–6**; this is likely due to the lower steric hindrance induced by the formation of a single metallacycle per ligand unit (*vs.* two in **3–6**). Overall, the bond distances and bond angles in **7** compare very well those observed in a related bis(aminophenolate)zinc complex reported by Lappert and colleagues.[9]

### Synthesis and structure of magnesium complexes

The synthesis of magnesium-enolate complexes was carried out in a one-pot, two-step procedure (Scheme 5). Tri- and diaminophenol pro-ligands [L$^1$]H and [L$^4$]H[17] were first reacted with one equiv. of Mg($n$,$s$Bu)$_2$ to generate the

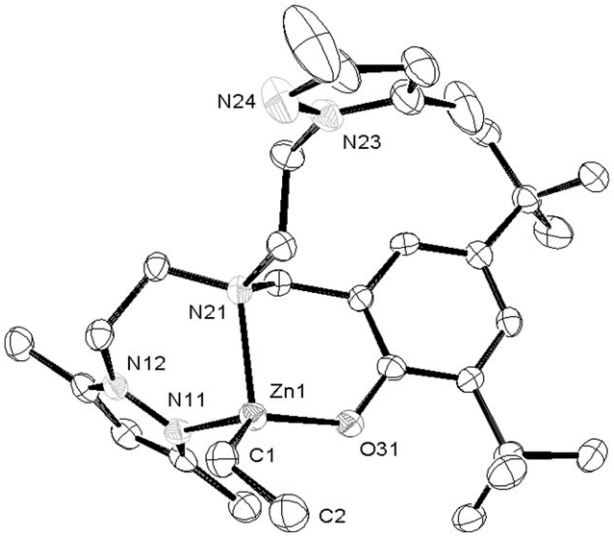



**Fig. 1** Solid-state structure of [L$^3$]ZnEt (**3**) (ellipsoids drawn at the 60% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Zn(1)–O(31), 1.909(1); Zn(1)–N(11), 2.100(2); Zn(1)–N(21), 2.206(2); Zn(1)–C(1), 1.978(2); O(31)–Zn(1)–C(1), 128.33(9); O(31)–Zn(1)–N(11), 100.93(7); O(31)–Zn(1)–N(21), 95.01(6); C(1)–Zn(1)–N(21), 117.09(8); C(1)–Zn(1)–N(11), 119.05(9); N(11)–Zn(1)–N(21), 86.86(7).

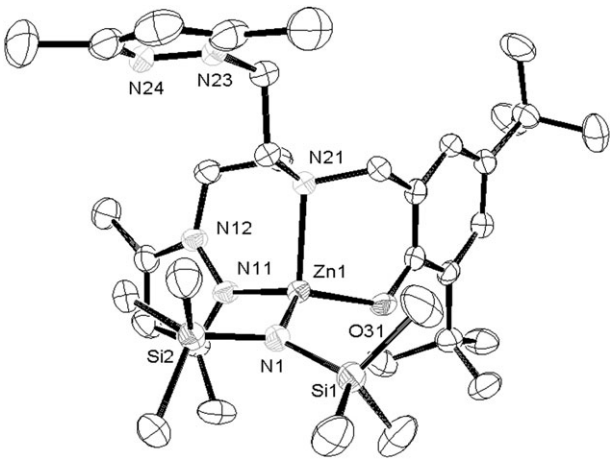
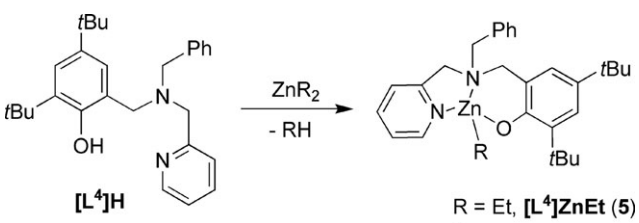



**Fig. 2** Solid-state structure of [L$^3$]Zn(N(SiMe$_3$)$_2$) (**4**) (ellipsoids drawn at the 60% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Zn(1)–O(31), 1.932(2); Zn(1)–N(11), 2.058(2); Zn(1)–N(21), 2.121(2); Zn(1)–N(1), 1.931(2); O(31)–Zn(1)–N(1), 121.17(7); O(31)–Zn(1)–N(11), 108.62(7); O(31)–Zn(1)–N(21), 95.71(6); N(1)–Zn(1)–N(21), 116.65(7); N(1)–Zn(1)–N(11), 116.17(7); N(11)–Zn(1)–N(21), 93.50(7).




**Scheme 3** Preparation of zinc aminophenolate complexes **5–6**.

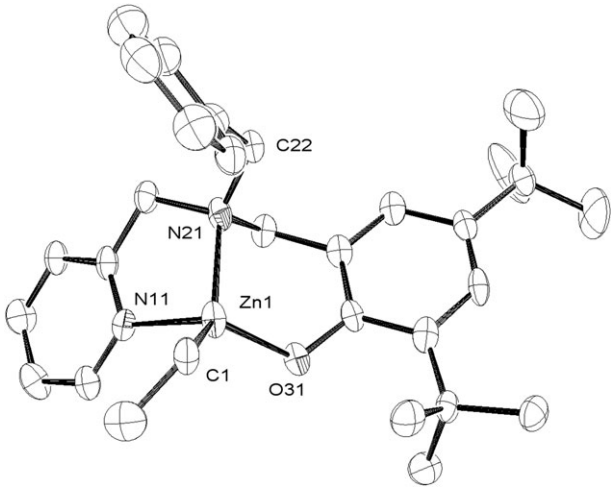



**Fig. 3** Solid-state structure of [L$^4$]ZnEt (**5**) (ellipsoids drawn at the 50% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°) (data given for the independent molecule depicted above, with [values] for the two other independent molecules): Zn(1)–O(31), 1.959(4) [1.935(5), 1.976(4)]; Zn(1)–C(1), 1.987(7) [1.969(7)]; Zn(1)–N(11), 2.146(5) [2.122(6), 2.136(6)]; Zn(1)–N(21), 2.179(6) [2.170(5), 2.187(5)]; O(31)–Zn(1)–C(1), 121.8(2) [119.7(9), 120.1(3)]; O(31)–Zn(1)–N(11), 106.0(2) [101.2(2), 104.4(2)]; O(31)–Zn(1)–N(21), 94.4(2) [94.6(2), 95.3(2)]; C(1)–Zn(1)–N(21), 134.1(3) [134.7(3), 135.0(3)]; C(1)–Zn(1)–N(11), 112.2(2) [114.8(3), 118.4(3)]; N(11)–Zn(1)–N(21), 79.1(2) [78.1(2), 79.0(2)]; C(22)–N(21)–Zn(1), 121.8(4) [119.7(4), 125.9(5)].

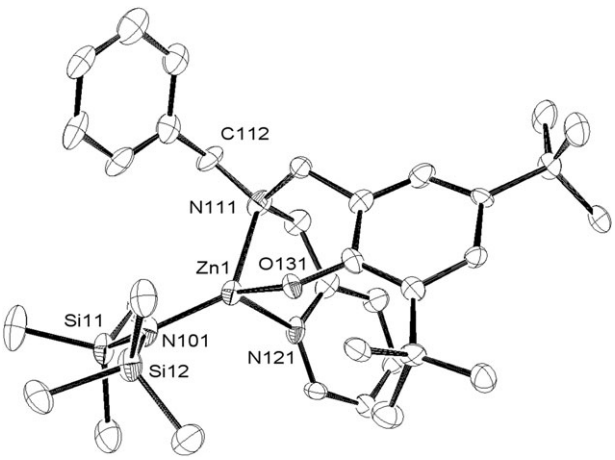
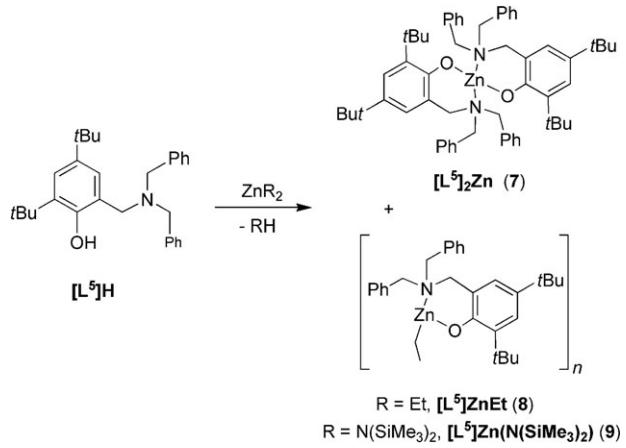



