Mono- and Binuclear Chiral N,N,O-Scorpionate Zinc Alkyls as Efficient Initiators for the ROP of *rac*-Lactide.

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ABSTRACT

The preparation of new chiral bis(pyrazol-1-yl)methane-based N,N,O-donor scorpionate ligands in the form of the alcohol compounds bpzampeH (**1**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(dimethylamino)phenyl]ethanol}, bpzaepeH (**2**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(diethylamino)phenyl]ethanol}, bpzimeH (**3**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[1-methyl-1H-imidazol-2-yl]ethanol} has been carried out by 1,2-addition reactions of a series of aldehydes. These new chiral heteroscorpionate ligands reacted with [ZnR$_2$] (R = Me, Et, CH$_2$SiMe$_3$) in a 1:1 molar ratio in toluene to give the mononuclear monoalkyl zinc complexes [Zn(R)(κ^3-NNO)] (**4–12**). When these reactions were carried out in a 1:2 molar ratio the binuclear trisalkyls [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] (**13–18**) were obtained. The structures of these complexes were elucidated by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and the X-ray crystal structures of **4** and **5** were also established.

Interestingly, alkyl-containing zinc complexes **4–13**, **15** and **17** act as efficient single-component initiators for the ring-opening polymerization of rac-lactide at 20 ºC to afford PLA materials with low molecular weights in a few hours. The dinuclear trisalkyls showed higher activity in comparison with the mononuclear zinc counterparts, suggesting a cooperative effect of the two remote metals. The narrow dispersity ranges (M_w/M_n = 1.05) of the isolated polymers in conjunction with the linear nature of the number average molecular weight versus conversion plot provided evidence for living behavior. Inspection of the kinetic parameters showed that the propagations have the usual pseudo-first-order dependence on rac-lactide and catalyst concentration. End-group analysis and MALDI-TOF mass spectrometry confirmed that the initiation occurs through nucleophilic attack of the alkyl on the lactide monomer. Microstructural analysis of poly(rac-lactide)s revealed that the most sterically hindered ligand on the alkoxide fragment exerts a moderate influence on the degree of stereoselectivity, with heteroenriched-PLAs (P_s = 0.68) produced at room temperature.

INTRODUCTION

During this decade, compounds derived from renewable resources have been applied in high priority industrial processes.[1] In particular, the production of the bio-based poly(lactide)s (PLAs) has been

extensively investigated in recent years[2,3] given that its renewability, biodegradability and biocompatibility make it a very attractive material with widespread biomedical/pharmaceutical applications[4,5,6] and these polymers have been used in packaging and agriculture as a commodity plastic.[7] In fact, bio-based polymers are expected to grow at a current annual rate of 3–4% until 2021[8a] and the estimated rate for the PLA market is even greater in the coming years, *i.e.*, close to 10%,[8a] with an approximate production close to 0.5 million tons by 2021.[8b] The synthesis of PLA polymers is performed by the ring-opening polymerization (ROP) of the inexpensive bioderived monomer lactide with the assistance of an organo-metallic complex as catalyst, which allows high-control over the process and leads to materials with the desired structure, stereochemistry, and molecular weight distribution. In addition, the search for biologically benign metal-based catalytic systems such as zinc,[9] magnesium[10] and calcium[11] compounds is desirable given the biocompatible nature of the bioassimilable PLAs.

In this context, a large number of highly effective organozinc initiators[12] supported by a rich variety of ancillary ligands has been described for the ROP of lactides, but very few examples of zinc catalysts that bear chiral auxiliaries have been reported to give both heterotactic[13] and isotactic[14] enriched materials in the polymerization of *rac*-lactide. Our research group has made significant contributions[15] in the preparation of efficient scorpionate-based catalysts for the well-controlled ROP of *rac*-LA, and we have reported highly effective single-component alkyl[16-18]-amide[19] and enantiopure mixed alkyl/alkoxo and thioalkoxo[20] zinc initiators to produce heterotactic[16-19] (up to P_s = 0.79)[19] and isotactic[17,20] (up to P_i = 0.77)[17]-enriched PLA materials in a living fashion under mild conditions. Very recently, we reported the random copolymerization of ε-CL and L-LA mediated by an enantiopure mixed alkyl/alkoxo bimetallic zinc catalyst[21a] and the production of aliphatic polycarbonates [21b] through the copolymerization of cyclohexene oxide and carbon dioxide assisted by acetate and trifluoroacetate bimetallic zinc complexes. With the challenging aim of identifying more efficient zinc-based catalysts for the synthesis of poly(*rac*-lactide)s with controlled architectures, we have now introduced additional groups into the chiral fragment of the scorpionate

to increase the steric hindrance of these ligands and have also designed alternative chiral N,N,O scorpionate mono- and binuclear zinc alkyls.

Herein, we describe the synthesis and structural characterization of a new family of more sterically demanding chiral N,N,O-scorpionate ligands, their transfer to zinc metal for the preparation of mononuclear alkyls and binuclear trisalkyls of the type $[Zn(R)(\kappa^3\text{-NNO})]$ and $[Zn(R)(\kappa^2\text{-NN}\mu\text{-O})Zn(R)_2]$, respectively, and their application as single-component living initiators to produce heterotactic-enriched polylactides.

RESULTS AND DISCUSSION

Synthesis of the Ligands

In an effort to increase the steric hindrance around the zinc metal center of the initiators, three new heteroscorpionate ligand precursors bearing more sterically encumbered substituents were designed and synthesized according to our previously reported synthetic route for the preparation of alcohol-containing heteroscorpionate ligands.[22] The bulkiness was incorporated in the alkoxide moiety. Thus, the one-pot reaction of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) with Bu^{n}Li, followed by the 1,2-addition of a series of aldehydes [4-(dimethylamino)benzaldehyde, 4-(diethylamino)benzaldehyde and 1-methyl-2-imidazolecarboxaldehyde] followed by treatment with saturated aqueous ammonium chloride solution afforded the chiral alcohol compounds bpzampeH (**1**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(dimethylamino)phenyl]ethanol}, bpzaepeH (**2**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(diethylamino)phenyl]ethanol}, bpzimeH (**3**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[1-methyl-1*H*-imidazol-2-yl]ethanol}, which were isolated as racemic mixtures in good yields (*ca*. 80%) after the appropriate workup (Scheme 1).

Scheme 1. Synthesis of the N,N,O-chiral heteroscorpionate ligands (**1**–**3**).

