Enantiopure N,N,O-Scorpionate Zinc Amide and Chloride Complexes as Efficient Initiators for the Heteroselective ROP of Cyclic Esters.

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Published article available at
https://pubs.rsc.org/en/content/articlelanding/2014/dt/c4dt02178a/unauth#!divAbstract
with DOI 10.1039/C4DT02178A

ABSTRACT

The reaction of bpzbeH, bpzteH (racemic mixture) or (*R*,*R*)-bpzmmH (enantiopure) with the amide complexes $Zn\{N(SiMe_3)_2\}_2$ or $Zn\{N(SiHMe_2)_2\}_2$ in a 1:1 molar ratio in toluene afforded the

mononuclear amide zinc complexes [Zn(NR_2)(κ^3-NNO)] (**1**–**6**) [κ^3-NNO = bpzbe, R = $SiMe_3$ **1**, $SiHMe_2$ **2**; bpzte, R = $SiMe_3$ **3**, $SiHMe_2$ **4**; (*R*,*R*)-bpzmm, $SiMe_3$ **5**, $SiHMe_2$ **6**]. These complexes were employed in a protonolysis reaction with HCl/Et_2O in a 2:1 molar ratio to yield the dinuclear amide/chloride zinc complexes [Zn(κ^2-NN-μ-O)$_2${ZnCl(NR_2)}] (**7**–**12**) [κ^2-NN-μ-O = bpzbe, R = $SiMe_3$ **7**, $SiHMe_2$ **8**; bpzte, R = $SiMe_3$ **9**, $SiHMe_2$ **10**; (*R*,*R*)-bpzmm, $SiMe_3$ **11**, $SiHMe_2$ **12**]. The mononuclear complexes **5** and **6** and dinuclear complexes **11** and **12** are the first enantiopure-scorpionate zinc amide complexes to be synthesized.

The single-crystal X-ray structures of derivatives **1** and **3** confirmed a monomeric 4-coordinative structure in which the heteroscorpionate ligands are in a κ^3 coordination mode, while **8** had a dimeric molecular disposition with two μ-bridging alkoxides of the heteroscorpionate ligands between the two six- and four-coordinate Zn(II) centers.

Interestingly, the chiral amide-containing zinc complexes **1**–**5** and **11** can act as single-component initiators for the ring-opening polymerization of ε-caprolactone and lactides under mild conditions, affording in a few hours medium/low molecular weight polymers with low polydispersity indexes. MALDI-ToF mass spectra confirmed that the initiation occurred through a nucleophilic attack by the amide on the lactide monomer and inspection of the kinetic parameters showed that propagations present the usual pseudo-first order dependence on monomer and catalyst concentrations. In addition, microstructural analysis of poly(*rac*-lactide)s revealed that the myrtenal substituent on the alkoxide fragment has a significant influence on the degree of stereoselectivity, producing enriched-heterotactic PLAs with a P_s value up to 0.79 under mild conditions.

INTRODUCTION

During the last decade our research group has contributed widely to the design of new heteroscorpionate ligands based on bis(pyrazol-1-yl)methane.[1] In recent years, we have been interested in the introduction of chirality into these systems in an effort to obtain new enantiopure scorpionate ligands.[2] For example, we have reported the preparation of new chiral bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands[3] (Fig. 1) in a single high-yielding step by the 1,2-

addition of organometallics to aldehydes to afford chiral secondary alcohols.[4] When this type of reaction was carried out with an enantiopure aldehyde [(1*R*)-(–)-myrtenal] as a possible chiral substrate to control the stereochemistry of the newly created asymmetric center,[5] we obtained an enantiopure scorpionate ligand (Fig. 1*c*) in one step with high stereoselectivity. Furthermore, these alcohol compounds were found to be excellent reagents for the introduction of scorpionate ligands into zinc metal complexes and a series of neutral alkyl[6] complexes were prepared by reaction with ZnR_2. Furthermore, alkoxide[7] and thioalkoxide[7] complexes were synthesized by subsequent alcoholysis or thioalcoholysis reactions.

Given the recent interest of our research group[8] in the preparation of efficient catalysts for the well-controlled ring-opening polymerization (ROP) of ε-caprolactone and lactide, and considering the biocompatible nature and the lack of toxicity to living tissue of the bioassimilable polylactides (PLAs),[9,10] we decided to take advantage of the biocompatible character[11] of these zinc-based metal complexes[6,7] and tested them as possible initiators in the ROP of lactides. Indeed, these chiral alkyl[6] and alkoxide/thioalkoxide[7] zinc complexes behaved as efficient living initiators for the ROP of lactides to afford heterotactic[6] (P_s = 0.77) and isotactic[7] (P_i = 0.74) enriched PLAs through a chain-end[12a] and enantiomorphic site[12b] control mechanism, respectively. In this context, several highly effective organo-zinc initiators[13] have also proven to be excellent initiators for the well-controlled ROP of lactides, with very high conversions achieved under mild conditions and with remarkable levels of stereoselectivity.[14] However, only a few examples of organo-zinc scorpionate complexes containing stereogenic centers have been reported[15] and, to the best of our knowledge, very few examples have succeeded in the stereoselective ROP of lactides[7,14,16]. For this reason, we turned our attention to the use of the same chiral alkoxide-based heteroscopionate ligands (Fig. 1) for the synthesis of a series of amide zinc complexes in order to compare their synthetic accessibility, structural arrangements, reactivity and catalytic behavior with those of the heteroscorpionate zinc alkyls,[6] alkoxides/thioalkoxides,[7] and analogous zinc derivatives.[13,14,16,17]

We present here the preparation and structural characterization of new chiral NNO-scorpionate mononuclear amide and dinuclear amide/chloride zinc complexes of the type [Zn(NR_2)(κ^3-NNO)] and [Zn(κ^2-NN-μ-O)$_2${ZnCl(NR_2)}], respectively, as single-component initiators for the efficient ROP of *rac*-lactide in the production of heterotactic-enriched polylactides.