**Fig. 4** Solid-state structure of [L$^4$]Zn(N(SiMe$_3$)$_2$) (**6**) (ellipsoids drawn at the 50% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°) (data given for the independent molecule depicted above, with [values] for the other independent molecule): Zn(1)–O(131), 1.936(5) [1.933(5)]; Zn(1)–N(101), 1.923(7) [1.916(6)]; Zn(1)–N(111), 2.160(7) [2.175(6)]; Zn(1)–N(121), 2.091(6) [2.087(6)]; O(131)–Zn(1)–N(101), 119.1(3) [118.7(2)]; O(131)–Zn(1)–N(121), 98.1(2) [98.0(2)]; O(131)–Zn(1)–N(111), 96.3(2) [96.3(2)]; N(101)–Zn(1)–N(121), 120.6(3) [121.9(2)]; N(101)–Zn(1)–N(111), 130.9(3) [130.6(2)]; N(121)–Zn(1)–N(111), 82.8(3) [82.2(2)]; C(112)–N(111)–Zn(1), 120.1(6) [121.5(4)].

corresponding {[L$^n$]Mg(*n*,*s*Bu)}$_n$ species, which were not isolated but further reacted with one equiv. of 2,4,6-Me$_3$C$_6$H$_2$-COMe. This sterically demanding ketone was selected for its




**Scheme 4** Formation of zinc aminophenolate complexes **7–9**.

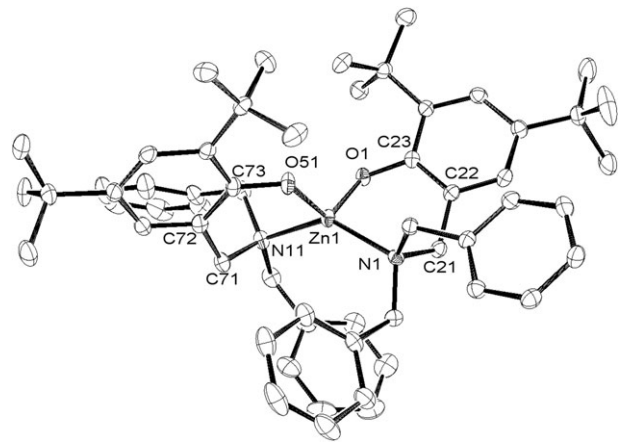
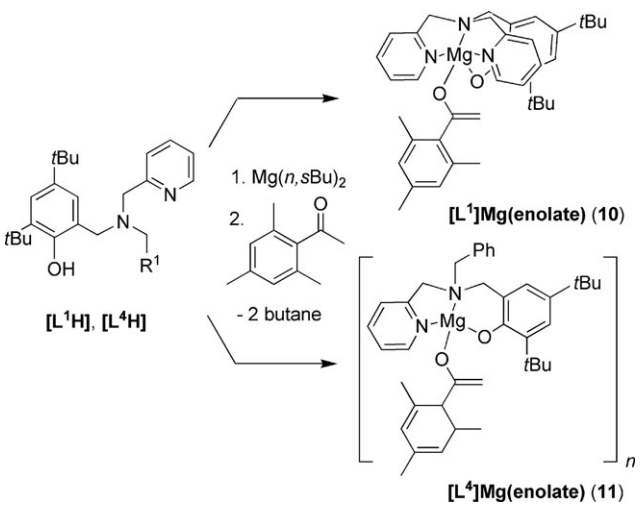



**Fig. 5** Solid-state structure of complex $[L^5]_2Zn$ (**7**) (ellipsoids drawn at the 50% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Zn(1)–O(1), 1.897(2); Zn(1)–O(51), 1.911(2); Zn(1)–N(1), 2.113(2); Zn(1)–N(11), 2.083(2); O(1)–Zn(1)–O(51), 119.62(6); O(1)–Zn(1)–N(11), 101.61(6); O(51)–Zn(1)–N(11), 94.39(6); O(1)–Zn(1)–N(1), 99.11(5); O(51)–Zn(1)–N(1), 106.95(6); N(11)–Zn(1)–N(1), 137.39(6).




**Scheme 5** Preparation of magnesium aminophenolate enolate complexes **10** and **11**.

well-known excellent crystallization properties that its metal enolates can have.[18] Actually, recrystallization of the crude products from toluene allowed isolating the desired enolate complexes $[L^n]Mg\{OC(=CH_2)Mes\}$ (Mes = 2,4,6-$Me_3C_6H_2$) **10** and **11** as white crystals in 63% and 21% yield, respectively. Both complexes were characterized in solution by $^1H$ and $^{13}C$ NMR spectroscopy and, in the case of **10**, by a single-crystal X-ray diffraction study.

The solid-state structure of **10** features a five-coordinated Mg center in a distorted trigonal-bipyramidal geometry, with coordination of the phenolato oxygen, the two pyridine nitrogens, the tertiary bridging nitrogen, and the enolate oxygen (Fig. 6). Complex **10** represents a rare example of a monomeric magnesium complex with a terminal O–bound enolate ligand, in addition to Mg(enolato)(dpp-bianH)$(THF)_2$ complexes (enolato = $OC(=CHPh)CH_2Ph$, $OC(=CPh_2)CH_3$, or camphor; dpp-bian = 1,2-bis{(2,6-diisopropylphenyl)-imino}acenaphthene) recently reported by Schumann and co-workers.[19] Other examples magnesium enolate complexes are concerned with dimeric or oligomeric structures with μ-bridging O(enolate) ligands,[20] as usually observed for oxophilic, hard metals.[21] The Mg–O(enolato) distance of 1.888(2) Å in **10** compares well with those observed in Mg(enolato)(dpp-bianH)$(THF)_2$ complexes (1.902(3), 1.921(2) and 1.890(2) Å, respectively), and lies in between those of 1.845(3) and 2.012(3) Å observed for the two terminally bound enolate groups in the tetrameric complex $[Mg_4\{OC(=CH_2)Mes\}_8\{O=C(Mes)Me\}_2(C_6H_5Me)_2]_5$.[20e]

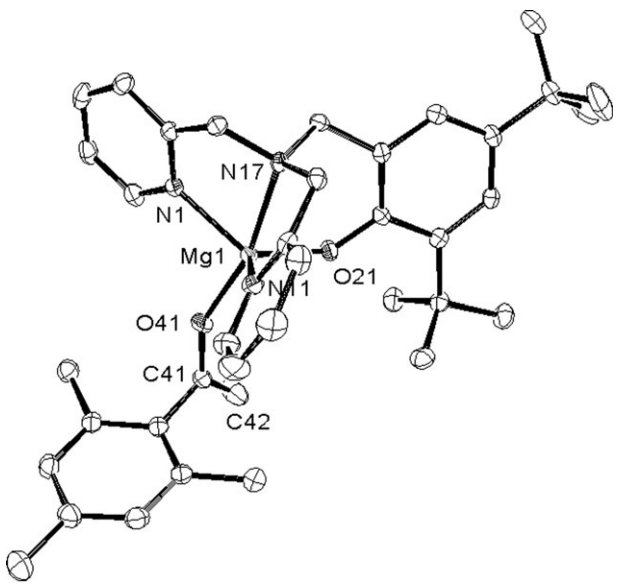



**Fig. 6** Solid-state structure of complex $[L^1]Mg\{OC(=CH_2)(2,4,6\text{-}Me_3C_6H_2)\}$ (**10**) (ellipsoids drawn at the 50% probability, H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Mg(1)–O(41), 1.888(2); Mg(1)–O(21), 1.903(2); Mg(1)–N(1), 2.143(2); Mg(1)–N(11), 2.178(2); Mg(1)–N(17), 2.273(2); O(41)–C(41), 1.319(2); C(41)–C(42), 1.333(3); O(41)–Mg–(1)–O(21), 107.61(7); O(41)–Mg(1)–N(1), 92.22(7); O(41)–Mg(1)–N(11), 102.00(7); O(41)–Mg(1)–N(17), 163.93(7); O(21)–Mg(1)–N(1), 120.64(7); O(21)–Mg(1)–N(11), 115.82(7); O(21)–Mg(1)–N(17), 87.79(6); N(1)–Mg(1)–N(11), 113.40(7); N(1)–Mg(1)–N(17), 75.56(6); N(11)–Mg(1)–N(17), 74.24(7); O(41)–C(41)–C(42), 126.0(2).

They are only slightly smaller than those of 1.908(2) and 1.921(2) Å observed for C,O-bridging enolate groups in the dimeric $[(BDI)Mg(\mu,\mu\text{-}OC(=CH_2)Mes)]_2$ (BDI = $HC(C(Me)=N\text{-}2,6\text{-}iPr_2C_6H_3)_2$).[20f] The bond distances and angles associated to the aminophenolate ligand are similar to those observed in a related $[N_3O]Mg(i\text{Pr})$ complex.[7] The two five-membered rings in **10** have an envelop conformation with the N(17) atom lying *ca.* 0.59 Å out of the Mg(1)–N(11)–C(15)–C(16) plane, and *ca.* 0.63 Å out of the Mg(1)–N(1)–C(5)–C(6) plane.