Aldehydes:

R = Me, Et

R = Me (**1**) bpzampeH
R = Et (**2**) bpzaepeH

(**3**) bpzimeH
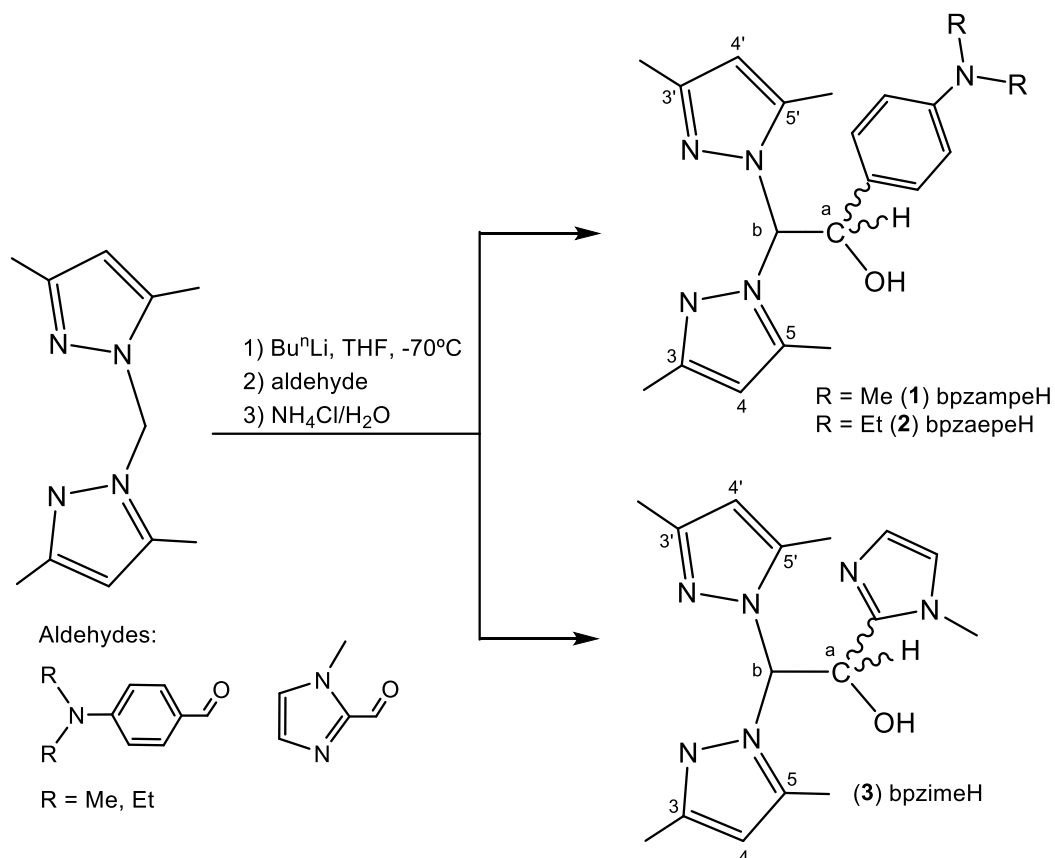
The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1–3** exhibit two distinct sets of pyrazole resonances, indicating the existence of two types of pyrazole ring. Furthermore, the ^1H NMR spectra show signals due to the moiety bound at the methylene bridge and the OH group. The phase-sensitive ^1H NOESY-1D spectra were also obtained in order to confirm the assignments of the signals for the Me^3, Me^5 and H^4 groups of each pyrazole ring. In compounds **1–3** the carbon atom (C^a) is a stereogenic center and the presence in solution of the corresponding two enantiomers was confirmed by adding a chiral shift reagent, namely (R)-(–)-(9-anthryl)-2,2,2-trifluoroethanol. This process gave rise to two signals for each proton in the ^1H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers.
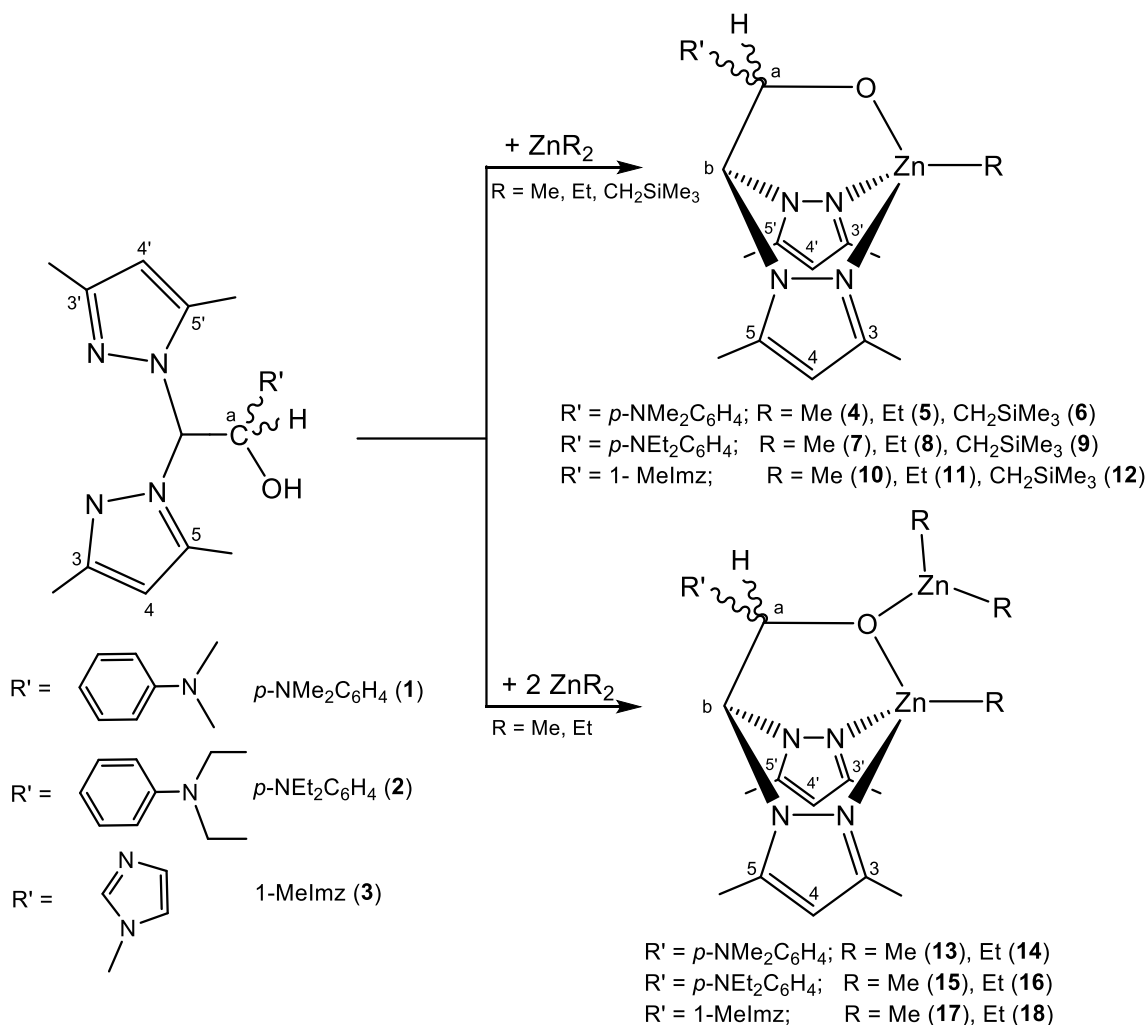
Zinc Complexes

Having prepared these new chiral heteroscorpionate ligands in the form of the alcohol compounds, we explored their potential utility as tridentate ligands in the preparation of chiral zinc metal complexes. The alcohols **1–3** (as racemic mixture) were reacted at room temperature with $[ZnR_2]$ (R = Me, Et, CH_2SiMe_3) in a 1:1 molar ratio in toluene to give, after the appropriate work-up, the

mononuclear monoalkyl zinc complexes [Zn(R)(κ^3-NNO)] (**4–12**) (κ^3-NNO = bpzampe, R = Me **4**, Et **5**, CH$_2$SiMe$_3$ **6**; bpzaepe, R = Me, **7**, Et **8**, CH$_2$SiMe$_3$ **9**; bpzime, R = Me, **10**, Et **11**, CH$_2$SiMe$_3$ **12**), which were isolated as white solids in good yield (*ca*. 90%) (Scheme 2).