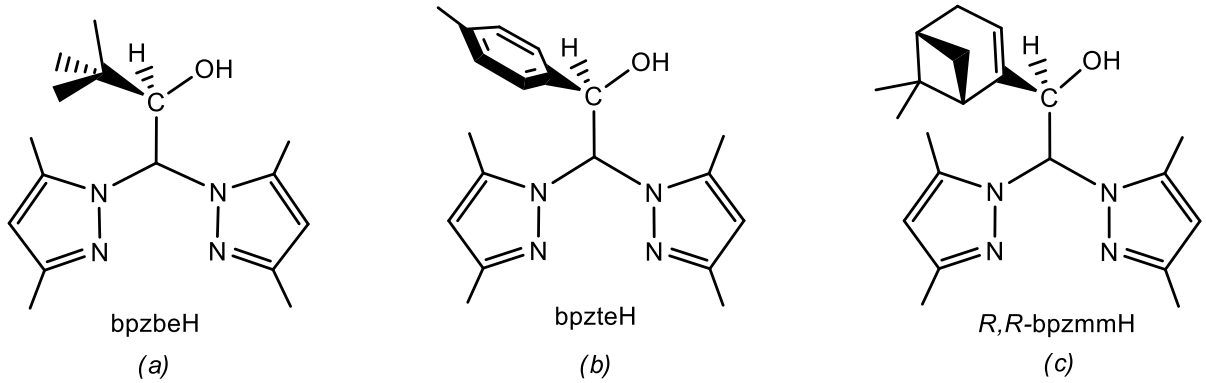


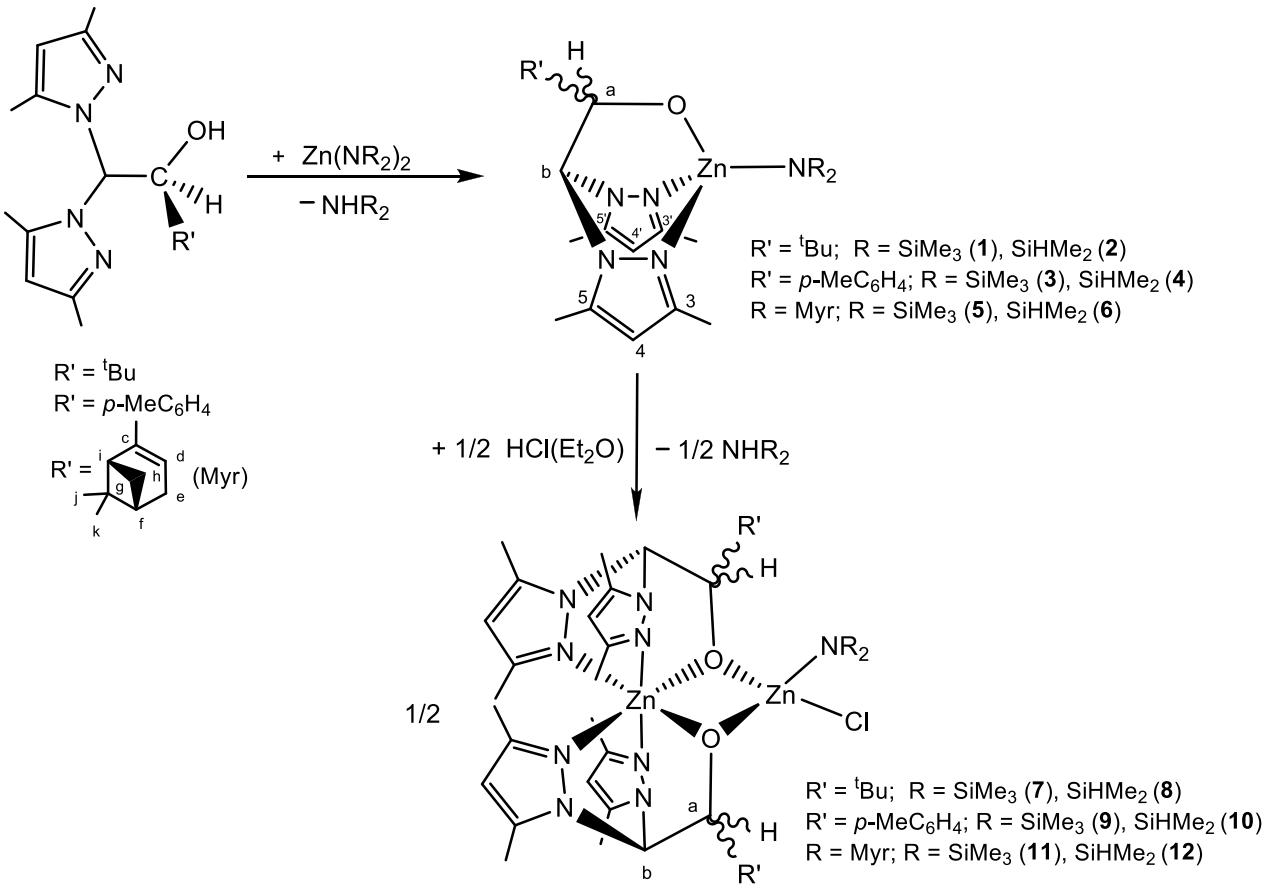
Figure 1. Previously reported bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands.

RESULTS AND DISCUSSION

Reaction of racemic alcohol-scorpionate compounds bpzbeH[3a] [bpzbeH = 1,1-bis(3,5-dimethylpyrazol-1-yl)-3,3-dimethyl-2-butanol] and bpzteH[3a] [bpzteH = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*para*-tolylethanol] or the enantiopure scorpionate (*R*,*R*)-bpzmmH[3b] {(*R*,*R*)-bpzmmH = (1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol} with the amide complexes Zn{N($SiMe_3$)$_2$}$_2$ or Zn{N($SiHMe_2$)$_2$}$_2$ in a 1:1 molar ratio in toluene afforded, after the appropriate work-up, the mononuclear amide zinc complexes [Zn(NR_2)(κ^3-NNO)] (**1**–**6**) [κ^3-NNO = bpzbe, R = $SiMe_3$ **1**, $SiHMe_2$ **2**; bpzte, R = $SiMe_3$ **3**, $SiHMe_2$ **4**; (*R*,*R*)-bpzmm, $SiMe_3$ **5**, $SiHMe_2$ **6**], which were isolated as white solids in good yield (*ca*. 90%) (see Scheme 1). The reactivity of these complexes (**1**–**6**) with hydrogen chloride was explored in order to obtain chloride derivatives as possible starting materials for further transformations and interestingly, new mixed-ligand complexes that contained amide and chloride ligands were isolated. Thus, the mononuclear amide zinc complexes **1**–**6** were employed in a protonolysis reaction with HCl/Et_2O in a 2:1 molar ratio to yield the dinuclear amide/chloride zinc complexes [Zn(κ^2-NN-μ-O)$_2${ZnCl(NR_2)}] (**7**–**12**)

[κ^2-NN-μ-O = bpzbe, R = $SiMe_3$ **7**, $SiHMe_2$ **8**; bpzte, R = $SiMe_3$ **9**, $SiHMe_2$ **10**; (*R*,*R*)-bpzmm, $SiMe_3$ **11**, $SiHMe_2$ **12**] in *ca*. 70% isolated yield (see Scheme 1). When these reactions were carried out in a 1:1 molar ratio, a complex mixture of products was obtained and these compounds could not be separated. The mononuclear [$Zn(NR_2)$(*R*,*R*-bpzmm)] (R = $SiMe_3$ **5**, $SiHMe_2$ **6**) and the dinuclear [Zn(*R*,*R*-bpzmm)$_2${$ZnCl(NR_2)$}] (R = $SiMe_3$ **11**, $SiHMe_2$ **12**) are the first enantiopure-scorpionate zinc amide complexes to be synthesized. Furthermore, the dinuclear [Zn(κ^2-NN-μ-O)$_2${$ZnCl(NR_2)$}] (**7**–**12**) are the first scorpionate zinc complexes to contain amide and chloride ligands simultaneously.

Scheme 1. Synthesis of NNO-scorpionate amide or amide/chloride zinc complexes (**1**–**12**).



The different complexes were characterized by spectroscopic methods. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**–**6** exhibit two distinct sets of pyrazole resonances, indicating the existence of two

types of pyrazole ring. The ^{1}H NMR spectra of these complexes show two singlets for the H^4, Me^3 and Me^5 pyrazole protons, one broad singlet for each of the methine groups (CH^b bridge of the pyrazole rings and CH^a) and the signals corresponding to the R' moieties of the scorpionate ligands and the amide ligands. The results are consistent with a tetrahedral environment for the zinc atoms in which the two pyrazole rings are located in *cis* and *trans* positions with respect to the *tert*-butyl group, *para*-tolyl group or bicyclic moiety (Myr) (see Scheme 1). The ^{1}H NOESY-1D experiments permitted the unequivocal assignment of all ^{1}H resonances and the $^{13}C\{^{1}H\}$ NMR signals were assigned on the basis of ^{1}H-^{13}C heteronuclear correlation (g-HSQC) experiments. In addition, the presence in solution of only one enantiomer for complexes **5** and **6** was confirmed by the addition of a chiral shift reagent – namely (*R*)-(–)-(9-anthryl)-2,2,2-trifluoroethanol – as this addition did not modify the ^{1}H NMR spectra of these compounds. However, in the rest of the complexes, which are racemic mixtures, the addition of the shift reagent gave rise to the appearance in the ^{1}H NMR spectra of two signals for each proton, resulting from the two diastereoisomers of the corresponding two enantiomers. The specific rotations of **5** and **6** were measured by polarimetry (see Experimental Section).

The crystal structures of complexes **1** and **3** were determined by X-ray diffraction studies and the ORTEP diagrams are shown in Figure S6 in the Electronic Supplementary Information (ESI†) and Figure 2, respectively. For complex **1**, the asymmetric unit is formed by an overlap of the two enantiomers in a 70/30 (S/R) ratio. This overlap prevented an anisotropical refinement of the minor enantiomer and thus the R values are high. For this reason, a detailed discussion of the distances and angles for this complex has not been included. These studies confirmed that the presence in solution of the corresponding two enantiomers for these compounds is maintained in the solid-state. The most representative bond lengths and angles are presented in Table 1 and the crystallographic details are reported in Table S3 in the ESI†. Complex **3** has a monomeric structure that consists of a heteroscorpionate ligand bonded to the zinc atom through the two nitrogen atoms and the oxygen atom of the alkoxide group in a κ^3-NNO-coordination mode. In addition, the zinc center is coordinated to one amide ligand. This center has a distorted tetrahedral environment due to the κ^3-

NNO-coordination of the scorpionate ligand with major distortions in the O–Zn(1)–N(1) and O–Zn(1)–N(3) angles, which have values of 91.9(5)º and 91.8(1)º. The Zn–N distances [2.079(3) Å, 2.111(3) Å] for Zn(1)–N(1) and Zn(1)–N(3) are in good agreement with other values determined for zinc scorpionate complexes such as [Zn(CH_3)(bpzbe)][6] or [Zn(CH_3)(pbp^{t}amd)][18] prepared by our research group.[6,18] The Zn(1)–N(5) bond length [1.903(3) Å] is similar to those in the complex [Zn{N($SiMe_3$)$_2$}(pbpamd)][17] and analogous aliphatic zinc amides reported previously [1.881(3)–1.923(3) Å].[19,20] Finally, the Zn–O distance [1.932(3) Å] is similar to that in another NNO-alkoxide scorpionate zinc complexes.[6,20]