The $^1H$ and $^{13}C$ NMR spectra of **10** contain each one set of well resolved resonances which were fully assigned on the basis of 2D $^1H$–$^1H$ COSY, and $^1H$–$^{13}C$ HMQC and HMBC experiments (see Experimental section). Key data include only one signal in both the $^1H$ and $^{13}C$ NMR spectra in $C_6D_6$ for magnetically equivalent C*HH*-pyridine groups. This is indicative that, in benzene solution, both pyridine groups are coordinated to the magnesium center, and that the structure found in the solid state is maintained in solution. Other important data for **10** include two finely-coupled $^1H$ NMR resonances ($J < 0.3$ Hz) at $\delta$ 5.10 and 4.47 ppm for the OC=C*HH* hydrogens of the enolate group. These resonances are more deshielded than those reported for the mixed Mg–Na–enolate complexes of the type $[Na_2Mg_x\{\mu\text{-}OC(=CH_2)Mes\}_y(TMEDA)_2]$ ($\delta$ 4.69–5.01 and 4.02–4.20 ppm in $C_6D_6$),[20e] $[(BDI)Mg\{\mu,\mu\text{-}OC(=CH_2)Mes\}]_2$ ($\delta$ 4.10 and 3.72 ppm in $C_6D_6$),[20f] and even more than for (BDI)Mg{OC(=$CH_2$)Mes}(THF) ($\delta$ 3.58 and 2.98 ppm in THF-$d_8$).[20f] Except in the latter case where change of the NMR solvent (THF for benzene) is likely to have a major impact on chemical shifts, we assume that these NMR trends reflect the different coordination modes of the enolate groups in those complexes. The latter trends are more obvious in $^{13}C$ NMR spectroscopy. In fact, the key $^{13}C$ NMR chemical shifts for **10** ($\delta$ (O(*C*=$CH_2$)) 166.86; $\delta$ (=*C*$H_2$) 81.80 ppm) compare well with those in (BDI)Mg{OC(=$CH_2$)Mes}(THF) ($\delta$ (O(*C*=$CH_2$)) 165.83; $\delta$ (=*C*$H_2$) 84.97 ppm),[20f] which has also a terminal O–bounded enolate group, while these for bridging enolate groups in $[Na_2Mg_x\{\mu\text{-}OC(=CH_2)Mes\}_y(TMEDA)_2]$ are more shielded ($\delta$ (O(*C*=$CH_2$)) 161.23, 163.12 and 165.17; $\delta$ (=*C*$H_2$) 89.74, 87.02 and 83.91 ppm).[20e]

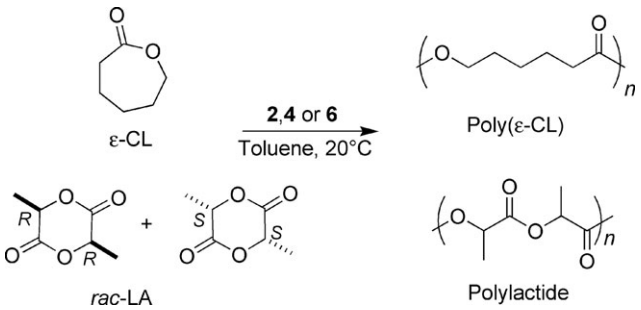
The 1D and 2D NMR spectra of **11** in either $C_6D_6$ (300 MHz) or $CD_2Cl_2$ (500 MHz) at 20 °C were much more complicated, and could not be fully interpreted. Though most of the resonances were relatively sharp, severe overlapping occurred and the chemical shifts of the many diastereotopic hydrogens appear to be significantly affected by anisotropic shielding of the aryl groups, hampering a straightforward interpretation. The number and similar intensity of $^1H$ NMR resonances for the *t*Bu and Ar–*Me* groups, and of the many AB systems [also identified in the $^1H$–$^1H$ COSY spectrum] for the C*HH* groups as well, suggest the existence of two sets of resonances in a *ca.* 1 : 1 ratio. This might be indicative of the presence of two [mononuclear] isomers in comparable proportions or, more likely, of a dinuclear species with non-equivalent ligands. Consistent with these hypotheses is the observation in the $^{13}C$ NMR spectrum of two resonances of similar intensity for the enolate methylenic group at $\delta$ 93.34 and 81.31 ppm. The latter resonances correlate in the $^1H$–$^{13}C$ HMQC spectrum with two sets of doublets [authenticated in the $^1H$–$^1H$ COSY spectrum in $CD_2Cl_2$] at $\delta$ 5.00 and 3.35 ppm ($J$ = 12.7 Hz) and $\delta$ 3.45 and 3.10 ppm ($J$ = 13.5 Hz), respectively. Unfortunately, attempts to grow suitable crystals of **11** for X-ray diffraction to assess the exact nuclearity of this compound in the solid state were unsuccessful. The formulation of complex **11** (as in Scheme 3) appears to be only possible on the basis of elemental analysis and by analogy with that of complex **10**.

### Preliminary studies on the reactivity towards polar monomers

Zinc and magnesium complexes modified by ancillary ligands have been used with great success for the controlled polymerization of polar monomers such as (meth)acrylates, lactide (LA), and lactones.[22–26] We are therefore interested in investigating the catalytic activity of the new mononuclear zinc and magnesium complexes that we have prepared and we report here some preliminary observations.

**Reactivity towards methyl methacrylate.** Zinc and magnesium enolate complexes have recently been shown to feature high performances for the polymerization of methyl methacrylate (MMA), affording PMMAs with a high degree of control in terms of molecular weight, molecular weight distribution, and tacticity.[21,25] The reactivity of the prepared complexes towards MMA was therefore investigated, either as single initiators or in combination with $Li[OC(=CH_2)\text{-}(2,4,6\text{-}Me_3C_6H_2)]$. Both zinc complexes **1** and **5** showed no activity, even when 1 equiv. of the bulky Li-enolate was added to produce *in situ* the enolate-zincate species. More surprisingly, isolated Mg-enolate complexes **10** and **11** also showed no activity towards MMA polymerization. Indeed, even though metal enolates are known to adopt a variety of structural motifs, which are dependent on the choice of metal, solvent, and steric bulk of the ligands,[27] enolates of electropositive metals such as **10** and **11** prefer O-bound structures,[28] and are usually reactive in MMA polymerizations.[29] More, Gibson reported recently very high activities for MMA polymerization with related imidinate-Mg-enolate $[(BDI)Mg(OC(=CH_2)(2,4,6\text{-}Me_3C_6H_2))]_2$. One might explain this inactivity by the high coordination number of the metal center in **10** and **11**, which would prevent coordination of the MMA monomer, compared to Gibson's initiator which is 3-coordinated.[25]

**Reactivity towards ε-caprolactone and *rac*-lactide.** The ability of the zinc complexes to catalyze the ROP of ε-caprolactone (ε-CL) and *rac*-lactide (*rac*-LA) was also preliminarily examined (Scheme 6). Some first results are given in Table 2. Zinc complexes **4** and **6** proved significantly active and productive initiators for the ROP of ε-CL, allowing conversions of 200–3700 equiv. of monomer at room temperature (Entries 1–4). The degree of control over the polymerization (as judged by the correspondence of experimental and theoretical molecular weights, and molecular weight distributions) was relatively good for **6** but appeared to be quite poor for **4**, presumably due to transesterification reactions and/or side reactions with impurities that act as transfer agents.[30] Complexes **2**, **4** and **6** are also active for the polymerization of *rac*-lactide at room temperature, affording atactic[31] PLAs




**Scheme 6** Ring-opening polymerization of ε-caprolactone (ε-CL) and *rac*-lactide (*rac*-LA).

(Entries 5–7). Significant differences in terms of activity and of degree of control were observed, suggesting a major influence of the substituents on the phenolate ligands and the nature of the *N*-donor fragments, as well.

These preliminary results indicate that some of the above systems feature high polymerization activity, good molecular weight control and give relatively narrow molecular weight distributions; this is notably the case of complex **6** for the ROP of lactide. Overall, such performances compare well with those reported for some related, efficient aminophenolate-zinc systems.[13] A somehow disappointing feature of these aminophenolate-zinc systems remains the absence of stereocontrol achieved in the ROP of racemic lactide, whatever the substituents on the phenolate ligands and the nature of the *N*-donor fragments, while other Zn(II) systems, such as those supported by BDI-type ligands (BDI = $CH(CMeNC_6H_3$-2,6-$iPr_2)_2$), lead to highly heterotactic PLAs.[23] These observations further confirm the crucial role of ancillary ligands in chain-end stereocontrolled ROP processes.