In addition, we were interested in exploring the effect that two remote zinc metals would have in the design of more efficient zinc initiators for the ROP of *rac*-LA. In this context, several interesting studies have recently demonstrated[23] the cooperative effect of two remote metal atoms, including aluminum,[23a,d] zinc[23b] or titanium,[23c] in a homo-binuclear species for the ROP of cyclic esters such as ε-caprolactone and lactides.

For this reason, we carried out the initial reaction described above in a 1:2 molar ratio and this gave the corresponding bimetallic trisalkyls [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] (**13–18**) [κ^2-NNμ-O = bpzampe, R = Me **13**, Et **14**; bpzaepe, R = Me **15**, Et **16**; bpzime, R = Me **17**, Et **18**] in good yield (*ca*. 80–90%) (Scheme 2).

Scheme 2. Synthesis of complexes [Zn(R)(κ^3-NNO)] (**4–12**) and [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] (**13–18**).

+ ZnR₂ → + ZnR$_2$

R = Me, Et, CH$_2$SiMe$_3$

R' = p-NMe$_2$C$_6$H$_4$; R = Me (**4**), Et (**5**), CH$_2$SiMe$_3$ (**6**)
R' = p-NEt$_2$C$_6$H$_4$; R = Me (**7**), Et (**8**), CH$_2$SiMe$_3$ (**9**)
R' = 1- MeImz;   R = Me (**10**), Et (**11**), CH$_2$SiMe$_3$ (**12**)

R' = p-NMe$_2$C$_6$H$_4$ (**1**)

R' = p-NEt$_2$C$_6$H$_4$ (**2**)

R' = 1-MeImz (**3**)

+ 2 ZnR$_2$

R = Me, Et

R' = p-NMe$_2$C$_6$H$_4$; R = Me (**13**), Et (**14**)
R' = p-NEt$_2$C$_6$H$_4$; R = Me (**15**), Et (**16**)
R' = 1-MeImz;   R = Me (**17**), Et (**18**)

The ¹H and ¹³C{¹H} NMR spectra of the monoalkyl zinc complexes **4–18** contain two singlets for each of the H⁴, Me³ and Me⁵ pyrazole protons, one broad singlet for each of the methine groups (CH bridge of the pyrazole rings and CHᵃ) and the signals corresponding to the (R') moieties of the scorpionate ligands and the alkyl substituents. It is worth noting that at room temperature the ¹H and ¹³C{¹H} NMR spectra of the binuclear trisalkyl zinc complexes **13–18** present two distinct broad sets of alkyl ligand resonances, with a 1:2 integral ratio, in the ¹H NMR spectra. This behavior indicates that two alkyl ligands exchange their positions rapidly at room temperature on one zinc atom and the third alkyl ligand is coordinated to the other zinc atom. ¹H NOESY-1D experiments permitted the unequivocal assignment of all ¹H resonances and the assignment of the ¹³C{¹H} NMR signals was made on the basis of ¹H-¹³C heteronuclear correlation (g-HSQC) experiments. In addition, the presence in solution of a racemic mixture was confirmed by the addition of a chiral shift reagent.

These results are consistent with a tetrahedral structure resulting from κ^3-NNO (in **4–12**) or κ^2-NNμ-O (in **13–18**) coordination of the scorpionate ligand to the metal center, in which the two pyrazole rings are located in *cis* and *trans* positions with respect to the R' group (Scheme 2). The existence of this geometry was also confirmed in the solid state by X-ray structural analysis of complexes **4** and **5**. The molecular views are shown in Figures 1 and 2, respectively. These studies confirmed that the presence in solution of the corresponding two enantiomers for these compounds ($R + S$) is maintained in the solid state. The most representative bond lengths and angles are presented in Table 1. Crystallographic details are reported in Table S1 in the ESI†. The structures of complexes **4** and **5** consist 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 an alkyl ligand. These centers have a distorted tetrahedral environment due to the κ^3-NNO-coordination of the scorpionate ligand, with major distortions in the O(1)–Zn(1)–N(1) and O(1)–Zn(1)–C(21) angles, which have values of 89.99(9)º and 133.5(1)º, respectively, for complex **4**. The Zn–N and Zn–C distances [2.142(3) Å, 2.094(3) Å and 1.954(3) Å for **4**] are in good agreement with others determined for zinc scorpionate complexes such as [Zn(Me)(bpzbe)][16] prepared by our research group. The Zn–O distance [1.929(2) Å] is similar to that described in analogous N,N,O-alkoxide scorpionate zinc complexes.[24] Complexes **13–18** have a similar structure to the complexes [Zn(CH$_2$SiMe$_3$)(bpzbe)Zn(CH$_2$SiMe$_3$)$_2$][18] or [Zn(Me)(bpzte)Zn(Me)$_2$],[21a] which were synthesized by our research group and characterized by single-crystal X-ray diffraction. The first zinc center has a distorted tetrahedral geometry with a heteroscorpionate ligand that acts in a tridentate fashion, and the second zinc center has a distorted trigonal geometry in which μ-O of the scorpionate ligand occupies one position and the alkyl groups the other two positions (see Scheme 2).

Table 1. Selected bond lengths (Å) and angles (º) for **4** and **5**.