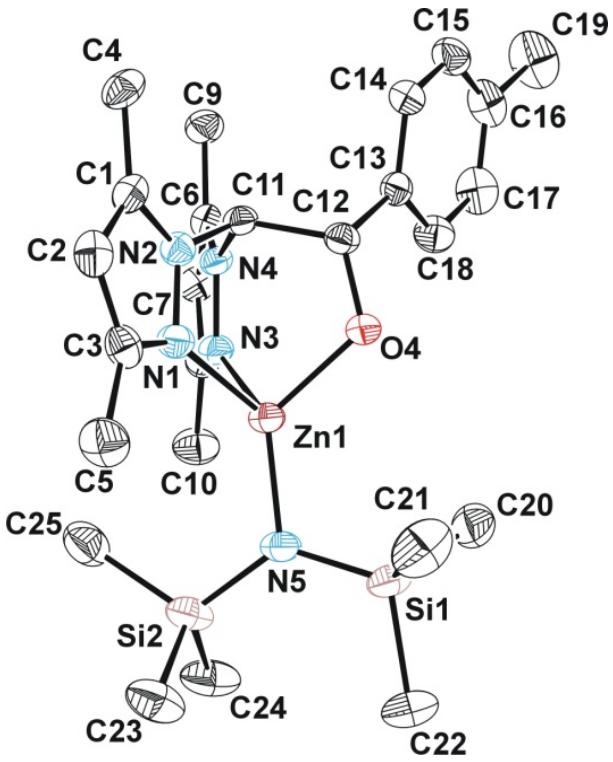


Figure 2. ORTEP view of the *R* enantiomer of [Zn{N($SiMe_3$)$_2$}(bpzte)] (**3**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

The ^{1}H and ^{13}C{^{1}H}-NMR spectra of complexes **7–12** show the resonances for four distinct sets of pyrazol-1-yl units, indicating the existence of four different pyrazole rings. Additional resonances corresponding to the R' moieties of the scorpionate ligands and the amide ligands are also present (see Experimental Section). A ^{1}H-^{13}C correlation experiment (*g*-HSQC) was carried out on these compounds and this allowed us to assign the resonances corresponding to the different types of

carbon atoms. An X-ray crystal structure determination was carried out for **8**. An ORTEP drawing is shown in Figure 3. A summary of bond lengths and angles is presented in Table 1 and the crystallographic details are reported in Table S3 in the ESI†. In this X-ray structure only one diastereoisomer, namely '*rac*', was present in the unit cell although the ^{1}H NMR spectrum of the bulk of the crystals corresponds to both diastereoisomers. The complexes have a dinuclear structure with two μ-bridging alkoxide groups from the scorpionate ligands between the two six- and four-coordinate Zn(II) centers. The first zinc center Zn(1) has a distorted octahedral geometry with a heteroscorpionate ligand that acts in a tridentate fashion. The pyrazolic nitrogens N(1), N(3), N(5) and N(7) occupy four positions and the alkoxide oxygen-bridges μ-O(1) and μ-O(2) occupy the other two positions. The second zinc center has a distorted tetrahedral geometry in which μ-O(1) and μ-O(2) occupy two positions and the amide and chloride groups the other two positions. Furthermore, the X-ray structure of **8** has a rhomboidal $(ZnO)_2$ core with Zn(1)–O(1), Zn(1)–O(2), Zn(2)–O(1) and Zn(2)–O(2) bond lengths ranging from 2.022(5) to 2.046(5) Å and the Zn···Zn diagonal (nearly 3 Å) is much longer than the O···O diagonal (nearly 2.7 Å). The dimeric aggregate is based on Zn_2O_2 four-membered rings, which have previously been observed in other zinc compounds that contain, for example, thiolate-oxo,[21] alkoxide-imino,[22a] aryloxide[22b] or aminoalcoholate[23] ligands. However, it should be noted that dinuclear compounds of zinc with two six- and four-coordinate Zn(II) atoms, based on Zn_2O_2 four-membered rings, containing a scorpionate ligand have not been reported in the literature.

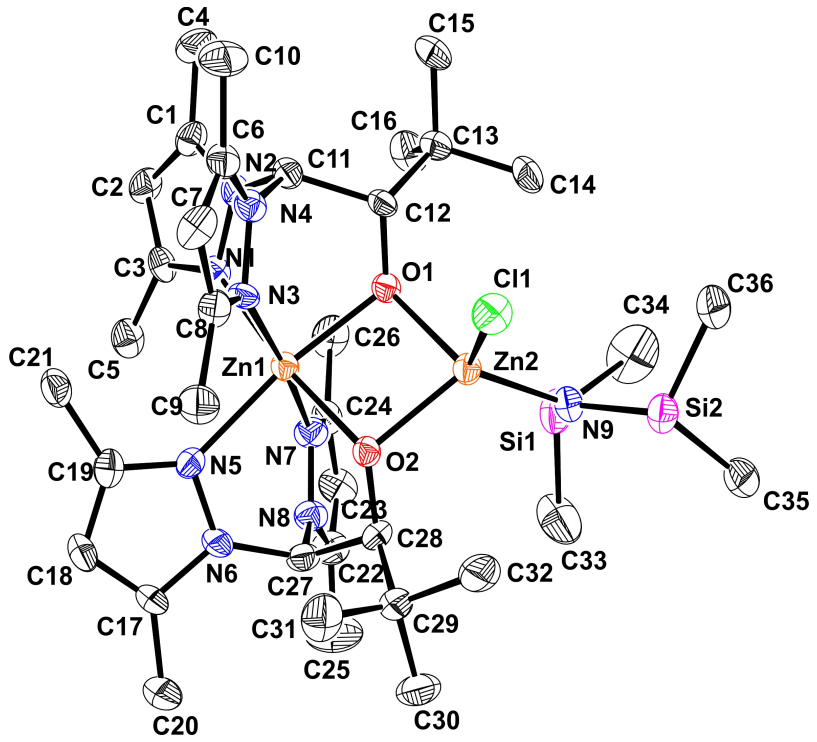


Figure 3. ORTEP view of the *S*,*S* enantiomer of [Zn(bpzbe)$_2$(ZnCl{N(SiHMe$_2$)$_2$})] (**8**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected geometrical parameters from the X-ray studies of compounds **3** and **8·2.5C$_7$H$_8$**. Distances in Å, angles in degrees.

3		**8·2.5C$_7$H$_8$**	
Bond Lengths			
Zn(1)–N(1)	2.079(3)	Zn(1)–N(1)	2.134(6)
Zn(1)–N(3)	2.111(3)	Zn(1)–N(3)	2.225(6)
Zn(1)–N(5)	1.902(3)	Zn(1)–N(5)	2.149(7)
Zn(1)–O(4)	1.932(3)	Zn(1)–O(1)	2.045(5)
N(5)–Si(1)	1.700(4)	Zn(1)–O(2)	2.046(5)
N(5)–Si(2)	1.714(4)	Zn(1)–N(7)	2.247(7)
O(4)–C(12)	1.373(4)	Zn(2)–O(1)	2.022(5)
		Zn(2)–O(2)	2.029(5)
		Zn(2)–N(9)	1.964(6)
		Zn(2)–Cl(1)	2.281(3)
		O(1)–C(12)	1.389(9)
		O(2)–C(28)	1.403(8)
Angles			
N(5)–Zn(1)–O(4)	125.5(1)	O(1)–Zn(1)–O(2)	84.9(2)

N(5)–Zn(1)–N(1)	124.0(1)	N(1)–Zn(1)–N(3)	82.9(2)
O(4)–Zn(1)–N(1)	91.8(1)	N(1)–Zn(1)–N(5)	101.0(2)
N(5)–Zn(1)–N(3)	125.2(1)	N(1)–Zn(1)–N(7)	94.1(2)
O(4)–Zn(1)–N(3)	91.8(1)	N(3)–Zn(1)–N(7)	174.8(2)
N(1)–Zn(1)–N(3)	87.7(1)	N(5)–Zn(1)–N(3)	94.1(2)
Si(1)–N(5)–Si(2)	127.6(2)	N(5)–Zn(1)–N(7)	82.3(3)
Si(1)–N(5)–Zn(1)	113.2(2)	N(9)–Zn(2)–O(1)	119.5(2)
Si(2)–N(5)–Zn(1)	119.2(2)	N(9)–Zn(2)–O(2)	118.0(2)
C(12)–O(4)–Zn(1)	119.1(2)	O(1)–Zn(2)–O(2)	85.9(2)
		Si(1)–N(9)–Zn(2)	116.4(3)
		Si(2)–N(9)–Si(1)	125.8(4)
		Si(2)–N(9)–Zn(2)	117.5(4)
		Zn(2)–O(1)–Zn(1)	94.7(2)
		Zn(2)–O(2)–Zn(1)	94.4(2)

Polymerization Studies

Complexes **1**–**5** and **11** were systematically assessed in the ring-opening polymerization of polar monomers such as *ε*-caprolactone and L-/*rac*-lactide (LA) for the production of poly(caprolactone)s (PCL)s and poly(lactide)s (PLA)s, respectively, in toluene and tetrahydrofuran under a nitrogen atmosphere and without the need for an activator. These reactivity studies also allowed the determination of kinetic parameters such as the reaction rate and the order dependence on monomer and catalyst concentration. Furthermore, a comparison could be made between these alkoxo-based heteroscorpionate Zn-amide complexes and other recently published analogous heteroscorpionate zinc-alkyl,[6,7] -amide[17] and -alkoxide[7] systems as initiating groups and also with other interesting and efficient systems reported to date.[13,14,16] Inspection of the experimental M_n values of the resulting PCLs and PLAs revealed, as a common trend, that the molecular weights of the polymer samples closely approximate the expected theoretical calculated values for one growing polymer chain per catalyst molecule [M_n(calcd)PCL_{200} = 22 800 g·mol^{-1} and M_n(calcd)PLA_{100} = 14 400 g·mol^{-1},

respectively]. Size exclusion chromatography (SEC) data for the resulting polyesters show a monomodal weight distribution for both monomers with polydispersities ranging from 1.07 to 1.32.