## Conclusions

In conclusion, we have reported a new series of magnesium enolato and zinc alkyl or amido complexes supported by readily available polydentate monoanionic aminophenolate ligands. The ligands designed confer interesting activity and productivity to the zinc derivatives, which readily initiate the ROP of ε-CL and *rac*-lactide. Thorough studies are currently being pursued to evaluate and rationalize the influence of the *N*-donor fragments and of the substituents on the phenolate ligands on the activity and degree of control in these polymerizations, and will be reported in due course.

## Experimental

### General procedures

All experiments involving metal complexes were carried out under purified argon using standard Schlenk techniques or in a glove box (<1 ppm $O_2$, 5 ppm $H_2O$). Hydrocarbon solvents, diethyl ether and tetrahydrofuran were distilled from Na/benzophenone, toluene and pentane were distilled from Na/K alloy under nitrogen and degassed by freeze-thaw-vacuum cycles prior to use. Methanol was distilled from Mg chips. Chlorinated solvents were distilled from calcium hydride. Deuterated solvents were purchased from Eurisotop and purified before use. 3,5-Di(*tert*-butyl)-2-hydroxybenzaldehyde, *N*,*N*-bis(picolyl)amine, *N*-benzyl-*N*-(2-methylpyridine), bis(2-chloroethyl)amine hydrochloride, $NaBH_3CN$, $ZnEt_2$ (15 wt% solution in hexane) and $Mg(n,s\text{-}Bu)_2$ (1.0 M solution in heptane) were purchased from Acros or Aldrich Co. and used as received. $Zn[N(SiMe_3)_2]_2$ was prepared following the reported procedure.[34] $ZnEt(OEt)_2$ was prepared by ethanolysis of $ZnEt_2$ in toluene. ε-Caprolactone was dried over calcium hydride and then distilled at reduced pressure (2 mmHg, 85 °C) before use.

NMR spectra were recorded on Bruker AC-200, AC-300 and AM-500 spectrometers (in Teflon-valved NMR tubes for complexes) at 20 °C otherwise stated. $^1H$ and $^{13}C$ NMR chemical shifts were determined using residual solvent resonances and are reported *vs.* $SiMe_4$. Assignment of signals was made from 2D $^1H$–$^1H$ COSY and $^1H$–$^{13}C$ HMQC and HMBC NMR experiments. Coupling constants are given in Hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. High resolution mass spectra of complexes were obtained by ESI in the positive mode (6 keV) using a Micromass ZabSpec TOF spectrometer. Size exclusion chromatography (SEC) of PCL and PLA polymers was performed in THF at 20 °C using a Polymer Laboratories PL-GPC 50 plus apparatus (PLgel 5 μm MIXED-C 300 × 7.5 mm, 1.0 ml $min^{-1}$, RI and Dual angle LS detector (PL-LS 45/90)). The number average molecular masses ($M_n$) and polydispersity index ($M_w/M_n$) of the polymers were calculated with reference to a universal calibration *vs.* polystyrene standards. $M_n$ values were corrected by a Mark–Houwink factor of 0.56 and 0.58 for PCL[32] and PLA,[33] respectively, due to the use of PS standards.

**Table 2** Preliminary results obtained in the ring-opening polymerization of ε-caprolactone and *rac*-lactide promoted by complexes **2**, **4**, and **6**[a]

| Entry | Monomer M | [I] | [M]/[I] | *t*/min | $M_{n,calc}$[b]/g $mol^{-1}$ | $M_{n,exp}$[c]/g $mol^{-1}$ | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|---|
| 1 | ε-CL | **4** | 200 | 2 | 22 800 | 7600 | 1.8 |
| 2 | ε-CL | **4** | 3700 | 210 | 422 000 | 14 700 | 1.6 |
| 3 | ε-CL | **6** | 500 | 1 | 57 000 | 65 500 | 1.6 |
| 4 | ε-CL | **6** | 1000 | 2 | 114 000 | 179 000 | 1.6 |
| 5 | *rac*-LA | **2** | 100 | 15 | 14 400 | 15 500 | 3.6 |
| 6 | *rac*-LA | **4** | 100 | 1440 | 14 400 | 6100 | 1.9 |
| 7 | *rac*-LA | **6** | 100 | 180 | 14 400 | 13 800 | 1.7 |

[a] All reactions performed at 20 °C in toluene at [monomer] = 1–2 M (*i.e.*, slurry for *rac*-lactide), until completion as determined by the integration of $^1H$ NMR methyl resonances of *rac*-LA and PLA or methylene resonances of ε-CL and PCL. [b] $M_n$ of PCL or PLA calculated from the monomer conversion: $M_{n,calc}$ = ([ε-CL or *rac*-LA]/[Zn]) × conversion × $M$(monomer). [c] $M_n$ and $M_w/M_n$ of polymer determined by SEC-RI in THF at RT using polystyrene standards; $M_n$ values were corrected by a Mark–Houwink factor of 0.56 and 0.58 for PCL[32] and PLA,[33] respectively, due to the use of PS standards.



## Syntheses

**[L$^1$]H.**[16] To a 100 mL Schlenk flask containing 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol) in anhydrous MeOH (60 mL), bis(picolyl)amine (1.99 g, 10.0 mmol) was added slowly at room temperature, followed by several drops of aqueous acetic acid as catalyst. After stirring at room temperature for about 1 h, $NaBH_3CN$ (0.63 g, 10.0 mmol) was slowly added in by portions, and the reaction mixture was stirred at room temperature for 3 days. The mixture was acidified by adding 4 M aqueous HCl (*ca.* 10 mL) and then evaporated to dryness under vacuum. The residue was dissolved in saturated aqueous $Na_2CO_3$ (*ca.* 50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were evaporated to dryness to give a brown oil, which was further purified by flash chromatography ($CHCl_3$–methanol = 3 : 1) to give [L$^1$]H as a pale yellow powder (2.71 g, 65%). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 1.29 (s, 9H, *t*Bu), 1.48 (s, 9H, *t*Bu), 3.83 (s, 2H, C$H_2$-phenyl), 3.90 (s, 4H, C$H_2$-pyridyl), 6.91 (b, 1H, phenyl-H), 7.18 (t, $J$ = 6.5, 2H, pyridyl-4H), 7.23 (s, 1H, phenyl-H), 7.41 (d, $J$ = 7.5, 2H, pyridyl-2H), 7.66 (t, $J$ = 7.5, 2H, pyridyl-3H), 8.59 (d, $J$ = 4.9, 2H, pyridyl-5H), 10.6 (br s, 1H, O*H*).

**[L$^2$]H.** Aminophenol [L$^2$]H was prepared following the procedure described above for [L$^1$]H, starting from 5-chloro-3-methyl-2-hydroxy-benzaldehyde (0.50 g, 2.9 mmol), bis-(picolyl)amine (0.64 g, 3.2 mmol), and $NaBH_4$ (0.50 g, 13.2 mmol), to give after workup [L$^2$]H as a white powder (0.76 g, 74%). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 2.29 (s, 3H, Me), 3.76 (s, 2H, C$H_2$-pyridyl), 3.89 (s, 4H, C$H_2$), 6.92 (s, 1H, phenol-H), 7.05 (s, 1H, phenol-H), 7.20 (t, $J$ = 7, 2H, pyridyl-4H), 7.36 (d, $J$ = 7.7, 2H, pyridyl-2H), 7.67 (t, $J$ = 7.5, 2H, pyridyl-3H), 8.62 (d, $J$ = 4.0, 2H, pyridyl-5H), 11.17 (s, 1H, OH). $^{13}$C{$^1$H} NMR ($CDCl_3$, 75 MHz): $\delta$ 16.18 (*C*H$_3$), 56.61 (*C*H$_2$), 59.10 (2*C*H$_2$), 122.32 (pyridyl-*C4*), 123.27 (pyridyl-*C2*), 127.20 (phenol-C), 129.79 (phenol-C), 136.83 (pyridyl-*C3*), 149.06 (pyridyl-*C5*), 154.40 (phenol-*C1*), 158.04 (pyridyl-*C1*). Anal. Calc. for $C_{20}H_{20}ClN_3O$ (353.85): C, 67.89; H, 5.70; N, 11.88. Found: C, 68.0; H, 5.9; N, 11.9.