4		**5**	
Bond lengths			
Zn(1)–O(1)	1.929(2)	Zn(1)–O(1)	1.918(4)
Zn(1)–C(21)	1.954(3)	Zn(1)–C(21)	1.949(7)
Zn(1)–N(1)	2.094(3)	Zn(1)–N(1)	2.110(5)
Zn(1)–N(3)	2.142(3)	Zn(1)–N(3)	2.114(4)
N(5)–C(19)	1.376(3)	N(5)–C(19)	1.401(9)
N(5)–C(16)	1.411(6)	N(5)–C(16)	1.401(8)
N(5)–C(20)	1.423(5)	N(5)–C(20)	1.420(8)
Angles			
O(1)–Zn(1)–C(21)	133.5(1)	O(1)–Zn(1)–C(21)	132.9(3)
O(1)–Zn(1)–N(3)	89.69(9)	O(1)–Zn(1)–N(1)	90.2(2)
C(21)–Zn(1)–N(3)	121.1(1)	C(21)–Zn(1)–N(1)	121.4(3)
O(1)–Zn(1)–N(1)	89.99(9)	O(1)–Zn(1)–N(3)	90.7(2)
C(21)–Zn(1)–N(1)	122.9(2)	C(21)–Zn(1)–N(3)	122.4(3)
N(3)–Zn(1)–N(1)	86.55(9)	N(1)–Zn(1)–N(3)	86.4(2)
C(12)–O(1)–Zn(1)	119.8(2)	C(12)–O(1)–Zn(1)	119.1(3)
C(16)–N(5)–C(19)	120.1(4)	C(19)–N(5)–C(16)	120.2(7)
C(16)–N(5)–C(20)	120.1(4)	C(19)–N(5)–C(20)	120.1(6)
C(19)–N(5)–C(20)	119.7(4)	C(16)–N(5)–C(20)	119.6(7)
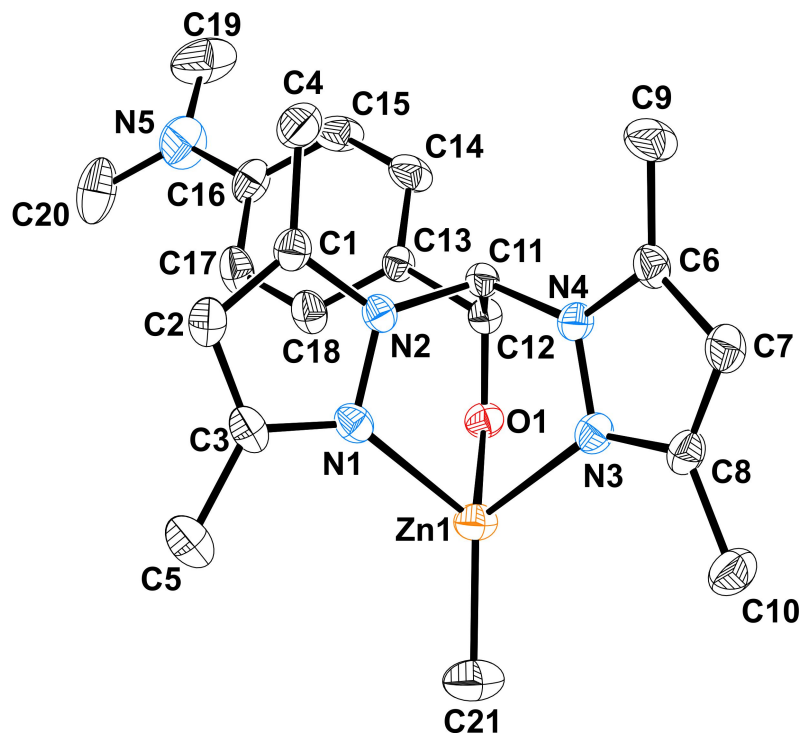
Figure 1. ORTEP view of the *S* enantiomer of [Zn(Me)(bpzampe)] (**4**). Ellipsoids are at the 30% probability level.
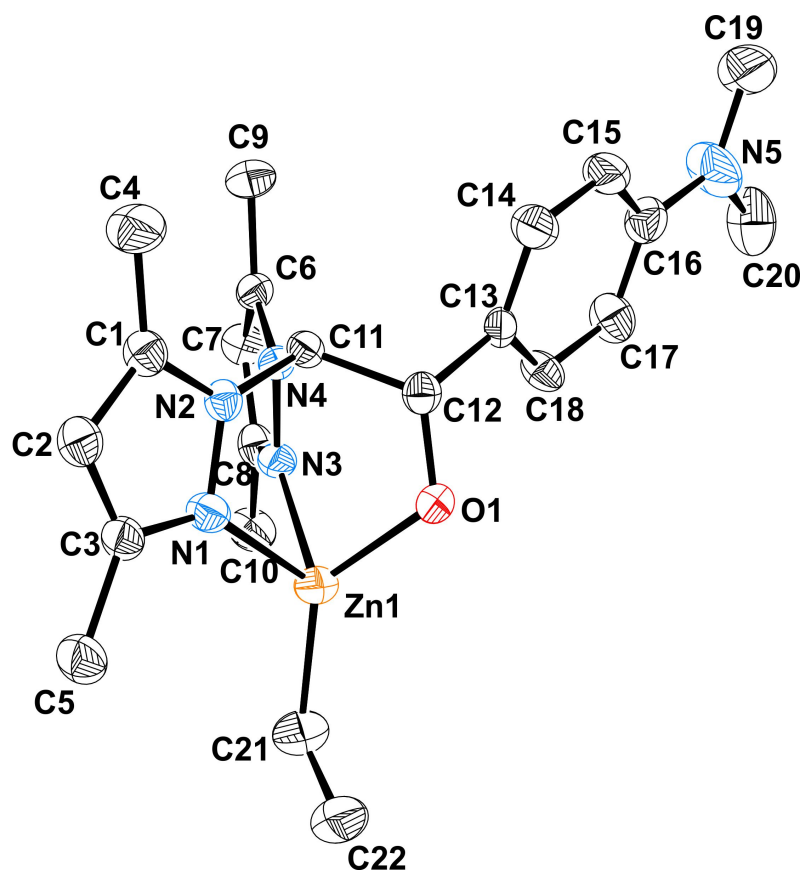
Figure 2. ORTEP view of the *S* enantiomer of [Zn(Et)(bpzampe)] (**5**). Ellipsoids are at the 30% probability level.

Polymerization Studies

The main aim of these studies was to compare the activity and stereoselectivity of both the mononuclear monoalkyls **4–12** and the binuclear trisalkyls **13**, **15** and **17** with those found for other zinc mononuclear monoalkyls[16,20] and binuclear trisalkyls[20] described by our group, and also to establish a comparison with some remarkable organozinc initiators bearing chiral auxiliary ligands,[13,14] and other asymmetrical N,N,O-tridentates[25] as well as achiral[26] scorpionate zinc analogs published to date.

Complexes **4–13**, **15** and **17** were systematically assessed in the ring-opening polymerization (ROP) of the polar monomer *rac*-lactide (*rac*-LA) in tetrahydrofuran as solvent at 20 and 60 °C under a nitrogen atmosphere for the production of poly(*rac*-lactide)s (PLAs) (Table 2). The experimental low-medium M_n values of the PLAs produced were in close agreement with the expected theoretical values considering one polymer chain per zinc center [M_n(calcd)PLA$_{100}$ = 14 400 g·mol^{-1}] (Table 2). In addition, analysis of the resulting polyesters by size exclusion chromatography (SEC) revealed a monomodal weight distribution, with dispersities ranging from 1.05 to 1.23 (Figure S1 in the ESI†).

The alkyl zinc mononuclear compounds **4–12** and the trisalkyl binuclear compounds **13**, **15** and **17** behaved as efficient single-component initiators and could polymerize 100 equivalents of *rac*-LA in tetrahydrofuran at 20 °C under otherwise identical conditions. In particular, the mononuclear complexes **4** and **10** transformed nearly 85% of the monomer after four hours while, interestingly, **7** gave almost complete conversion in four hours (entries 1, 12 and 18, respectively). The effect of the alkyl substituents on the zinc metal center were also evident. For example, in these mononuclear alkyls, the Me alkyl derivatives proved to be significantly more active than the Et- and CH$_2$SiMe$_3$-substituted initiators. For instance, whereas initiator **7** gave 98% conversion at 20 °C after four hours, analogs **8** and **9** converted nearly 60% of the monomer under the same conditions (entries 12, 15 and 16, respectively). Nonetheless, this behavior was opposite to that found for the analogs previously reported by our group, such as the chiral N,N,O-scorpionate zinc alkyls, in the ROP of L-LA.[16]

More importantly, the bimetallic trisalkyl complexes **13**, **15** and **17** significantly out-performed the mononuclear monoalkyls **4–12** described above in terms of activity. For instance, initiators **13** and **17** gave nearly 70% conversion after three hours at 20 ℃ (entries 22 and 27, respectively) while derivative **15** transformed 93% of the monomer in three hours (entry 25), with this complex again being the most active of this family due to the presence of the p-NEt$_2$C$_6$H$_4$ group. This behavior is probably the result of the beneficial cooperative effect of the two remote alkylzinc centers in the initiators, as previously observed for bis(trimethylsilyl)amide and isopropoxide zinc complexes bearing bis(imino)diphenylamido ancillary ligands.[23b]