Initiators **1**–**5** act as rapid single-component catalysts for the polymerization of *ε*-caprolactone (CL) in toluene to give medium-low molecular weight polymers in Table S1 (ESI†). A variety of polymerization conditions were explored. The zinc amide derivatives **1**–**5** effectively polymerized 200 equivalents of CL at room temperature in 3 hours. The polymerization was well controlled and gave low-medium molecular weight polymers with low polydispersity indexes. Not unexpectedly, the productivity increased markedly on heating (50°C) but the characteristics and the molecular weight distributions remained unchanged. It was also found that the nature of the NNO heteroscorpionate alkoxide and the amide substituents (Scheme 1) affects the catalytic activity as follows: (*R*,*R*)-bpzmm >> bpzbe ≈ bpzte and $N(SiHMe_2)_2$ > $N(SiMe_3)_2$. Additionally, when tetrahydrofuran was employed as solvent, all initiators markedly reduced the rate of polymerization, possibly as a result of the competition between the coordinating tetrahydrofuran solvent and the monomer moiety for the metal center. At this point, it is worth highlighting the fact that their NNO heteroscorpionate zinc-alkyl[6,7] counterparts are not active in the polymerization of this monomer under any conditions.

Compounds **1**, **3**–**5** and **11** acted as active single-component catalysts for the well-controlled polymerization of L-LA in toluene at room temperature and the results of these experiments are collected in Table 2. For instance, the zinc amide derivative **5** polymerized 91% of the monomer after 4 hours (entry 9) to yield a low molecular weight polymer with a narrow molecular weight distribution (M_n = 11 800, M_w/M_n = 1.14). As one would expect, an increase in the reaction temperature (50ºC) led to an increase in productivity (entry 10) without any changes in the polymer features (see Figure S1 on the ESI†). The employment of tetrahydrofuran as solvent decreases the productivity as for the case of *ε*-CL monomer. The analogous NNO-donor amide catalysts **3**–**5** gave comparable productivity values under similar conditions (entries 4, 7 and 9). These reactions afforded highly crystalline, isotactic polymers (T_m = 168–171ºC)[24] with medium-low molecular

weights. A low molecular weight material produced by initiator **2** was studied by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS)[25] (see Figure S2 on the ESI†) and this provided evidence that the ring-opening of L-LA occurs by the initial addition of the amide fragment to the monomer in the materials produced, with cleavage of the acyl-oxygen bond[26] followed by further monomer additions to the (macro)alcohols. Kinetic studies conducted on the ROP of L-LA employing **3** and **4** at 50ºC established that the reaction order with respect to monomer and catalyst concentration follows a first-order dependence (square correlation coefficients ≥ 0.97), (see Figures S3, S4 and Table S2 on the ESI†). Interestingly, the experimentally obtained k_{app} value for initiator **3** is slightly higher than that obtained for **4** at each $[catalyst]_0$ studied (see Table S2 on the ESI†), which provides evidence that the initiation step in the ROP of lactide mediated by the $–N(SiMe_3)_2$ derivatives is slightly faster than in the cases of the $–N(SiHMe_2)_2$ analogs. It is also noteworthy that the pseudo-first-order rate constants, k_{app}, for each initiator are significantly higher than those measured for the analogous chiral monoalkyls $[Zn(R)(NNO)]_2$[6] ($k_{app,50ºC} = 8.3 \pm 0.3 \times 10^{-4}$ s^{-1}, NNO = bpzte, R = CH_2SiMe_3 *vs* $k_{app,50ºC} = 13.8 \pm 0.2 \times 10^{-4}$ s^{-1} for **3**, at a $[Zn]_0 = 20$ mM).

Finally, initiators **5** and **11** were also tested in the polymerization of *rac*-lactide in toluene under mild conditions (Table 2). For example, the amide and the dinuclear amide/chloride zinc catalysts **5** and **11**, respectively, proved to be active at 50ºC, with conversions of 79% and 57% achieved, respectively, after a reaction time of 2.5 hours to produce low molecular weight materials with very narrow polydispersity values (M_n = 12 000, M_w/M_n = 1.09, entry 12). In contrast, the catalytic activity decreased markedly again when tetrahydrofuran was employed under identical polymerization conditions (entry 13), as occurred for the ε-CL and L-LA monomers. For the sake of comparison, the new heteroscorpionate alkoxo-based amide zinc derivatives **1**, **3**–**5** and **11** proved to be more active for the ROP of lactides than the analogous heteroscorpionate alkyl derivatives,[6] the amidinate-based zinc alkyl[18]-amides[17] [Zn(R)(κ^3-NNN)] and the hybrid scorpionate/cyclopentadienyl-based alkyl zinc initiators [Zn(R)(κ^2-π-bpzcp)],[27] which were previously described by our group, or the recently reported robust zinc guanidine complexes of the

type [Zn(guanidine)$_2$OTf]OTf[28] and the zinc alkyls supported by *N*,*O*-bidentate ligands [(κ^2-N,O)ZnEt],[29] which require more energetic conditions and longer reaction times to produce lower conversions of material.

Microstructural analysis by homonuclear decoupled ^{1}H NMR spectroscopy of the poly(*rac*-lactide)s revealed that initiator **11** leads to a moderate level of heterotacticity (Table 2, entry 14, P_s = 0.74), while initiator **5**, despite its enantiopure nature, did not impart an enantiomorphic site control mechanism[12b] although it does show a preference for heterotactic dyad enchainment (Table 2, entry 12, P_s = 0.79, see Figure S5 on the ESI†), possibly through a chain-end control mechanism.[12a] The influence of solvent on the level of stereoselectivity was also studied but an improvement in the heterotacticity value was not observed (Table 2, entry 13, P_s = 0.76). This behavior, while still far from that shown by the most heralded organo-zinc initiators[14] reported in the literature, signifies an interesting improvement in comparison with the previous results obtained with alkyl zinc initiators supported by sterically hindered amidinate[18] or alkoxo[6]-based heteroscorpionates previously described by our group, where the levels of heterotacticity achieved were clearly lower, with P_s values of 0.68[18] and 0.77,[6] respectively. The improvement obtained with **5** under these conditions is most probably the result of the high steric demand of the myrtenal fragment in the NNO-heteroscorpionate ligand.

Table 2. Polymerization of L-/*rac*-Lactide Catalyzed by 1, 3–5 and 11.[a]

entry	initiator	monomer	temp (°C)	time (h)	yield (g)	conv (%)[b]	$M_{n(theor)}$ (Da)[c]	M_n (Da)[d]	M_w/M_n[d]	P_s[e]
1	**1**	L-LA	20	4	1.10	85	12 200	10 400	1.17	
2	**1**	L-LA	50	2.5	0.97	75	10 800	11 400	1.26	
3	**1**[f]	L-LA	50	2.5	traces	-	-	-	-	
4	**3**	L-LA	20	4	0.98	76	10 900	9 900	1.17	
5	**3**	L-LA	50	2.5	1.08	83	12 000	11 600	1.11	
6	**3**[f]	L-LA	50	2.5	0.35	27	3 900	5 900	1.32	
7	**4**	L-LA	20	4	0.81	63	9 000	9 800	1.25	
8	**4**	L-LA	50	2.5	1.09	84	12 100	10 000	1.09	
9	**5**	L-LA	20	4	1.18	91	13 100	11 800	1.14	
10	**5**	L-LA	50	2.5	1.16	90	13 000	12 800	1.14	
11	**5**[f]	L-LA	50	2.5	0.84	65	9 400	8 700	1.07	
12	**5**	*rac*-LA	50	2.5	1.03	79	11 400	12 000	1.09	0.79
13	**5**[f]	*rac*-LA	50	2.5	0.48	37	5 300	5 900	1.10	0.76
14	**11**	*rac*-LA	50	2.5	0.74	57	8 200	7 800	1.12	0.74

[a] Polymerization conditions: 90 μmol of catalyst, 40 mL of toluene as solvent, $[\text{L-/}rac\text{-lactide}]_0/[Zn]_0 = 100$. [b] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100]. [c] Theoretical M_n = [(monomer/catalyst) × (% conversion) × (M_w of lactide)]/100. [d] Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[30] for M_n [M_n(obsd) = 0.56 × M_n(GPC)]. [e] The parameter P_s (s = syndiotactic) is the probability of forming a new *s*-dyad. P_s is the probability of syndiotactic (racemic) linkages between monomer units and is determined from the relative intensity in the tretrads obtained in the decoupled ^{1}H NMR experiment by $P_s = 2I_1/(I_1+I_2)$, with I_1 = δ 5.20–5.25 ppm (*sis*, *sii*/*iis*) and I_2 = δ 5.13–5.20 ppm (*iis*/*sii*, *iii*, *isi*). P_s = 0.5 means atactic polymer.[31] [f] 10 mL of tetrahydrofuran as solvent.