***N*,*N*-Bis[2-(3,5-dimethyl-1-pyrazole)ethyl]amine.** To a 100 mL Schlenk containing a suspension of NaH (1.38 g, 57.4 mmol) in DMF (50 mL) was added dropwise a solution of 3,5-dimethylpyrazole (3.68 g, 38.3 mmol) in DMF (10 mL). The reaction mixture was stirred for 2 h at room temperature. Then a solution of bis(2-chloroethyl)amine hydrochloride (3.41 g, 19.1 mmol) in DMF (10 mL) was added dropwise to the mixture. The reaction mixture was further stirred for 2 h at 70 °C, yielding a cream white dispersion which was cooled and filtered. The filtrate was evaporated to dryness *in vacuo*, and hot water (80 °C, 100 mL) was added. Cooling to room temperature gave white needle crystals. Finally, a colorless oil-like product (2.20 g, 45%) was obtained by further removing the residual water by azeotropic distillation overnight. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 2.16 (s, 6H, pyraz-C$H_3$), 2.19 (s, 6H, pyraz-C$H_3$), 2.95 (t, $^3J$ = 6.0, 4H, N(C$H_2$C$H_2$-pyraz)$_2$), 4.01 (t, $^3J$ = 6.0, 4H, N(C$H_2$C$H_2$-pyraz)$_2$), 5.74 (s, 2H, pyraz-*H*). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 1.81 (s, 6H, pyraz-C$H_3$), 2.29 (s, 6H, pyraz-C$H_3$), 2.70 (t, $^3J$ = 6.0, 4H, N(C$H_2$C$H_2$-pyraz)$_2$), 3.61 (t, $^3J$ = 6.0, 4H, N(C$H_2$C$H_2$-pyraz)$_2$), 5.69 (s, 2H, pyraz-*H*).

**2,4-Di(*tert*-butyl)-6-{bis[(3,5-dimethyl-1-pyrazole)ethylamino]-aminomethyl}phenol ([L$^3$]H).** To a solution of 3,5-di-(*tert*-butyl)-2-hydroxylbenzaldehyde (1.96 g, 8.4 mmol) in methanol (20 mL) were added bis[2-(3,5-dimethyl-1-pyrazole)-ethyl]amine (2.20 g, 8.4 mmol) and a small amount of acetic acid. Sodium cyanotrihydroborate (0.53 g, 8.4 mmol) was added by portions to the resulting solution with stirring. After the solution was stirred for three days at room temperature, it was acidified by adding 4 M aqueous HCl (*ca.* 10 mL) and then evaporated under reduced pressure. The residue was dissolved in saturated aqueous $Na_2CO_3$ (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated under vacuum to give a brown oil which was purified on a silica-gel column with chloroform–methanol to give [L$^3$]H as a colorless powder (1.60 g, 40%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.65 (s, 1H, PhO*H*), 7.23 (d, $J$ = 2.4, 1H, phenol-C*H*), 6.82 (d, $J$ = 2.4, 1H, phenol-C*H*), 5.76 (s, 2H, pyr-C*H*), 4.03 (t, 4H, $J$ = 6.6, NC$H_2$CH$_2$NCH$_2$C$H_2$N), 3.81 (s, 2H, NC$H_2$PhOH), 2.98 (t, $J$ = 6.6, 4H, NCH$_2$C$H_2$NC$H_2$CH$_2$N), 2.19 (s, 6H, C$H_3$-pyraz), 2.07 (s, 6H, C$H_3$-pyraz), 1.39 (s, 9H, phenol-*tBu*), 1.29 (s, 9H, phenol-*tBu*). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 10.81 (*C*H$_3$-pyraz), 13.45 (*C*H$_3$-pyraz), 29.59 (C(*C*H$_3$)$_3$), 37.67 (*C*(CH$_3$)$_3$), 46.12 (N*C*H$_2$CH$_2$NCH$_2$*C*H$_2$N), 53.94 (NCH$_2$*C*H$_2$N*C*H$_2$CH$_2$N), 59.51 (Zn*C*H$_2$-phenol), 105.16 (*C*H-pyraz), 123.41 (*C*-pyraz), 123.83 (*C*-pyraz). ESI-HRMS: calcd for [M + H]$^+$: 480.37024; found: 480.3711; calc. for [M + Na]$^+$: 502.35218; found: 502.3519.

***N*-Benzyl-*N*-(2-methylpyridine).** This compound was prepared using a modified procedure from that reported in the literature.[35] To a 100 mL Schlenk flask containing 2-aminomethyl(pyridine) (7.55 g, 70 mmol) in anhydrous MeOH (50 mL), benzaldehyde (7.45 g, 70 mmol) was added slowly in at room temperature. Then, several drops of aqueous acetic acid were added as catalyst. After stirring at room temperature for about 1 h, the solution was cooled to 0 °C and then $NaBH_4$ (3.97 g, 105 mmol) was slowly added in by portions. After stirring for 30 min, the solution was poured into a flask and acidified with 4 M HCl till pH = *ca.* 1. KOH pellets were then added to the solution until pH = 14 was reached, and the solution was extracted with $CH_2Cl_2$ (*ca.* 50 mL). The organic phases were combined, dried over $Na_2SO_4$ and the solvents were removed under vacuum to give yellowish oil. The oil was distilled under vacuum (180 °C/0.1 mmHg) to afford *N*-benzyl-*N*-(2-methylpyridine) as a colorless oil (11.1 g, 80%). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 8.56 (d, $J$ = 4.2, 1H, pyridyl-2H), 7.63 (t, $J$ = 6.3, 1H, pyridyl-3H), 7.17–7.32 (m, 7H, pyridyl-H and phenyl-H), 3.92 (s, 2H, C$H_2$-pyridyl), 3.84 (s, 2H, C$H_2$-phenyl), 2.14 (br s, 1H, N*H*).

**[L$^4$]H.** Aminophenol [L$^3$]H was prepared following the procedure described above for [L$^1$]H, starting from 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol), *N*-benzyl-*N*-(2-methylpyridine) (1.98 g, 10.0 mmol), and $NaBH_3CN$ (0.63 g, 10.0 mmol), to give after workup [L$^4$]H as a white powder (1.58 g, 38%). $^1$H NMR ($CDCl_3$, 300 MHz):

$\delta$ 1.29 (s, 9H, *t*Bu), 1.47 (s, 9H, *t*Bu), 3.71 (s, 2H, C$H_2$-pyridyl), 3.80 (s, 4H, C$H_2$), 6.88 (d, $J$ = 2.4, 1H, Ph-2,6-*H*), 7.10–7.40 (m, 7H, pyridyl-H and phenyl-H), 7.68 (t, $J$ = 17.1, 1H, pyridyl-5H), 8.58 (d, $J$ = 5.0, 1H, pyridyl-6H). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): $\delta$ 29.60 (C($CH_3$)$_3$), 31.66 (C($CH_3$)$_3$), 34.13 ($C$(CH$_3$)$_3$), 34.91 ($C$(CH$_3$)$_3$), 57.90 (CH$_2$), 59.36 (CH$_2$), 122.30 (pyridyl-*C5*), 122.94 (Ph-C), 124.13 (pyridyl-*C3*), 128.49 (Ph-C), 129.93 (Ph-C), 135.48 (phenol-*C6*), 136.62 (pyridyl-*C4*), 140.63 (phenol-*C4*), 149.13 (pyridyl-*C6*), 157.92 (pyridyl-*C2*). ESI-HRMS: calc. for $C_{28}H_{37}N_2O$ [M + H]$^{\bullet+}$, 417.2906; found, 417.2893; calc. for $C_{28}H_{36}N_2ONa$ [M + Na]$^{\bullet+}$, 439.2725; found, 439.2725.

**[L$^5$]H.** Aminophenol [L$^4$]H was prepared following the procedure described above for [L$^1$]H, starting from 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10.0 mmol), *N*,*N*-dibenzylamine (1.97 g, 10.0 mmol), and $NaBH_3CN$ (0.63 g, 10.0 mmol), to give after workup [L$^3$]H as a white powder (1.89 g, 46%). $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 1.37 (s, 9H, *t*Bu), 1.69 (s, 9H, *t*Bu), 3.31 (s, 4H, C$H_2$), 3.46 (s, 2H, C$H_2$), 6.9–7.5 (m, 12H, phenyl-H). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): $\delta$ 29.58 (C($CH_3$)$_3$), 31.69 (C($CH_3$)$_3$), 34.13 ($C$(CH$_3$)$_3$), 34.91 ($C$(CH$_3$)$_3$), 57.61 (CH$_2$), 58.07 (CH$_2$), 121.23, 122.88, 123.84, 127.51, 129.69, 128.51, 129.69, 137.04, 140.50, 153.85 (C arom). ESI-HRMS: calc. for $C_{29}H_{38}NO$ [M + H]$^{\bullet+}$, 416.2953; found, 416.2960.

**[L$^1$]ZnEt (1).** Complex **1** was prepared according to the reported method.[2] To a 50 mL Schlenk flask were added [L$^1$]H (0.200 g, 0.48 mmol), toluene (10 mL), and $ZnEt_2$ (0.390 g of a 15 wt% solution in hexane, 0.48 mmol). The reaction mixture was stirred at room temperature overnight. After evaporation of volatiles under vacuum, the residue was washed with pentane at −78 °C to give **1** as a white powder (0.205 g, 84%). $^1H$ NMR ($C_6D_6$, 200 MHz): $\delta$ 0.76 (q, $J$ = 8.2, 2H, ZnC$H_2$CH$_3$), 1.37 (s, 9H, *t*Bu), 1.71 (t, $J$ = 8.2, 3H, ZnCH$_2$C$H_3$), 1.85 (s, 9H, *t*Bu), 3.45 (s, 2H, CH$_2$-phenolate), 3.74 (d, $J$ = 15.0, 2H, C$H_2$-pyridyl), 4.04 (d, $J$ = 15.0, 2H, C$H_2$-pyridyl), 6.40-7.40 (m, 8H, arom), 8.19 (d, $J$ = 4.6, 2H, pyridyl-5H).