It is also worth noting that both families of mono- and binuclear initiators proved to be significantly more active than the analogous chiral N,N,O-scorpionate zinc alkyls[16] and trisalkyls,[18] since polymerization activity was not detected at 20 ℃ in the latter cases. These compounds are more active than the asymmetrical N,N,O-tridentate zinc analogs[25] (15 h, 25 ℃, 78% conversion) and enantiopure amido-oxazolinate based zinc analogs (*i.e.*; 13 h, 23 ℃, 91% conversion),[14a] a finding that is consistent with the results obtained for alternative organozinc initiators bearing chiral auxiliary ligands[13] (*i.e.*; 2–3 h, 20–23 ℃, > 90% conversion) and for achiral scorpionate zinc[26] zwitterionic systems (3 h, 30 ℃, 90% conversion), but they are less active than enantiopure aminophenolate-based zinc complexes with multiple stereogenic centers (10–30 min, 25 ℃, > 95% conversion).[14b]

The effect of temperature and solvent on the catalytic activity was also investigated. As one would expect, the activities increased for all catalysts on increasing the temperature to 60 ℃. In contrast, when the reaction temperature was 0 ℃, all catalysts showed dramatically reduced catalytic activity and only traces of product were found. Interestingly, however, catalysts **7** and **15**, which contain the NEt$_2$ substituent, converted 37 and 52% of the monomer at 0 ℃ after 24 and 14 hours, respectively (entries 7 and 24, respectively). In addition, the catalytic activity was markedly lower in all cases when toluene was employed as the solvent, since complete dissolution of the catalyst was not achieved. This situation is in contrast with the complete dissolution of all initiators in tetrahydrofuran in conjunction with the cooperative effect that the zinc ions are probably complexed

by this coordinating solvent, thus leading to an increase in the nucleophilicity of the alkyl initiating group and the alkoxide propagating chains.

The good level of control afforded by these initiators was also evidenced by the linear correlations between M_n and percentage conversion found in the case of initiator **7** (entries 8–12) (R^2 = 0.993) (Figure S2 in the ESI†) in conjunction with the narrow molecular weight distributions. A double-feed experiment confirmed the living behavior of catalyst **7** (entries 12 and 13), which resulted in a polymer chain extension with similar polymer features. This behavior is representative of well-behaved living propagations and the existence of a single type of reaction site.

MALDI-ToF MS (Figure S3 in the ESI†) and end-group analysis by ^{1}H NMR spectroscopy (Figure S4 in the ESI†) of low molecular weight poly(*rac*-lactide) oligomers obtained with **8** and **7** were also carried out. Both techniques provided evidence for the initial addition of an alkyl fragment to the monomer in the materials produced, with subsequent cleavage of the acyl-oxygen bond[27] and further monomer additions to the (macro)alcohols.

In an effort to gain further insights into the polymerization process, a kinetic study was conducted with the mononuclear initiator **7** to establish the reaction order with respect to *rac*-LA monomer and catalyst concentration and also to determine the reaction rate constant. The polymerization experiments were performed at 20 ºC, using tetrahydrofuran as solvent and without cocatalyst or activator, and the yields were determined at stated intervals (Figure S4 in the ESI†). In all cases, the semilogarithmic plots of ln[*rac*-LA]$_0$/[*rac*-LA]$_t$ as a function of time for different catalyst concentrations gave a good linear relationship (Figure S4 in the ESI†) and these findings imply a first-order disappearance of the monomer concentration. Thus, a rate law of $-\mathrm{d}[\textit{rac}\text{-LA}]/\mathrm{d}t = k_{app}[\textit{rac}\text{-LA}]_t$ is suggested, where k_{app} denotes the apparent polymerization rate constant. Interestingly, the pseudo-first-order rate constant, k_{app}, for this initiator at 20 ºC has an order that is consistent with that measured for the analogous chiral monoalkyls [Zn(R)(NNO)]$_2$[16] at much higher temperature (k_{app}(50 °C) = (8.3 ± 0.3) × 10^{-4} s^{-1}, R = CH$_2$SiMe$_3$, vs k_{app}(20 °C) = (2.37 ± 0.08) × 10^{-4} s^{-1} for **7**, at [Zn]$_0$ = 20 mM in both cases). The kinetic dependence on the catalyst concentration (*n*)

and the propagation rate constant (k_p) were also determined (Figure S5 in the ESI†) and these confirmed that the reaction is also first-order in catalyst **7** at this temperature (Table S1 in the ESI†). The values obtained prove that the polymerization of *rac*-LA mediated by [Zn(Me)(bpzaepe)] (**7**) obeys an overall second-order kinetic rate law.

Finally, inspection of the microstructure by analysis of the methine region in the homonuclear decoupled ^{1}H NMR spectrum of the poly(*rac*-lactide)s produced revealed that the mononuclear initiators **4**–**12** exerted a low level of heterotactic enrichment on the growing polymer chains at 20 ºC – similar to asymmetrical N,N,O-tridentate zinc complexes (P_s = 0.62)[25] – but initiator **7** afforded a higher heterotactic dyad enchainment [P_s value up to 0.68; Table 2, entry 7, see Figure S6 (ESI†)]. On the other hand, the bimetallic initiators **13**, **15** and **17** provided similar values of heteroactivity to the mononuclear analogs, but lower values than **7** (P_s~0.62, Table 2, entry 25) and the heteroactive chiral zinc catalysts described above.[13] The effect of lower temperatures on the reaction did not improve the heterotacticity values in the polymer microstructures (Table 2, entries 7 and 24) whereas, as one would expect, the effect of higher temperatures clearly reduced this value and resulted in almost atactic materials (Table 2, entries 2, 14, 18 and 26). These findings suggest that for both families of initiators a chain-end control mechanism predominates for the production of heterotactic poly(*rac*-lactide)s.

Table 2. Polymerization of *rac*-Lactide Catalyzed by 4–13, 15 and 17.[a]

entry	initiator	T(°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	4	20	4	1.10	85	12 200	12 300	1.15	0.62
2	4	60	3	1.21	93	13 400	14 300	1.21	0.58
3	5	20	4	0.91	70	10 000	9 200	1.20	0.60
5	6	20	4	0.88	68	9 800	9 000	1.14	0.59
7	7	0	24	0.48	37	5 300	6 100	1.12	0.68
8	7	20	0.5	0.15	12	1 700	1 900	1.05	0.67
9	7	20	1	0.27	21	3 000	3 600	1.07	0.68
10	7	20	2	0.83	64	9 200	8 700	1.06	0.68
11	7	20	3	0.91	70	10 100	9 500	1.09	0.67
12	7	20	4	1.27	98	14 100	13 100	1.12	0.68
13	7	20	8	2.46	95	27 400	25 900	1.15	0.67
14	7	60	3	1.21	93	13 400	14 100	1.23	0.64
15	8	20	4	0.80	62	8 900	9 300	1.05	0.63
16	9	20	4	0.75	58	8 400	8 000	1.09	0.64
18	10	20	4	1.08	83	12 000	11 200	1.11	0.59
18	10	60	3	1.18	91	13 100	12 100	1.15	0.58
19	11	20	4	0.60	46	6 600	7 800	1.17	0.61
21	12	20	4	0.67	52	7 500	8 100	1.15	0.59

22	**13**	20	3	0.91	70	10 100	9 200	1.07	0.59
24	**15**	0	14	0.67	52	7 500	7 700	1.10	0.62
25	**15**	20	3	1.21	93	13 400	14 000	1.11	0.62
26	**15**	60	2	1.28	99	14 300	13 400	1.15	0.58
27	**17**	20	3	0.88	68	9 800	9 300	1.17	0.57