CONCLUSIONS

In conclusion, we have explored the reactivity of our previously described racemic and enantiopure bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands in the form of the alcohol compounds with $Zn(NR_2)_2$. These reactions yielded monomeric heteroscorpionate zinc amide complexes $[Zn(NR_2)(\kappa^3\text{-NNO})]$ and these complexes were used in a protonolysis reaction with HCl/Et_2O to obtain the dinuclear amide/chloride zinc complexes $[Zn(\kappa^2\text{-NN-}\mu\text{-O})_2\{ZnCl(NR_2)\}]$. Some of the complexes reported are the first enantiopure scorpionate zinc amide complexes to be synthesized. Single-crystal X-ray diffraction studies on derivatives **1**, **3** and **8** confirmed that in the structures the heteroscorpionate ligands are arranged in both coordination modes.

Both families of chiral amide zinc complexes can act as single-site initiators for the well-controlled polymerization of ε-caprolactone and lactides under mild conditions in a few hours to give medium-low molecular weight polymers with narrow molecular-weight distributions. The MALDI-ToF mass spectra suggest that the initiation process is mediated by amide transfer to the monomer and initial studies of the kinetic parameters revealed that propagations present the usual first order dependence on monomer and catalyst concentrations. Additionally, the myrtenal-substituted initiator **5** exerts significant levels of stereocontrol in the polymerization of *rac*-lactide to give heterotactic-enriched PLAs ($P_s = 0.79$).

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded on a Varian Inova FT-500 spectrometer and are referenced to the residual deuterated solvent. ^{1}H NMR

homodecoupled and NOESY-1D spectra were recorded on the same instrument with the following acquisition parameters: irradiation time 2 s and 256 scans, using standard VARIAN-FT software. 2D NMR spectra were acquired using the same software and were processed using an IPC-Sun computer. Microanalyses were performed with a Perkin-Elmer 2400 CHN analyzer. Gel Permeation Chromatography (GPC) measurements were performed on a Shimadzu LC-20AD instrument equipped with a TSK-GEL $G_{3000}H$ column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 60ºC at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da. MALDI-ToF MS data were acquired with a Bruker Autoflex II ToF/ToF spectrometer using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700–3 200 Da) and Protein Calibration Standard I (covered mass range: 5 000–17 500 Da). The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^1H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Varian Inova FT-500 spectrometer. PLA melting temperatures were measured using a melting point Block (SMP 10). The sample was heated at a rate of 5ºC/min up to 185ºC and then the sample was left to cool down to room temperature. After that, the sample was heated at rate of 2ºC/min up to 185ºC. This second step was carried out twice. The starting materials bpzbeH,[3a] bpzteH[3a] and (*R*,*R*)-bpzmmH[3] were prepared according to literature procedures. Anhydrous $ZnCl_2$, $HN(SiHMe_2)_2$ and HCl (1.0 M in Et_2O) were used as purchased from Aldrich. The reagent $LiN(SiMe_3)_2$ was purified by sublimation under reduced pressure and stored in a glovebox. Starting materials $LiN(SiMe_3)_2$,[32] $Zn(N(SiMe_3)_2)_2$[33] and $Zn(N(SiHMe_2)_2)_2$[22] were prepared according to literature procedures. L-Lactide and *rac*-lactide were sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Preparation of compounds 1–12

Synthesis of [Zn{N(SiMe$_3$)$_2$}(bpzbe)] (1). In a 250 cm^3 Schlenk tube, bpzbeH (1.0 g, 3.44 mmol) was dissolved in dry toluene (30 mL) and the solution was cooled to −30 ºC. A solution of Zn{N(SiMe$_3$)$_2$}$_2$ (1.32 g, 3.44 mmol) in toluene (30 mL) was added and the mixture was allowed to warm up to room temperature and stirred for 2 h. The resulting white light suspension was filtered through Celite and the filtrate was evaporated to dryness under reduced pressure to yield a sticky white product. The product was washed with *n*-hexane (1 × 20 mL) to give compound **1** as a white solid. Colorless crystals of compound **1** suitable for X-ray diffraction were obtained from a toluene solution at −26 ºC. Yield: 1.57 g (89%). ^{1}H NMR (C_6D_6, 297 K), δ 5.85 (bs, 1H, CH^b), 5.38 (s, 1H, H$^{4'}$), 5.35 (s, 1H, H^4), 3.78 (bs, 1H, CH^a), 2.34 (s, 3H, Me$^{3'}$), 2.32 (s, 3H, Me^3), 1.56 (s, 3H, Me^5), 1.55 (s, 3H, Me$^{5'}$), 0.85 (s, 9H, ^{t}Bu), 0.59 (s, 18H, Zn-N(SiMe$_3$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 148.8–137.9 (C$^{3,3'}$, C$^{5,5'}$), 106.4 (C$^{4'}$), 105.8 (C^4), 88.2 (C^a), 65.0 (C^b), 36.5 (C-Me$_3$), 26.1 (C-Me$_3$), 13.6 (Me$^{3'}$), 13.5 (Me^3), 10.5 (Me^5), 10.2 (Me$^{5'}$), 5.7 (Zn-N(SiMe$_3$)$_2$). Elemental analysis (%) calcd. for $C_{22}H_{43}N_5OSi_2Zn$: C, 51.29; H, 8.41; N, 13.59. Found: C, 51.36; H, 8.35; N, 13.63.

Synthesis of [Zn{N(SiHMe$_2$)$_2$}(bpzbe)] (2). The synthesis of **2** was carried out in an identical manner to **1**, using bpzbeH (1.0 g, 3.44 mmol), Zn{N(SiHMe$_2$)$_2$}$_2$ (1.13 g, 3.44 mmol). Compound **2** was obtained as a white solid. Yield: 1.52 g (91%). ^{1}H NMR (C_6D_6, 297 K), δ 5.90 (bs, 1H, CH^b), 5.49 (m, 2H, Zn-N(SiHMe$_2$)$_2$), 5.34 (s, 1H, H$^{4'}$), 5.29 (s, 1H, H^4), 3.87 (bs, 1H, CH^a), 2.30 (s, 3H, Me$^{3'}$), 2.29 (s, 3H, Me^3), 1.60 (s, 3H, Me^5), 1.58 (s, 3H, Me$^{5'}$), 0.85 (s, 9H, ^{t}Bu), 0.59 (d, 12H, $^3J_{H-H}$= 14.1 Hz, Zn-N(SiHMe$_2$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 149.0–137.9 (C$^{3,3'}$, C$^{5,5'}$), 106.5 (C$^{4'}$), 105.7 (C^4), 88.2 (C^a), 65.0 (C^b), 36.6 (C-Me$_3$), 26.2 (C-Me$_3$), 13.3 (Me$^{3'}$), 13.1 (Me^3), 10.6 (Me^5), 10.3 (Me$^{5'}$), 3.6 (Zn-N(SiHMe$_2$)$_2$). Elemental analysis (%) calcd. for $C_{20}H_{39}N_5OSi_2Zn$: C, 49.31; H, 8.07; N, 13.38. Found: C,

49.36; H, 8.15; N, 13.33.

Synthesis of [Zn{N(SiMe$_3$)$_2$}(bpzte)] (3). The synthesis of **3** was carried out in an identical manner to **1**, using bpzteH (1.0 g, 3.0 mmol), Zn{N(SiMe$_3$)$_2$}$_2$ (1.12 g, 3.0 mmol). Compound **3** was obtained as a white solid. Yield: 1.43 g (91%). ^{1}H NMR (C_6D_6, 297 K), δ 7.17 (d, 2H, $^3J_{H-H}$= 8 Hz, *o*-H-Ph), 6.93 (d, 2H, $^3J_{H-H}$= 8 Hz, *m*-H-Ph), 5.70 (bs, 1H, CH^b), 5.49 (bs, 1H, CH^a), 5.42 (s, 1H, H$^{4'}$), 5.21 (s, 1H, H^4), 2.39 (s, 3H, Me$^{3'}$), 2.38 (s, 3H, Me^3), 2.09 (s, 3H, Me-Ph), 1.55 (s, 3H, Me^5), 1.09 (s, 3H, Me$^{5'}$), 0.64 (s, 18H, Zn-N(SiMe$_3$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 149.1–139.1 (C$^{3,3'}$, C$^{5,5'}$), 140.4 (*p*-C-Ph), 136.2 (*ipso*-C-Ph), 126.2 (*o*-C-Ph), 128.7 (*m*-C-Ph), 106.0 (C$^{4'}$), 105.0 (C^4), 82.2 (C^a), 70.4 (C^b), 21.0 (Me-Ph), 13.7 (Me$^{3'}$), 13.5 (Me^3), 10.2 (Me^5), 9.7 (Me$^{5'}$), 5.8 (Zn-N(SiMe$_3$)$_2$). Elemental analysis (%) calcd. for $C_{25}H_{41}N_5OSi_2Zn$: C, 53.01; H, 7.16; N, 13.44. Found: C, 53.15; H, 7.21; N, 13.55.