**[L$^2$]ZnN(SiMe$_3$)$_2$ (2).** To a solution of [L$^2$]H (0.400 g, 0.83 mmol) in toluene (10 mL) was added a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (0.320 g, 0.83 mmol) in toluene (5 mL). The mixture was stirred for 24 h at room temperature and volatiles were removed *in vacuo* leaving a powder, which was washed by a minimum amount of cold pentane to give **2** as a colorless powder (0.310 g, 65%). $^1H$ NMR ($C_6D_6$, 500 MHz): $\delta$ 0.60 (s, 18H, N(SiMe$_3$)$_2$), 2.33 (s, 3H, Me), 3.04 (s, 2H, C$H_2$), 3.26 (d, $J$ = 15, 2H, C$H_2$-pyridyl), 3.38 (d, $J$ = 15, 2H, C$H_2$-pyridyl), 6.33 (d, $J$ = 7.5, 2H, pyridyl-3H), 6.66 (t, $J$ = 6.5, 2H, pyridyl-5H ), 6.82 (s, 1H, phenol-H), 7.02 (s, 1H, phenol-H), 6.91 (t, $J$ = 7.5, 2H, pyridyl-4H), 9.13 (d, $J$ = 4.0, 2H, pyridyl-2H). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): $\delta$ 6.09 (N(SiMe$_3$)$_2$), 17.65 ($C$H$_3$), 60.04 ($C$H$_2$), 115.55 (phenol-C), 121.40 (phenol-C), 122.39 (pyridyl-*C4*), 123.07 (pyridyl-*C2*), 127.14 (phenol-C), 130.15 (phenol-C), 138.06 (pyridyl-*C3*), 148.90 (pyridyl-*C5*), 153.77 (pyridyl-*C1*), 165.38 (phenol-*C1*). Anal. Calc. for $C_{26}H_{37}ClN_4OSi_2Zn$ (578.60): C, 53.97; H, 6.45; N, 9.68. Found: C, 54.1; H, 6.5; N, 9.8.

**[L$^3$]ZnEt (3).** *Synthesis from ZnEt$_2$*: Complex **3** was prepared in 87% yield following a protocol similar to that described above for **1**. *Synthesis from EtZnOEt*: To a solution of zinc ethylethoxide (0.072 g, 0.52 mmol) in toluene (3 mL) was slowly added [L$^2$]H (0.248 g, 0.52 mmol) in toluene (5 mL) at −78 °C. The mixture was stirred for 24 h at room temperature. The volatiles were removed *in vacuo* leaving a viscous oil, which was further recrystallized from pentane at −30 °C to give **3** as a pale yellow crystalline solid (0.050 g, 17%). $^1H$ NMR (500 MHz, $C_6D_6$): $\delta$ 0.76 (q, 2H, $J$ = 8.0, ZnC$H_2$CH$_3$), 1.59 (s, 6H, C$H_3$-pyraz), 1.62 (s, 9H, *tBu*), 1.89 (t, 3H, $J$ = 8.0, ZnCH$_2$C$H_3$), 1.95 (s, 9H, *tBu*), 2.34 (s, 6H, C$H_3$-pyraz), 2.79 (m, 4H, NCH$_2$C$H_2$NC$H_2$CH$_2$N), 3.53 (t, 4H, $J$ = 5.5, NC$H_2$CH$_2$NCH$_2$C$H_2$N), 3.62 (s, NC$H_2$-phenol), 5.55 (s, 2H, pyraz-C*H*), 7.05 (d, 1H, $J$ = 2.6, phenol-C*H*), 7.76 (d, 1H, $J$ = 2.6, phenol-C*H*). $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$): $\delta$ −0.47 (Zn$C$H$_2$CH$_3$), 10.12 (C$H_3$-pyraz), 13.16 (C$H_3$-pyraz), 13.75 (ZnCH$_2$$C$H$_3$), 29.86 (C($CH_3$)$_3$), 32.22 (C($CH_3$)$_3$), 33.96 ($C$(CH$_3$)$_3$), 35.57 ($C$(CH$_3$)$_3$), 44.50 (NCH$_2$$C$H$_2$NCH$_2$CH$_2$N), 55.44 (NCH$_2$CH$_2$NCH$_2$$C$H$_2$N), 63.69 (phenol-$C$H$_2$), 105.42 (pyraz-*C*H), 124.34 (phenol-*C*H), 125.67 (phenol-*C*H). Anal. Calc. for $C_{31}H_{49}N_5OZn$ (573.14): C, 64.96; N, 12.22; H, 8.62. Found: C, 65.1; N, 11.9; H, 8.8.

**[L$^3$]ZnN(SiMe$_3$)$_2$ (4).** This compound was prepared in a similar manner to [L$^2$]ZnN(SiMe$_3$)$_2$ (**2**) starting from [L$^3$]H (0.400 g, 0.83 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (0.320 g, 0.83 mmol) in toluene (5 mL). Compound **4** was obtained as a colorless powder (0.380 g, 65%). $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 0.51 (s, 18H, N(SiMe$_3$)$_2$), 1.14 (s, 3H, C$H_3$-pyraz), 1.59 (s, 9H, *t*Bu), 1.85 (s, 9H, *t*Bu), 2.08 (s, 3H, CH$_3$-pyraz), 2.28 (m, 1H, NCH$_2$CH$_2$NCH$_2$C*H*HN), 2.38 (s, 3H, C$H_3$-pyra), 2.57 (s, 3H, C$H_3$-pyra), 2.92 (m, 1H, NCH$_2$CH$_2$NCH$_2$CH*H*N), 3.11 (d, 1H, $J$ = 1.9, ZnCH*H*-phenol), 3.24 (m, 4H, ZnCH*H*-phenol, NCH$_2$C*H*HNC*H*HC*H*HN), 3.93 (m, 1H, NCH$_2$CH$_2$N-CH*H*CH$_2$N), 4.18 (m, 1H, NCH*H*CH$_2$NCH$_2$CH$_2$N), 4.47 (m, 1H, NCH*H*CH$_2$NCH$_2$CH$_2$N), 4.63 (d, 1H, $J$ = 1.9, ZnCH*H*-phenol), 5.33 (s, 1H, pyraz-C*H*), 5.83 (s, 1H, pyraz-C*H*), 7.03 (d, 1H, $J$ = 2.4, phenol-C*H*), 7.66 (d, $J$ = 2.4, 1H, phenol-C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 5.87 (N(SiMe$_3$)$_2$), 9.92 ($C$H$_3$-pyraz), 10.36 ($C$H$_3$-pyraz), 13.75 ($C$H$_3$-pyraz), 13.81 ($C$H$_3$-pyraz), 29.96 (C($CH_3$)$_3$), 32.17 (C($CH_3$)$_3$), 33.93 ($C$(CH$_3$)$_3$), 35.42 ($C$(CH$_3$)$_3$), 42.32 (NCH$_2$CH$_2$NCH$_2$CH$_2$N), 42.61 (NCH$_2$$C$H$_2$NCH$_2$CH$_2$N), 53.05 (NCH$_2$CH$_2$NCH$_2$CH$_2$N), 56.44 (NCH$_2$CH$_2$NCH$_2$-$C$H$_2$N), 61.84 (Zn$C$H$_2$-phenol), 105.55 (pyraz-*C*H), 105.94 (pyraz-*C*H), 124.66 (phenol-*C*H), 125.35 (phenol-*C*H). Anal. Calc. for $C_{35}H_{62}N_6OSi_2Zn$ (704.46): C, 59.67; N, 11.93; H, 8.87. Found: C, 59.4; N, 11.8; H, 9.0.