[a] Polymerization conditions: 90 μmol of zinc centers; $[rac\text{-LA}]_0/[\text{Zn}]_0 = 100$; 20 mL of tetrahydrofuran. [b] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) $\times$ 100]. [c] Theoretical $M_n = (rac\text{-LA}/\text{Zn}) \times (\% \text{ conversion}) \times (M_w \text{ of } rac\text{-LA})$. [d] Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[28] for M_n [$M_n(\text{obsd}) = 0.58 \times M_n(\text{GPC})$].[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 tetrads obtained in the decoupled ^{1}H NMR experiment by $P_s = 2I_1/(I_1+I_2)$, with $I_1 = \delta$ 5.20–5.25 ppm (*sis*, *sii/iis*) and $I_2 = \delta$ 5.13–5.20 ppm (*iis/sii*, *iii*, *isi*).[29]

CONCLUSIONS

We report here the preparation of new chiral bis(pyrazol-1-yl)methane-based N,N,O-donor scorpionate ligands in the form of the alcohol compounds bpzampeH, bpzaepeH and bpzimeH through the 1,2-addition reaction of a series of aldehydes. We also describe the reactivity of the resulting ligands with $[ZnR_2]$ (R = Me, Et, CH_2SiMe_3) in different stoichiometries. The initial equimolecular reactions produced the expected mononuclear monoalkyl zinc complexes $[Zn(R)(\kappa^3\text{-NNO})]$, whereas a 1:2 molar ratio afforded the corresponding binuclear trisalkyls $[Zn(R)(\kappa^2\text{-NN}\mu\text{-O})Zn(R)_2]$.

Interestingly, the mononuclear and binuclear alkyl-containing zinc complexes can act as efficient single-component living initiators for the well-controlled ROP of *rac*-LA, with the binuclear species exhibiting a cooperative effect between the two metal centers that increases the activity in comparison with the mononuclear systems to produce medium-low molecular weight PLA materials in only a few hours at room temperature. In addition, kinetic studies confirmed that propagations follow a pseudo-first-order dependence on monomer and catalyst concentration. Furthermore, a combination of end-group analysis and MALDI-TOF mass spectrometry provided evidence that the polymerization process is initiated by alkyl transfer to the monomer. More importantly, the sterically more demanding mononuclear alkyl **7** moderately promoted the formation heterotactic poly(*rac*-lactide)s, with a P_s value of 0.68.

EXPERIMENTAL SECTION

General Procedures

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. The starting material bdmpzm was prepared as reported previously[30]. The aldehydes [4-(dimethylamino)benzaldehyde, 4-(diethylamino)benzaldehyde and 1-methyl-2-imidazolecarboxaldehyde)], Bu^nLi and ZnR_2 (R = Me, Et) were used as purchased (Aldrich). *rac*-Lactide was sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Instruments and Measurements

NMR spectra were recorded on a Varian Inova FT-500 spectrometer and were referenced to the residual deuterated solvent signal. ^1H 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 processed using an IPC-Sun computer. Microanalyses were performed with a Perkin-Elmer 2400 CHN analyzer. The molecular weights (M_n) and the molecular mass distributions (M_w/M_n) of polymer samples were measured by Gel Permeation Chromatography (GPC) performed on a Shimadzu LC-20AD GPC equipped with a TSK-GEL G3000Hxl column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 40 ℃ 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. Samples were prepared as follows: PLA (20 mg) was dissolved in HPLC quality THF with matrix and NaI in a 100:5:5 ratio. Prior to evaporation, 10 μL of the mixture solution was deposited on the sample

plate. 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). All values are the average of two independent measurements.

The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in CDCl$_3$ on a Varian Inova FT-500 spectrometer with concentrations in the range 1.0 to 2.0 mg/mL.

Preparation of compounds 1–18

Synthesis of bpzampeH (1). In a 250 cm^3 Schlenk tube, bdmpzm (4.00 g, 19.6 mmol) was dissolved in dry THF (125 cm^3) and cooled to –70 ºC. A 2.5 M solution of Bu^{n}Li (7.84 cm^3, 19.6 mmol) in hexane was added and the suspension was stirred for 1 h. The reaction mixture was warmed to 0 ºC and the resulting yellow suspension was treated with 4-(dimethylamino)benzaldehyde (2.93 g, 19.6 mmol). After 5 min the reaction mixture was treated with saturated aqueous ammonium chloride (50 cm^3). The product was extracted and dried over MgSO$_4$, filtered and the solvent was removed to give a white solid. This solid was crystallized from n-hexane. Yield 90% (6.23 g, 17.65 mmol). Anal. Calcd for C$_{20}$H$_{27}$N$_5$O: C, 67.96; H, 7.70; N, 19.81; Found: C, 68.07; H, 7.53; N, 20.01; ^{1}H NMR (CDCl$_3$, 297 K): δ 6.99 (d, 2 H, N-Ph^o), 6.65 (d, 2 H, N-Ph^m), 5.86 (d, 1 H, CH^a), 5.85 (s, 1 H, H$^{4'}$), 5.80 (d, 1 H, CH^b), 5.61 (s, 1 H, H^4), 4.93 (bs, 1 H, OH), 2.91 (s, 6 H, NMe$_2$), 2.28 (s, 3 H, Me$^{3'}$), 2.17 (s, 3 H, Me^3), 1.95 (s, 3 H, Me$^{5'}$), 1.73 (s, 3 H, Me^5). ^{13}C-{^{1}H} NMR (CDCl$_3$, 297 K): δ 150.5, 148.5, 148.4, 140.6 (C$^{3\ or\ 5}$), 139.7, 126.2 (C^{ph}), 127.5 (C^o), 112.3 (C^m), 106.5, 105.5 (C$^{4-4'}$), 76.8 (CH^a), 74.3 (CH^b), 40.6 (N-Me), 13.7, 13.8 (Me$^{3-3'}$), 10.7, 10.5 (Me$^{5-5'}$).

Synthesis of (bpzaepeH) (2). The synthetic procedure was the same as for **1**, using bdmpzm (4.00 g, 19.6 mmol), a 2.5 M solution of Bu^{n}Li (7.84 cm^3, 19.6 mmol) and 4-(diethylamino)benzaldehyde (3.47 g, 19.6 mmol), to give **2** as a white solid. Yield 92% (6.88 g, 18.0 mmol). Anal. Calcd for C$_{22}$H$_{31}$N$_5$O: C, 69.26; H, 8.19; N, 18.36; Found: C, 69.37; H, 8.07; N, 18.47; ^{1}H NMR (CDCl$_3$, 297 K): δ 6.94 (d, 2 H, N-Ph^o), 6.53 (d, 2 H, N-Ph^m), 5.85 (d, 1 H, CH^b), 5.84 (s, 1 H, H$^{4'}$), 5.75 (dd, 1 H, CH^a), 5.60 (s, 1 H, H^4), 4.88 (bs, 1 H, OH), 3.31 [q, 4 H, N(C̲H̲$_2$-CH$_3$)$_2$], 2.27 (s, 3 H, Me$^{3'}$), 2.16 (s, 3 H, Me^3), 1.94

(s, 3 H, Me$^{5'}$), 1.73 (s, 3 H, Me^5), 1.11 [t, 6 H, N(CH$_2$-$\underline{CH_3}$)$_2$]. ^{13}C-{^{1}H} NMR (CDCl$_3$, 297 K): δ 148.5, 148.4, 147.7, 140.6 (C$^{3\text{ or }5}$), 139.7, 125.0 (C^{ph}), 127.6 (C^o), 111.9 (C^m), 106.5, 105.5 (C$^{4\text{-}4'}$), 74.5 (CH^a), 74.0 (CH^b), 44.4 N($\underline{CH_2}$-CH$_3$)$_2$, 13.7 (Me$^{3\text{-}3'}$), 12.4 N(CH$_2$-$\underline{CH_3}$)$_2$, 10.7, 10.4 (Me$^{5\text{-}5'}$).