Synthesis of [Zn{N(SiHMe$_2$)$_2$}(bpzte)] (4). The synthesis of **4** was carried out in an identical manner to **1**, using bpzteH (1.0 g, 3.0 mmol), Zn{N(SiHMe$_2$)$_2$}$_2$ (0.96 g, 3.0 mmol). Compound **4** was obtained as a white solid. Yield: 1.33 g (88%). ^{1}H NMR (C_6D_6, 297 K), δ 7.11 (d, 2H, $^3J_{H-H}$= 8 Hz, *o*-H-Ph), 6.96 (d, 2H, $^3J_{H-H}$= 8 Hz, *m*-H-Ph), 5.60 (bs, 1H, CH^b), 5.43 (bs, 1H, CH^a), 5.36 (m, 2H, Zn-N(SiHMe$_2$)$_2$), 5.32 (s, 1H, H$^{4'}$), 5.25 (s, 1H, H^4), 2.31 (s, 3H, Me$^{3'}$), 2.30 (s, 3H, Me^3), 2.11 (s, 3H, Me-Ph), 1.63 (s, 3H, Me^5), 1.02 (s, 3H, Me$^{5'}$), 0.71 (d, 12H, $^3J_{H-H}$= 14.1 Hz, Zn-N(SiHMe$_2$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 153.6–138.1 (C$^{3,3'}$, C$^{5,5'}$), 142.4 (*p*-C-Ph), 136.1 (*ipso*-C-Ph), 129.1 (*m*-C-Ph), 126.4 (*o*-C-Ph), 106.8 (C$^{4'}$), 106.7 (C^4), 75.5 (C^a), 72.3 (C^b), 20.8 (Me-Ph), 13.6 (Me$^{3'}$), 13.5 (Me^3), 10.8 (Me^5), 10.1 (Me$^{5'}$), 0.4 (Zn-N(SiMe$_3$)$_2$). Elemental analysis (%) calcd. for $C_{23}H_{37}N_5OSi_2Zn$: C, 53.01; H, 7.16; N, 13.44. Found: C, 53.15; H, 7.21; N, 13.55.

Synthesis of [Zn{N(SiMe$_3$)$_2$}(*R,R*-bpzmm)] (5). The synthesis of **5** was carried out in an identical manner to **1**, using *R,R*-bpzmmH (1.0 g, 2.80 mmol), Zn{N(SiMe$_3$)$_2$}$_2$ (1.08 g, 2.80 mmol). Compound **5** was obtained as a white solid. Yield: 1.43 g (87%). ^{1}H NMR (C_6D_6, 297 K), δ 5.61 (bs, 1H, CH^b), 5.40

(s, 1H, $H^{4'}$), 5.39 (s, 1H, H^{4}), 5.34 (s, 1H, H^{d}), 4.82 (bs, 1H, CH^{a}), 2.36 (s, 3H, $Me^{3'}$), 2.30 (s, 3H, Me^{3}), 2.26-2.15 (m, 3H, $H^{e,f}$), 2.03 (bs, 1H, H^{i}), 1.84 (m, 1H, H^{h}), 1.63 (s, 3H, Me^{5}), 1.57 (s, 3H, $Me^{5'}$), 1.36 (s, 3H, Me^{b}), 1.09 (s, 3H, Me^{a}), 0.77 (d, 1H, $^{2}J_{H-H}$ = 8.4 Hz, H^{h}), 0.58 (s, 18H, Zn-N($SiMe_3$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 153.6–138.6 ($C^{3,3'}$, $C^{5,5'}$), 148.9 (C^{d}), 139.2 (C^{c}), 105.9 ($C^{4'}$), 105.7 (C^{4}), 83.2 (C^{a}), 69.8 (C^{b}), 41.7 (C^{f}), 40.7 (C^{i}), 38.2 (C^{g}), 32.2 (C^{e}), 31.8 (C^{h}), 26.3 (Me^{b}), 21.4 (Me^{a}), 13.6 (Me^{3}), 13.4 ($Me^{3'}$), 10.5 (Me^{5}), 10.2 ($Me^{5'}$), 5.7 (Zn-N($SiMe_3$)$_2$). Elemental analysis (%) calcd for $C_{27}H_{47}N_5OSi_2Zn$: C, 55.98; H, 8.18; N, 12.09. Found: C, 56.11; H, 8.31; N, 12.18. $[\alpha]_D^{25}$ = +32.1 (*c* 10^{-3} g/mL in toluene).

Synthesis of [Zn{N($SiHMe_2$)$_2$}(*R*,*R*-bpzmmH)] (6). The synthesis of **6** was carried out in an identical manner to **1** using *R*,*R*-bpzmmH (1.0 g, 2.80 mmol), Zn{N($SiHMe_2$)$_2$}$_2$ (0.92 g, 2.80 mmol). Compound **6** was obtained as a white solid. Yield: 1.42 g (92%). ^{1}H NMR (C_6D_6, 297 K), δ 5.63 (bs, 1H, CH^{b}), 5.45 (s, 1H, $H^{4'}$), 5.39 (s, 1H, H^{4}), 5.38 (bs, 1H, H^{d}), 5.23 (m, 2H, Zn-N($Si\underline{H}Me_2$)$_2$), 4.88 (bs, 1H, CH^{a}), 2.41 (s, 3H, $Me^{3'}$), 2.29 (s, 3H, Me^{3}), 2.25–2.13 (m, 3H, $H^{e,f}$), 2.04 (bs, 1H, H^{i}), 1.82 (m, 1H, H^{h}), 1.69 (s, 3H, Me^{5}), 1.66 (s, 3H, $Me^{5'}$), 1.33 (s, 3H, Me^{b}), 1.12 (s, 3H, Me^{a}), 0.75 (d, 1H, $^{2}J_{H-H}$ = 8.4 Hz, H^{h}), 0.67 (d, 12H, $^{3}J_{H-H}$ = 14.1 Hz, Zn-(N($SiH\underline{Me}_2$)$_2$)). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 153.2–138.1 ($C^{3,3'}$, $C^{5,5'}$), 148.6 (C^{d}), 140.0 (C^{c}), 106.7 ($C^{4'}$), 106.1 (C^{4}), 81.3 (C^{a}), 68.8 (C^{b}), 41.7 (C^{f}), 40.9 (C^{i}), 38.1 (C^{g}), 32.1 (C^{e}), 31.5 (C^{h}), 26.1 (Me^{b}), 21.2 (Me^{a}), 13.4 (Me^{3}), 13.2 ($Me^{3'}$), 10.5 (Me^{5}), 10.1 ($Me^{5'}$), 0.5 (Zn-N($SiMe_3$)$_2$). Elemental analysis (%) calcd. for $C_{23}H_{43}N_5OSi_2Zn$: C, 54.47; H, 7.86; N, 12.71. Found: C, 54.29; H, 7.95; N, 12.66. $[\alpha]_D^{25}$ = +31.4 (*c* 10^{-3} g/mL in toluene).

Synthesis of [Zn(bpzbe)$_2$(ZnCl{N($SiMe_3$)$_2$})] (7). In a 250 cm^3 Schlenk tube, [Zn{N($SiMe_3$)$_2$}(bpzbe)] (**1**) (1.0 g, 1.94 mmol) was dissolved in dry toluene (70 mL) and the solution was cooled to –50 ºC. A solution of HCl (1.0 M in Et_2O) (1.32 mL, 0.97 mmol), previously dissolved in dry toluene (20 mL) and cooled to –50 ºC, was added. The resulting mixture was stirred at –20 ºC during 1 h, after which a white suspension had formed. The reaction mixture was concentrated to 10 mL under reduced pressure and the supernatant was removed by filtration. The resulting white solid was dried *in vacuo* and corresponds to

complex **7**. Yield: 1.23 g (70%). ^{1}H NMR (C_6D_6, 297 K), δ 6.26 (bs, 1H, CH^{b}), 6.18 (bs, 1H, CH^{b}), 5.75 (s, 1H, $H^{4'}$), 5.61 (s, 1H, $H^{4'}$), 5.50 (s, 1H, H^{4}), 5.36 (s, 1H, H^{4}), 4.72 (bs, 1H, CH^{a}), 4.49 (bs, 1H, CH^{a}), 2.21 (s, 3H, $Me^{3'}$), 2.12 (s, 3H, $Me^{3'}$), 1.90 (s, 3H, Me^{3}), 1.88 (s, 3H, Me^{3}), 1.75 (s, 3H, Me^{5}), 1.69 (s, 3H, Me^{5}), 1.60 (s, 3H, $Me^{5'}$), 1.19 (s, 9H, ^{t}Bu), 1.13 (s, 3H, $Me^{5'}$), 1.12 (s, 9H, ^{t}Bu), 0.57 (s, 18H, Zn-N($SiMe_3$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 150.3–140.8 ($C^{3,3'}$, $C^{5,5'}$), 103.2–102.0 ($C^{4'}$,C^{4}), 85.3; 84.1 (C^{a}), 66.9; 65.1 (C^{b}), 31.9; 27.2 (C-Me_3), 23.0; 22.2 (C-Me_3), 13.9; 13.8; 12.9; 12.6 (Me^{3},$Me^{3'}$), 11.8; 11.0; 10.6; 10.3 (Me^{5},$Me^{5'}$), 5.6 (Zn-N($SiMe_3$)$_2$). Elemental analysis (%) calcd. for $C_{38}H_{68}ClN_9O_2Si_2Zn_2$: C, 50.41; H, 7.57; N, 13.92. Found: C, 50.54; H, 7.63; N, 14.07.