**[L$^3$]ZnEt (5).** Complex **5** was prepared following the procedure described above for **3**, starting from [L$^3$]H (0.200 g, 0.48 mmol), toluene (10 mL), and $ZnEt_2$ (0.390 g of a 15 wt% solution in hexane, 0.48 mmol). Recrystallization of the final solid from pentane at −30 °C gave **5** as colorless crystals (0.210 g, 84%). $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 0.76 (m, 2H, ZnC$H_2$CH$_3$), 1.34 (s, 9H, *t*Bu), 1.71 (m, 3H, ZnCH$_2$C$H_3$), 1.88 (s, 9H, *t*Bu), 3.02–3.70 (m, 4H, C$H_2$-pyridyl and

$CH_2$-phenol), 3.80 (s, 2H, $CH_2$-phenyl), 5.90–7.20 (m, 8H, arom), 7.40 (m, 1H, pyridyl-3H), 7.82 (d, $J$ = 2.3, 1H, pyridyl-6H). $^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 0.34 (m, $J$ = 8.1, 2H, $ZnCH_2CH_3$), 1.20 (s, 9H, *t*Bu), 1.30 (t, $J$ = 8.1, 3H, $ZnCH_2CH_3$), 1.39 (s, 9H, *t*Bu), 3.40 (d, $J$ = 11.6, 1H, C*H*H), 3.63 (d, $J$ = 15.5, 1H, C*H*H), 3.90 (d, $J$ = 11.6, 1H, C*H*H), 4.19 (d, $J$ = 2.5, 2H, $CH_2$Ph), 4.22 (d, $J$ = 15.5, 1H, C*H*H), 6.67 (d, $J$ = 2.6, 1H, H arom), 6.97 (d, $J$ = 2.6, 1H, H arom), 7.01 (d, $J$ = 7.8, 1H, H arom), 7.21 (dt, $J$ = 1.6 and 6.3, 1H, pyridyl-5H), 7.45–7.50 (m, 5H, H arom Ph), 7.64 (dt, $J$ = 1.6 and 6.3, 1H, pyridyl-4H), 8.35 (d, $J$ = 4.6, 1H, pyridyl-6H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 75 MHz): $\delta$ −1.72 ($ZnCH_2CH_3$), 13.86 ($ZnCH_2CH_3$), 30.09 ($C(CH_3)_3$), 32.26 ($C(CH_3)_3$), 33.83 ($C(CH_3)_3$), 35.58 ($C(CH_3)_3$), 58.28 ($CH_2$), 60.29 ($CH_2$), 71.76 ($CH_2$), 121.71, 122.67, 123.48, 125.63, 126.73, 128.11, 131.35, 138.20, 147.69, 150.48 (C arom). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 125 MHz): $\delta$ −2.68 ($ZnCH_2CH_3$), 13.07 ($ZnCH_2CH_3$), 29.37 ($C(CH_3)_3$), 31.60 ($C(CH_3)_3$), 33.53 ($C(CH_3)_3$), 34.89 ($C(CH_3)_3$), 58.64 ($CH_2$), 59.55 ($CH_2$), 61.13 ($CH_2$Ph), 121.75, 122.22, 123.11 (pyridyl-C5), 123.55, 125.55, 128.39, 128.48, 131.39, 133.20, 134.18, 136.90, 138.78 (pyridyl-C4), 147.81, 156.05, 164.26 (pyridyl-C6). Anal. Calc. for $C_{30}H_{40}N_2OZn$ (510.01): C, 70.65; N, 5.49; H, 7.90. Found: C, 70.5; N, 5.6; H, 8.0.

**[L$^4$]ZnN(SiMe$_3$)$_2$ (6).** This compound was prepared in a similar manner to [L$^2$]ZnN(SiMe$_3$)$_2$ (**2**) starting from [L$^4$]H (0.310 g, 0.74 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (0.278 g, 0.72 mmol) in toluene (15 mL). Compound **5** was obtained as a colorless powder (0.350 g, 76%). $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ 0.55 (s, 18 H, N(SiMe$_3$)$_2$), 1.18 (s, 9H, *tBu*), 1.59 (s, 9H, *tBu*), 2.97 (d, 1H, $J$ = 11.4, NCH*H*Ph), 3.07 (d, 1H, $J$ = 15.5, NCH*H*-phenol), 3.83 (d, 1H, $J$ = 15.5, NCH*H*-phenol), 4.08 (d, 1H, $J$ = 11.4, NCH*H*Ph), 4.13 (d, 1H, $J$ = 13.7, NCH*H*-pyridyl), 4.26 (d, 1H, $J$ = 13.7, NCH*H*-pyridyl), 5.95 (d, 1H, $J$ = 7.8, pyridyl-C*H*), 6.22 (t, 1H, $J$ = 6.3, pyridyl-C*H*), 6.33 (d, 1H, $J$ = 2.5, pyridyl-C*H*), 6.61 (dt, 1H, $^2J$ = 7.7, $^3J$ = 1.6, pyridyl-C*H*), 7.00 (d, 1H, $J$ = 2.6, phenol-C*H*), 7.89 (d, 1H, $J$ = 4.7, pyridyl-C*H*). $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): $\delta$ 6.02 (N(SiMe$_3$)$_2$), 29.65 ($C(CH_3)_3$), 31.83 ($C(CH_3)_3$), 33.39 ($C(CH_3)_3$), 35.04 ($C(CH_3)_3$), 58.69 (N$CH_2$-phenolate), 61.33 (N$CH_2$Ph), 63.48 (N$CH_2$-pyridyl), 121.11 (pyridyl-*C*H), 122.60 (pyridyl-*C*H), 123.49 (phenolate-*C*H), 124.75 (pyridyl-*C*H), 127.88, 131.34, 132.65, 134.22, 137.90 (pyridyl-*C*H), 147.47 (pyridyl-*C*H), 154.54 (phenolate-*C*), 164.31 (pyridyl-C6). Anal. Calc. for $C_{34}H_{53}N_3OSi_2Zn$ (641.37): C, 63.67; N, 6.55; H, 8.33. Found: C, 63.4; N, 6.5; H, 8.4.

**1 : 1 Reaction of [L$^5$]H with ZnEt$_2$. Generation of [L$^5$]$_2$Zn (7) and {[L$^4$]ZnEt}$_n$ (8).** To a 50 mL Schlenk flask containing [L$^4$]H (0.199 g, 0.48 mmol) in toluene (10 mL), $ZnEt_2$ (0.390 g of a 15 wt% solution in hexane, 0.48 mmol) was slowly added in at −78 °C. The solution was warmed to room temperature and stirred overnight. After evaporation of volatiles under vacuum, the residue was recrystallized from pentane at −30 °C to give white crystals (0.190 g), which proved by $^1$H NMR to be a mixture of [L$^4$]$_2$Zn (**7**, 23%) and [L$^4$]ZnEt (**8**, 77%). $^1$H NMR ($C_6D_6$, 500 MHz) **7**: $\delta$ 1.61 (s, 18H, *t*Bu), 1.87 (s, 18H, *t*Bu), 3.22 (br d, 2H, C*H*H), 3.83 (d, $J$ = 14.5, 4H, C*H*H), 4.19 (d, $J$ = 12.6, 2H, C*H*H), 4.58 (br d, $J$ = 13.5, 2H, C*H*H), 4.90 (br d, $J$ = 13.5, 2H, C*H*H), 7.10–7.40 (m, 20H, H arom), 7.77 (d, $J$ = 2.5, 2H, H phenolato). **8** (selected key resonances): $\delta$ 0.61 (q, $J$ = 8.1, 2H, $ZnCH_2CH_3$), 1.31 (t, $J$ = 8.1, 3H, $ZnCH_2CH_3$), 1.53 (s, 9H, *t*Bu), 1.97 (s, 9H, *t*Bu), 3.45 (d, $J$ = 13, 2H, C*H*H), 3.65 (m, 4H, 2 C*H*H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 125 MHz): **7**: $\delta$ 29.95 ($C(CH_3)_3$), 32.03 ($C(CH_3)_3$), 34.04 ($C(CH_3)_3$), 35.53 ($C(CH_3)_3$), 55.63 (N$CH_2$-phenolate)), 61.07 (N$CH_2$Ph), 119.58, 124.06, 128.93, 130.18, 132.07, 135.09, 135.31, 138.59, 163.41 (C arom). **8** (selected key resonances) $\delta$ 0.55 ($ZnCH_2CH_3$), 12.23 ($ZnCH_2CH_3$), 29.88 ($C(CH_3)_3$), 32.01 ($C(CH_3)_3$), 33.89 ($C(CH_3)_3$), 35.63 ($C(CH_3)_3$), 57.73 ($CH_2$), 60.09 ($CH_2$).

**1 : 1 Reaction of [L$^5$]H with Zn(N(SiMe$_3$)$_2$). Generation of [L$^5$]$_2$Zn (7) and {[L$^5$]Zn(N(SiMe$_3$)$_2$)}$_n$ (9).** This reaction was carried out as described above, starting from [L$^4$]H (0.200 g, 0.48 mmol), Zn(N(SiMe$_3$)$_2$)$_2$ (0.185 g, 0.48 mmol) in toluene (15 mL). Workup afforded a colorless powder (0.100 g), which proved to be by $^1$H NMR a *ca.* 80 : 20 mixture of **7** and **9**. $^1$H NMR (200 MHz, $C_6D_6$) for {[L$^4$]Zn(N(SiMe$_3$)$_2$)}$_n$ (**9**): $\delta$ 0.31 (s, 18H, ZnN(Si*Me*$_3$)$_2$), 1.45 (s, 9H, *t*Bu), 1.78 (s, 9H, *t*Bu), 3.53 (s, 2H, NC$H_2$-phenol), 3.62 (s, 2H, NC$H_2$Ph), 3.81 (s, 2H, NC$H_2$Ph), 6.85 (m, 2H, H-Ph), 7.07 (m, 4H, H-Ph), 7.10 (m, 4H, H-Ph), 7.61 (2 overl. s, 2 × 1H, H-phenolate).