Synthesis of (bpzimeH) (3). The synthetic procedure was the same as for **1**, using bdmpzm (4.00 g, 19.6 mmol), a 2.5 M solution of Bu^{n}Li (7.84 cm^3, 19.6 mmol) and 1-methyl-2-imidazolecarboxaldehyde (2.16 g, 19.6 mmol), to give **3** as a white solid. Yield 88% (5.41 g, 17.2 mmol). Anal. Calcd for C$_{16}$H$_{22}$N$_6$O: C, 61.13; H, 7.05; N, 26.73; Found: C, 61.01; H, 7.11; N, 26.89; ^{1}H NMR (CDCl$_3$, 297 K): δ 6.92 (s, 1 H, C=C$_{im}$), 6.68 (s, 1 H, C=C$_{im}$), 6.54 (s, 1 H, CH^a), 6.14 (s, 1 H, CH^b), 5.84 (s, 1 H, H$^{4'}$), 5.60 (s, 1 H, H^4), 4.77 (bs, 1 H, OH), 3.48 (s, 3 H, NMe$_{im}$), 2.27 (s, 3 H, Me$^{3'}$), 2.14 (s, 3 H, Me^3), 2.13 (s, 3 H, Me$^{5'}$), 2.12 (s, 3 H, Me^5). ^{13}C-{^{1}H} NMR (CDCl$_3$, 297 K): δ 149.3, 148.9, 145.5, 141.0 (C$^{3\text{ or }5}$), 140.3 (C^{im}), 124.7, 121.7 (C=C$_{im}$), 106.5, 106.0 (C$^{4\text{-}4'}$), 70.4 (CH^a), 66.4 (CH^b), 33.5 (NMe$_{im}$), 13.7 (Me$^{3\text{-}3'}$), 10.7, 10.4 (Me$^{5\text{-}5'}$).

Synthesis of [Zn(Me)(bpzampe)] (4). In a 250 cm^3 Schlenk tube, bpzampeH (1.0 g, 2.83 mmol) was dissolved in dry toluene (60 mL) and the solution was cooled to −70 ºC. A solution of ZnMe$_2$ (2.0 M in toluene) (1.42 mL, 2.83 mmol) was added and the mixture was allowed to warm up to room temperature and stirred during 1 h. The solvent was evaporated to dryness under reduced pressure to yield a white product. The product was washed with *n*-hexane (1 × 25 mL) and recrystallized from toluene at −26 ºC to give compound **4** as colorless crystals. Yield: 90% (1.10 g, 2.54 mmol). Anal. Calcd. for C$_{21}$H$_{29}$N$_5$OZn : C, 58.27; H, 6.75; N, 16.18; Found: C, 58.42; H, 6.88; N, 16.14; ^{1}H NMR (C$_6$D$_6$, 297 K), δ 7.37 (d, 2H, N-Ph^o), 6.62 (d, 2H, N-Ph^m), 5.92 (s, 1H, CH^b), 5.89 (s, 1H, CH^a), 5.43 (s, 1H, H$^{4'}$), 5.27 (s, 1H, H^4), 2.52 (s, 6H, NMe$_2$), 2.15 (s, 3H, Me$^{5'}$), 2.13 (s, 3H, Me^5), 1.66 (s, 3H, Me$^{3'}$), 1.26 (s, 3H, Me^3), 0.20 (s, 3H, Zn-CH$_3$). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 297 K), δ 150.5−135.0 (C$^{3\text{ or }5}$), 139.2, 125.8 (C^{ph}), 127.0 (C^o), 112.2 (C^m), 105.1, 104.4 (C$^{4\text{-}4'}$), 81.6 (C^a), 71.0 (C^b), 40.1 (NMe$_2$), 12.6 (Me^5), 12.5 (Me$^{5'}$), 10.3 (Me^3), 9.58 (Me$^{3'}$), −2.4 (Zn-Me).

Synthesis of [Zn(Et)(bpzampe)] (5). The synthesis of **5** was carried out in an identical manner to **4**, using bpzampeH (1.0 g, 2.83 mmol), ZnEt$_2$ (1.0 M in hexane) (2.83 mL, 2.83 mmol). Yield: 91%

(1.15 g, 2.57 mmol). Anal. Calcd. for $C_{22}H_{31}N_5OZn$: C, 59.13; H, 6.99; N, 15.67; Found: C, 59.29; H, 6.84; N, 15.61; ^1H NMR (C_6D_6, 297 K), δ 7.31 (d, 2H, N-Ph^o), 6.58 (d, 2H, N-Ph^m), 5.92 (s, 1H, CH^b), 5.85 (s, 1H CH^a), 5.44 (s, 1H, H$^{4'}$), 5.30 (s, 1H, H^4), 2.52 (s, 6H, NMe$_2$), 2.18 (s, 6H, Me$^{5-5'}$), 1.98 (t, 3H, Zn-CH$_2$C$\underline{H}_3$), 1.68 (s, 3H, Me$^{3'}$), 1.30 (s, 3H, Me^3), 1.07 (q, 2H, Zn-C$\underline{H}_2$CH$_3$). ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 148.0–135.5 (C$^{3\ or\ 5}$) 138.6, 124.5 (C^{Ph}), 127.2 (C^o), 112.1 (C^m), 105.5, 104.6 (C$^{4-4'}$), 80.3 (C^a), 70.2 (C^b), 44.2 (NMe$_2$), 13.8 (Zn-CH$_2$C$\underline{H}_3$), 13.5–9.9 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), −0.2 (Zn-C$\underline{H}_2$CH$_3$).

Synthesis of [Zn(CH$_2$SiMe$_3$)(bpzampe)] (6). A solution of [(trimethylsilyl)methyllithium, Li(CH$_2$SiMe$_3$)] 0.7 M in hexane (8.1 mL, 5.67 mmol) was added to a cooled (–40 ºC), stirred suspension of ZnCl$_2$ (0.39 g, 2.83 mmol) in diethyl ether (50 mL) in a 250 cm^3 Schlenk tube. The mixture was allowed to warm up to room temperature and stirred for 1 h. An increase in turbidity was observed and this finally led to the formation of a white suspension. The suspension was filtered and the filtrate, corresponding to Zn(CH$_2$SiMe$_3$)$_2$, was added to a 250 cm^3 Schlenk tube containing a precooled (–20 °C) solution of bpzampeH (1.0 g, 2.83 mmol) in diethyl ether (50 mL). The mixture was allowed to warm up to room temperature and stirred during 2 h. The ether was evaporated to dryness under reduced pressure to yield a white product. The product was washed with cold hexane (1 × 20 mL) and recrystallized from hexane to give compound **6** as colorless crystals. Yield: 90% (1.29 g, 2.55 mmol). Anal. Calcd. For $C_{24}H_{37}N_5OSiZn$: C, 57.08; H, 7.38; N, 13.87; Found: C, 57.25; H, 7.46; N, 13.61; ^1H NMR (C_6D_6, 297 K), δ 7.32 (d, 2H, N-Ph^o), 6.59 (d, 2H, N-Ph^m), 5.88 (s, 1H, CH^a), 5.78 (s, 1H, CH^b), 5.42 (s, 1H, H$^{4'}$), 5.24 (s, 1H, H^4), 2.52 (s, 6H, NMe$_2$), 2.18 (s, 6H, Me$^{5,5'}$), 1.67 (s, 3H, Me$^{3'}$), 1.22 (s, 3H, Me^3), 0.66 (s, 9H, Zn-CH$_2$Si$\underline{Me}_3$), −0.10 (s, 2H, Zn-C$\underline{H}_2$SiMe$_3$). ^{13}C{^1H} NMR (C_6D_6, 297 K), δ 149.4–135.3 (C$^{3\ or\ 5}$), 139.1, 124.7 (C^{Ph}), 126.9 (C^o), 112.2 (C^m) 105.2, 104.4 (C$^{4-4'}$), 81.5 (C^a), 70.8 (C^b), 40.1 (NMe$_2$), 12.8, 12.7 (Me$^{3,3'}$), 10.0 (Me^5), 9.6 (Me$^{5'}$), 3.3 (Zn-CH$_2$Si$\underline{Me}_3$), −9.7 (Zn-C$\underline{H}_2$SiMe$_3$).