Synthesis of [Zn(bpzbe)$_2$(ZnCl{N(SiHMe$_2$)$_2$})] (8). The synthesis of **8** was carried out in an identical manner to **7**, using [Zn{N($SiHMe_2$)$_2$}(bpzbe)] (**2**) (1.0 g, 2.05 mmol) and HCl (1.0 M in Et_2O) (1.40 mL, 1.03 mmol). Compound **8** was obtained as a white solid. Colorless crystals suitable for X-ray diffraction were obtained from a concentrated solution of **8** in toluene at –26 ºC. Yield: 1.22 g (68%). ^{1}H NMR (C_6D_6, 297 K), δ 6.19 (bs, 1H, CH^{b}), 6.14 (bs, 1H, CH^{b}), 5.73 (s, 1H, $H^{4'}$), 5.62 (bs, 2H, Zn-N(Si<u>H</u>Me_2)$_2$), 5.57 (s, 1H, $H^{4'}$), 5.44 (s, 1H, H^{4}), 5.43 (s, 1H, H^{4}), 4.71 (bs, 1H, CH^{a}), 4.70 (bs, 1H, CH^{a}), 2.32 (s, 3H, $Me^{3'}$), 2.09 (s, 3H, $Me^{3'}$), 1.86 (s, 3H, Me^{3}), 1.75 (s, 3H, Me^{3}), 1.73 (s, 3H, Me^{5}), 1.60 (s, 3H, Me^{5}), 1.58 (s, 3H, $Me^{5'}$), 1.22 (s, 9H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu), 1.07 (s, 3H, $Me^{5'}$), 0.70 (m, 6H, Zn-N(SiH<u>Me</u>$_2$)$_2$), 0.66 (m, 6H, Zn-N(SiH<u>Me</u>$_2$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 150.1–141.0 ($C^{3,3'}$, $C^{5,5'}$), 103.9–102.6 ($C^{4'}$,C^{4}), 84.9; 83.2 (C^{a}), 66.8; 66.7 (C^{b}), 31.6; 28.4 (C-Me_3), 23.3; 22.2 (C-Me_3), 13.6; 13.3; 13.0; 12.8 (Me^{3},$Me^{3'}$), 11.7; 11.0; 10.5; 10.4 (Me^{5},$Me^{5'}$), 2.9 (Zn-N($SiHMe_2$)$_2$). Elemental analysis (%) calcd. for $C_{36}H_{64}ClN_9O_2Si_2Zn_2$: C, 49.28; H, 7.35; N, 14.37. Found: C, 49.40; H, 7.47; N, 14.30.

Synthesis of [Zn(bpzte)$_2$(ZnCl{N(SiMe$_3$)$_2$})] (9). The synthesis of **9** was carried out in an identical manner to **7**, using [Zn{N($SiMe_3$)$_2$}(bpzte)] (**3**) (1.0 g, 1.82 mmol) and HCl (1.0 M in Et_2O) (1.24 mL, 0.91 mmol). Compound **9** was obtained as a white solid. Yield: 1.42 g (80%).^{1}H NMR (C_6D_6, 297 K), δ 7.62 (d, 2H, $^{3}J_{H-H}$= 8 Hz, *o*-<u>H</u>-Ph), 7.19 (d, 2H, $^{3}J_{H-H}$= 8 Hz, *o*-<u>H</u>-Ph), 7.05 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-<u>H</u>-

Ph), 6.93 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-H-Ph), 6.23 (s, 1H, CH^{b}), 6.06 (s, 1H, CH^{b}), 5.71 (s, 1H, CH^{a}), 5.51 (s, 2H, $H^{4'}$), 5.54 (s, 1H, CH^{a}), 5.43 (s, 1H, H^{4}), 5.21 (s, 1H, H^{4}), 2.54 (s, 3H, $Me^{3'}$), 2.39 (s, 6H, $Me^{3,3'}$), 2.27 (s, 3H, Me^{3}), 2.16 (s, 3H, Me-Ph), 2.10 (s, 3H, Me-Ph), 1.77 (s, 3H, Me^{5}), 1.56 (s, 3H, Me^{5}), 1.39 (s, 3H, $Me^{5'}$), 1.09 (s, 3H, $Me^{5'}$), 0.64 (s, 18H, Zn-N($SiMe_3$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 149.3–138.1 ($C^{3,3'}$, $C^{5,5'}$), 140.5; 140.3 (*p*-C-Ph), 137.3; 136.3 (*ipso*-C-Ph), 135.6; 129.3 (*o*-C-Ph), 128.8; 126.5 (*m*-C-Ph), 106.1–104.9 ($C^{4,4'}$), 82.6; 82.4 (C^{a}), 71.9; 70.6 (C^{b}), 21.2; 21.0 (Me-Ph), 14.3; 13.8; 13.6; 13.3 ($Me^{3,3'}$), 10.6; 10.3; 10.2; 9.8 ($Me^{5,5'}$), 5.9 (Zn-N($SiMe_3$)$_2$). Elemental analysis (%) calcd. for $C_{44}H_{64}ClN_9O_2Si_2Zn_2$: C, 54.29; H, 6.63; N, 12.95. Found: C, 54.35; H, 6.67; N, 13.00.

Synthesis of [Zn(bpzte)$_2$(ZnCl{N(SiHMe$_2$)$_2$})] (10). The synthesis of **10** was carried out in an identical manner to **7**, using [Zn{N(SiHMe$_2$)$_2$}(bpzte)] (**4**) (1.0 g, 1.92 mmol) and HCl (1.0 M in Et_2O) (1.31 mL, 0.96 mmol). Compound **10** was obtained as a white solid. Yield: 1.40 g (77%).^{1}H NMR (C_6D_6, 297 K), δ 7.55 (d, 2H, $^{3}J_{H-H}$= 8 Hz, *o*-H-Ph), 7.21 (d, 2H, $^{3}J_{H-H}$= 8 Hz, *o*-H-Ph), 7.02 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-H-Ph), 6.99 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-H-Ph), 6.21 (s, 1H, CH^{b}), 6.12 (s, 1H, CH^{b}), 5.72 (s, 1H, CH^{a}), 5.60 (bs, 2H, Zn-(N(SiHMe$_2$)$_2$)), 5.59 (s, 1H, $H^{4'}$), 5.56 (s, 1H, CH^{a}), 5.48 (s, 1H, H^{4}), 5.43 (s, 1H, H^{4}), 5.42 (s, 1H, H^{4}), 2.54 (s, 3H, $Me^{3'}$), 2.43 (s, 6H, $Me^{3,3'}$), 2.19 (s, 3H, Me^{3}), 2.15 (s, 3H, Me-Ph), 2.13 (s, 3H, Me-Ph), 1.73 (s, 3H, Me^{5}), 1.58 (s, 3H, Me^{5}), 1.39 (s, 3H, $Me^{5'}$), 1.13 (s, 3H, $Me^{5'}$), 0.66 (m, 6H, Zn-N(SiHMe$_2$)$_2$), 0.63 (m, 6H, Zn-N(SiHMe$_2$)$_2$). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 148.3–138.6 ($C^{3,3'}$, $C^{5,5'}$), 140.6; 140.0 (*p*-C-Ph), 137.8; 136.4 (*ipso*-C-Ph), 136.1; 130.0 (*o*-C-Ph), 128.8; 126.5 (*m*-C-Ph), 106.1-104.9 ($C^{4,4'}$), 82.9; 82.1 (C^{a}), 72.2; 70.6 (C^{b}), 21.5; 21.4 (Me-Ph), 14.3; 13.1; 13.0; 12.7 ($Me^{3,3'}$), 11.6; 10.9; 10.7; 10.1 ($Me^{5,5'}$), 3.5 (Zn-N(SiHMe$_2$)$_2$). Elemental analysis (%) calcd. for $C_{42}H_{60}ClN_9O_2Si_2Zn_2$: C, 53.36; H, 6.40; N, 13.33. Found: C, 53.50; H, 6.33; N, 13.42.