**[L$^1$]Mg{OC(=CH$_2$)(2,4,6-Me$_3$C$_6$H$_2$)} (10).** To a 50 mL Schlenk flask containing [L$^1$]H (0.200 g, 0.48 mmol) in toluene (10 mL), Mg(*n*,*s*Bu)$_2$ (0.48 mL of a 1.0 M solution in heptane, 0.48 mmol) was added slowly in at −78 °C. The solution was slowly warmed to room temperature for 30 min; then, under stirring, 2,4,6-Me$_3$C$_6$H$_2$COMe (0.077 g, 0.48 mmol) was added in *via* syringe under argon. A white precipitate formed after 10 min. The solution was concentrated under vacuum to *ca.* 5 mL, and the white residue was recrystallized from toluene (*ca.* 30 mL) at −30 °C to give **10** as white crystals (0.190 g, 63%). $^1$H NMR ($C_6D_6$, 500 MHz): $\delta$ 1.63 (s, 9H, *t*Bu), 2.06 (s, 9H, *t*Bu), 2.45 (s, 3H, *p*-Me), 2.84 (d, $J$ = 15.5, 2H, $CH_2$-phenolate), 3.11 (s, 6H, 2 × *o*-Me), 3.45 (m, 4H, $CH_2$-pyridyl), 4.47 (s, 1H, OC=CH*H*), 5.10 (s, 1H, OC=C*H*H), 6.23 (d, $J$ = 7.7, 2H, pyridyl-3H), 6.56 (t, $J$ = 12.5, 2H, pyridyl-5H), 6.83 (t, $J$ = 15.3, 2H, pyridyl-4H), 7.12 (s, 1H, phenolate-5H), 7.17 (s, 2H, phenyl-3,5-H), 7.74 (s, 1H, phenolate-3H), 9.30 (d, 2H, $J$ = 5.0, 2H, pyridyl-6H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 125 MHz): $\delta$ 20.80 (*o*-Me), 21.12 (*p*-Me), 30.07 ($C(CH_3)_3$), 32.34 ($C(CH_3)_3$), 33.83 ($C(CH_3)_3$), 35.74 ($C(CH_3)_3$), 57.52 ($CH_2$-phenolate), 60.79 ($CH_2$-pyridyl), 81.80 (C=$CH_2$), 122.00 (pyridyl-*C3*), 123.20 (pyridyl-*C4*), 124.32 (phenolate-*C3*), 124.95 (phenolate-*C5*), 128.00 (phenyl-3,5-C), 133.21 (phenolate-*C4*), 134.03 (phenyl-*C4*), 135.21 (phenyl-2,6-C), 138.52 (pyridyl-*C5*), 138.89 (phenolate-*C6*), 144.89 (phenyl-*C1*), 151.13 (pyridyl-*C6*), 156.83 (pyridyl-*C2*), 164.57 (phenolate-*C1*), 166.86 (*C*OMg). Anal. Calc. for $C_{38}H_{47}MgN_3O_2$ (602.10): C, 75.80; N, 6.98; H, 7.87. Found: C, 75.7; N, 7.1; H, 8.1.

**[L$^4$]Mg{OC(=CH$_2$)(2,4,6-Me$_3$C$_6$H$_2$)} (11).** Complex **11** was prepared following the procedure described above for **10**, starting from [L$^4$]H (0.199 g, 0.48 mmol), (*n*,*s*Bu)$_2$Mg (0.48 mL of a 1.0 M solution in heptane, 0.48 mmol), and

2,4,6-$Me_3C_6H_2COMe$ (0.077g, 0.48 mmol), to give **11** as a white powder (0.062 g, 21%). 1H NMR ($CD_2Cl_2$, 500 MHz), selected resonances: $\delta$ 1.1–1.8 (several singlets, *t*Bu), 2.1–2.5 (several singlets, *o*-Me and *p*-Me), 3.10 (d, $J$ = 12.7, 1H, OC=CH*H*), 3.35 (d, $J$ = 12.7, 1H, OC=CH*H*), 3.45 (d, $J$ = 13.5, 1H, OC=CH*H*), 3.50 (d, $J$ = 13.6, 1H, C*H*H), 3.90 (d, $J$ = 15.5, 1H, C*H*H), 4.30 (br d, $J$ = *ca.* 12, 1H, C*H*H), 4.43 (br d, $J$ = *ca.* 11, 1H, C*H*H), 4.70 (d, $J$ = 13.6, 1H, C*H*H), 5.00 (d, $J$ = 12.7, 1H, OC=CH*H*), 5.15 (d, $J$ = 15.5, 1H, C*H*H), 6.2-8.0 (m, H arom), 8.20 (d, 1H, $J$ = 4.9), 8.35 (br d, 1H), 9.38 (d, 2H, $J$ = 4.4, 1H, pyridyl-6H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 125 MHz), selected resonances: $\delta$ 18.80 (*p*-Me), 20.78 (*o*-Me), 28.17 ($C(CH_3)_3$), 29.40 ($C(CH_3)_3$), 31.71 ($C(CH_3)_3$), 33.50 ($C(CH_3)_3$), 34.40 ($C(CH_3)_3$), 35.74 ($C(CH_3)_3$), 50.05, 55.72, 58.24, 62.64 ($CH_2$-phenolate and $CH_2$-pyridyl), 81.31 (C=$CH_2$), 93.34 (C=$CH_2$), 122.31, 124.97, 127.83, 128.37, 131.94, 135.43, 137.17, 138.50, 140.00, 148.45, 159.08, 164.36 (C arom). Anal. Calc. for $C_{39}H_{50}MgN_2O_2$ (603.13): C, 77.66; N, 4.64; H, 8.36. Found: C, 77.2; N, 4.9; H, 8.2.

### Solid-state structure determination of complexes 3–7 and 10

Suitable single crystals of **3**, **4**, **5**, **6**, **7** and **10** were mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100 K using an APEXII Bruker-AXS diffractometer with graphite-monochromatized Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). A combination of $\omega$- and $\varphi$-scans was carried out to obtain at least a unique data set. The structure was solved by direct methods using the SIR97 program,[36] and then refined with full-matrix least-square methods based on $F^2$ (SHELX-97)[37] with the aid of the WINGX[38] program. Many hydrogen atoms could be found from the Fourier Difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystals of **5** and **6** were found to contain lattice disordered solvent molecules, which could not be sufficiently modeled in the refinement cycles. These molecules were removed using the SQUEEZE procedure[39] implemented in PLATON package.[40] In **7**, one *tert*-butyl group per phenolate ring (*i.e.*, **2** *t*Bu groups in the crystal structure) was found to be disordered and accordingly modelled. Crystal data and details of data collection and structure refinement for the different compounds are given in Table 1.

### General procedure for ε-caprolactone polymerization

A Schlenk flask was charged with a 0.050 M solution of the selected complex in dry toluene. To this solution was added a 2.0 M solution of ε-caprolactone in toluene ([monomer]/[Zn] = 200, 1000, 4000). The reaction mixture was stirred at 20 °C for the desired reaction time. After a small aliquot of crude product was sampled for determining the monomer conversion by $^1$H NMR, the reaction mixture was quenched by adding acidified methanol (*ca.* 10 mL). The polymer was obtained as a white precipitate, which was filtered out, washed with methanol and dried *in vacuo* to dryness.

### General procedure for lactide polymerization

In the glovebox, a Schlenk flask was charged with a solution of the initiator in toluene (0.2 mL) or THF (0.2 mL). To this solution was added rapidly a slurry of the monomer (*rac*-LA) in the appropriate ratio in toluene (3.0 mL). The mixture was immediately stirred with a magnetic stir bar at room temperature. Aliquots were periodically removed with a pipette for monitoring by $^1$H NMR. After the desired time, the reaction was quenched with acidic methanol (0.5 mL of a 1.2 M HCl solution), and the polymer was precipitated with excess methanol (100 mL). The polymer was then dried under vacuum to constant weight.

## Acknowledgements

We thank Arkema Co. for a postdoctoral fellowship grant to ZZ, the *Centre National de la Recherche Scientifique*, and CAPES-COFECUB (grant 556/07) for financial support of this work. J. F. C. gratefully thanks the *Institut Universitaire de France* for a Junior IUF fellowship (2005–2009).

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