Synthesis of [Zn(*R*,*R*-bpzmm)$_2$(ZnCl{N(SiMe$_3$)$_2$})] (11). The synthesis of **11** was carried out in an identical manner to **7**, using [Zn{N(SiMe$_3$)$_2$}(*R*,*R*-bpzmm)] (**5**) (1.0 g, 1.73 mmol) and HCl (1.0 M in Et_2O) (1.17 mL, 0.86 mmol). Compound **11** was obtained as a white solid. Yield: 1.16 g (65%). ^{1}H

NMR (C_6D_6, 297 K), δ 6.00 (bs, 1H, CH^b), 5.99 (bs, 1H, CH^b), 5.96 (bs, 1H, CH^a), 5.88 (bs, 1H, CH^a), 5.33 (s, 1H, $H^{4'}$), 5.32 (s, 1H, $H^{4'}$), 5.21 (s, 1H, H^4), 5.16 (s, 1H, H^4), 5.12 (bs, 2H, H^d), 2.20–2.16 (m, 8H, $H^{e,f,i}$), 2.11 (s, 6H, Me^3), 1.99 (s, 6H, $Me^{3'}$), 1.88 (bs, 2H, H^h), 1.66 (s, 3H, Me^5), 1.58 (s, 3H, Me^5), 1.15 (s, 3H, $Me^{5'}$), 1.11 (s, 3H, $Me^{5'}$), 1.02 (s, 6H, Me^b), 0.99 (d, 2H, $^2J_{H-H}$ = 8.4 Hz, H^h), 0.75 (s, 6H, Me^a), 0.54 (s, 18H, Zn-N($SiMe_3$)$_2$). ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 151.6–139.9 ($C^{3,3'}$, $C^{5,5'}$), 149.6; 149.0 (C^d), 140.5; 140.1 (C^c), 107.1–105.1 ($C^{4,4'}$), 80.3; 79.9 (C^a), 69.3; 68.6 (C^b), 42.3; 41.8 (C^f), 41.6; 41.5 (C^i), 39.2 (C^g), 39.1; 38.9 (C^e), 31.6; 31.4 (C^h), 26.9 (Me^b), 21.0 (Me^a), 13.9; 13.6; 13.3; 12.6 ($Me^{3,3'}$), 11.8; 10.9; 10.1; 9.6 ($Me^{5,5'}$), 5.6 (Zn-N($SiMe_3$)$_2$). Elemental analysis (%) calcd. for $C_{48}H_{76}ClN_9O_2Si_2Zn_2$: C, 53.36; H, 6.40; N, 13.33. Found: C, 53.50; H, 6.33; N, 13.42. $[\alpha]_D^{25}$ = +21.1 (*c* 10^{-3} g/mL in toluene).

Synthesis of [Zn(*R*,*R*-bpzmm)$_2$(ZnCl{N($SiHMe_2$)$_2$})] (12). The synthesis of **12** was carried out in an identical manner to **7**, using [Zn{N($SiHMe_2$)$_2$}(*R*,*R*-bpzmm)] (**6**) (1.0 g, 1.81 mmol) and HCl (1.0 M in Et_2O) (1.24 mL, 0.91 mmol). Compound **12** was obtained as a white solid. Yield: 1.20 g (66%). ^1H NMR (C_6D_6, 297 K), δ 6.09 (bs, 1H, CH^b), 6.03 (bs, 1H, CH^b), 5.99 (bs, 1H, CH^a), 5.78 (bs, 1H, CH^a), 5.41 (bs, 2H, Zn-(N(Si<u>H</u>Me_2)$_2$)), 5.36 (s, 1H, $H^{4'}$), 5.29 (s, 1H, $H^{4'}$), 5.26 (s, 1H, H^4), 5.20 (s, 1H, H^4), 5.17 (bs, 2H, H^d), 2.23–2.15 (m, 8H, $H^{e,f,i}$), 2.11 (s, 6H, Me^3), 2.08 (s, 3H, $Me^{3'}$), 2.00 (s, 3H, $Me^{3'}$), 1.96 (bs, 2H, H^h), 1.69 (s, 3H, Me^5), 1.66 (s, 3H, Me^5), 1.28 (s, 3H, $Me^{5'}$), 1.19 (s, 3H, $Me^{5'}$), 1.18 (s, 6H, Me^b), 1.02 (d, 2H, $^2J_{H-H}$ = 8.4 Hz, H^h), 0.90 (s, 6H, Me^a), 0.69 (m, 6H, Zn-N(SiH<u>Me</u>$_2$)$_2$), 0.66 (m, 6H, Zn-N(SiH<u>Me</u>$_2$)$_2$). ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 151.1–139.9 ($C^{3,3'}$, $C^{5,5'}$), 150.0; 149.1 (C^d), 141.2; 140.8 (C^c), 107.3–106.1 ($C^{4,4'}$), 80.6; 70.1 (C^a), 70.0; 69.4 (C^b), 43.3; 42.1 (C^f), 41.6; 41.5 (C^i), 39.1 (C^g), 39.2; 39.0 (C^e), 31.6 (C^h), 27.2; 26.6 (Me^b), 21.8; 21.6 (Me^a), 14.1; 14.0; 13.5; 13.0 ($Me^{3,3'}$), 11.6; 10.5; 9.8; 9.3 ($Me^{5,5'}$), 3.8 (Zn-N($SiHMe_2$)$_2$). Elemental analysis (%) calcd. for $C_{48}H_{76}ClN_9O_2Si_2Zn_2$: C, 55.78; H, 7.41; N, 12.20. Found: C, 55.84; H, 7.47; N, 12.10. $[\alpha]_D^{25}$ = +24.1 (*c* 10^{-3} g/mL in toluene).

General Polymerization Procedures. Polymerizations of L-lactide and *rac*-lactide (LA) were

performed on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of lactide and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in the appropriate amount of solvent and temperature equilibration was ensured in both Schlenk flasks by stirring the solutions for 15 min in a temperature-controlled bath. The appropriate amount of initiator was added by syringe and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of hydrochloric acid in methanol. Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol and finally dried in vacuo to constant weight.

Typical Kinetic Procedure. A solution of catalyst in toluene (2.5 mL) was added to a solution of monomer (40 mL) in the same solvent to give an $[\text{L-LA}]_0 = 0.72$ M. The initial ratio monomer/catalyst was $[\text{L-LA}]_0/[\text{catalyst}]_0 = 90$ and the initial $[\text{catalyst}]_0 = 8$ mM was adjusted to 20 mM. The resulting mixture was stirred at 50ºC under an N_2 atmosphere. At appropriate time intervals, 0.5 mL aliquots were removed using a syringe and quickly quenched into 5 mL vials with wet methanol (3 drops). The aliquots were then dried to constant weight *in vacuo* and analyzed by ^{1}H NMR spectroscopy. The standard error associated with the kinetic parameters was calculated by the standard deviation in the slope and intercept for each regression analysis.

X-ray Crystallographic Structure Determination. The single crystals of **1**, **3** and **8·2.5C$_7$H$_8$** were mounted on a glass fiber and transferred to a Bruker X8 APEX II diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream Cooler Device. Data were integrated using the SAINT[34] program and were corrected for absorption effects with the semi-empirical from equivalents method using SADABS.[35] Details of crystal data, data collection, and refinement can be found in Table S3 in the ESI†. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using the software package SHELXTL version 6.10.[36] For

complex **1**, the asymmetric unit is formed by an overlap of the two enantiomers in a 70/30 (S/R) ratio. This overlap prevented an anisotropical refinement of the minor enantiomer and thus the R values are high. Complex **8** crystallized with 2.5 toluene solvent molecules. In the refinement only two molecules could be refined isotropically with restraints and the rest were squeezed[37] due to the higher level of disorder. A potential solvent volume of 273 $Å^3$ was found and 54 electrons per unit cell were located in the void. The derived quantities (Mr), F(000), and Dx in the crystal data were corrected with the contribution from this disordered solvent. For complex **3**, all non-hydrogen atoms were refined with anisotropic displacement coefficients. For all structures, the hydrogen atoms were added to their geometrically ideal positions.

Acknowledgments

We gratefully acknowledge financial support from the Ministerio de Economia y Competitividad (MINECO), Spain (Grant No. CTQ2011-22578/BQU).

†Electronic supplementary information (ESI) available:

Kinetic parameters carried out for complex **3** and **4**, as well as figures, text and tables giving experimental details. Details of data collection, refinement, for complexes **1**, **3** and **8**. CCDC, 1012781, 1012782, and 1012783.

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GRAPHIC TABLE OF CONTENTS ENTRY

Enantiopure N,N,O-Scorpionate Zinc Amide and Chloride Complexes as Efficient Initiators for the Heteroselective ROP of Cyclic Esters.

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The reaction of racemic and enantiopure bis(pyrazol-1-yl)methane-based NNO-donor scorpionate alcohols with $Zn(NR_2)_2$ in a 1:1 molar ratio afforded high yields of the mononuclear amide zinc complexes $[Zn(NR_2)(\kappa^3\text{-NNO})]$ or, by protonolysis reaction, the dinuclear species $[Zn(\kappa^2\text{-NN-}\mu\text{-O})_2\{ZnCl(NR_2)\}]$. These amide or amide/chloride-containing zinc heteroscorpionates can act as single-component initiators for the well-controlled ring-opening polymerization of lactides to produce heterotactic-enriched poly(*rac*-lactide) materials ($P_r = 0.79$).