Synthesis of [Zn(Me)(bpzaepe)] (7). The synthesis of **7** was carried out in an identical manner to **4**, using bpzaepeH (1.0 g, 2.62 mmol), ZnMe$_2$ (2.0 M in toluene) (1.31 mL, 2.62 mmol). Yield: 89%

(1.08 g, 2.34 mmol). Anal. Calcd. For $C_{23}H_{33}N_5OZn$: C, 59.93; H, 7.22; N, 15.19; Found: C, 60.21; H, 6.99; N, 15.42; ^{1}H NMR (C_6D_6, 297 K) δ 7.32 (d, 2H, N-Ph^o), 6.59 (d, 2H, N-Ph^m), 5.95 (s, 1H, CH^b), 5.89 (s, 1H, CH^a), 5.48 (s, 1H, H$^{4'}$), 5.29 (s, 1H, H^4), 2.99 [q, 4H, N($\underline{CH_2}$CH$_3$)$_2$], 2.16 (s, 3H, Me$^{5'}$), 2.14 (s, 3H, Me^5), 1.69 (s, 3H, Me$^{3'}$), 1.31 (s, 3H, Me^3), 0.91 [t, 6H, N(CH$_2\underline{CH_3}$)$_2$], 0.19 (s, 3H, Zn-Me). ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 150.5–135.0 (C$^{3\ or\ 5}$), 139.4, 125.2 (C^{Ph}), 127.3 (C^o), 112.1 (C^m), 105.1, 104.5 (C$^{4\text{-}4'}$), 81.5 (C^a), 71.2 (C^b), 40.0 (N$\underline{CH_2}$CH$_3$), 12.3 (NCH$_2\underline{CH_3}$), 12.6 (Me$^{5,5'}$), 10.1 (Me^3), 9.6 (Me$^{3'}$), −2.4 (Zn-Me).

Synthesis of [Zn(Et)(bpzaepe)] (8). The synthesis of **8** was carried out in an identical manner to **4**, using bpzaepeH (1.0 g, 2.62 mmol), ZnEt$_2$ (1.0 M in hexane) (2.62 mL, 2.62 mmol). Yield: 88% (1.09 g, 2.29 mmol). Anal. Calcd. For $C_{24}H_{35}N_5OZn$: C, 60.69; H, 7.43; N, 14.75; Found: C, 60.71; H, 7.58; N, 14.62; ^{1}H NMR (C_6D_6, 297 K), δ 7.31 (d, 2H, N-Ph^o), 6.58 (d, 2H, N-Ph^m), 5.92 (s, 1H, CH^b), 5.85 (s, 1H CH^a), 5.44 (s, 1H, H$^{4'}$), 5.30 (s, 1H, H^4), 3.00 [q, 4H, N-($\underline{CH_2}$CH$_3$)$_2$], 2.18 (s, 6H, Me$^{5\text{-}5'}$), 1.68 (s, 3H, Me$^{3'}$), 1.30 (s, 3H, Me^3), 1.98 (t, 6H, Zn-CH$_2\underline{CH_3}$), 1.07 (q, 4H, Zn-$\underline{CH_2}$CH$_3$), 0.91 [t, 6H, N-(CH$_2\underline{CH_3}$)$_2$]. ^{13}C {^{1}H} NMR (C_6D_6, 297 K), δ 148.0–135.5 (C$^{3\ or\ 5}$), 139.2, 124.1 (C^{Ph}), 127.2 (C^o), 112.1 (C^m), 105.5, 104.6 (C$^{4\text{-}4'}$), 80.3 (C^a), 70.2 (C^b), 44.2 (N$\underline{CH_2}$CH$_3$), 13.5–9.9 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), 13.8 (Zn-CH$_2\underline{CH_3}$), 12.2 (NCH$_2\underline{CH_3}$), −0.22 (Zn-$\underline{CH_2}$CH$_3$).

Synthesis of [Zn(CH$_2$SiMe$_3$)(bpzaepe)] (9). The synthesis of **9** was carried out in an identical manner to **6**, using bpzaepeH (1.0 g, 2.62 mmol), Li(CH$_2$SiMe$_3$) 0.7 M in hexane (7.48 mL, 5.24 mmol) and ZnCl$_2$ (0.36 g, 2.62 mmol). Yield: 84% (1.18 g, 2.21 mmol). Anal. Calcd. For $C_{26}H_{41}N_5OSiZn$: C, 58.58; H, 7.75; N, 13.14. Found: C, 58.55; H, 7.59; N, 13.41; ^{1}H NMR (C_6D_6, 297 K), δ 7.28 (d, 2H, N-Ph^o), 6.57 (d, 2H, N-Ph^m), 5.87 (s, 1H, CH^a), 5.76 (s, 1H, CH^b), 5.42 (s, 1H, H$^{4'}$), 5.26 (s, 1H, H^4), 2.99 [q, 4H, N-($\underline{CH_2}$CH$_3$)$_2$], 2.19 (s, 6H, Me$^{5,5'}$), 1.66 (s, 3H, Me$^{3'}$), 1.24 (s, 3H, Me^3), 0.90 [t, 6H, N-(CH$_2\underline{CH_3}$)$_2$], 0.66 (s, 9H, Zn-CH$_2$Si$\underline{Me_3}$), −0.10 (s, 2H, Zn-$\underline{CH_2}$SiMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K), δ 149.4–135.3 (C$^{3\ or\ 5}$), 139.5, 124.7 (C^{Ph}), 126.9 (C^o), 112.2 (C^m) 105.2 ,104.4 (C$^{4\text{-}4'}$), 81.5 (C^a), 70.8 (C^b), 44.2 (N-CH$_2\underline{CH_3}$), 12.8, 12.7 (Me$^{3,3'}$), 12.3 (NCH$_2\underline{CH_3}$), 10.0 (Me^5), 9.6 (Me$^{5'}$), 0.3 (Zn-CH$_2\underline{Si}$Me$_3$), −9.7 (Zn-$\underline{CH_2}$SiMe$_3$).

Synthesis of [Zn(Me)(bpzime)] (10). The synthesis of **10** was carried out in an identical manner to **4**, using bpzimeH (1.0 g, 3.18 mmol), ZnMe$_2$ (2.0 M in toluene) (1.60 mL, 3.18 mmol). Yield: 89% (1.12 g, 2.84 mmol). Anal. Calcd. For C$_{17}$H$_{24}$N$_6$OZn: C, 51.85; H, 6.14; N, 21.34; Found: C, 51.69; H, 6.30; N, 21.41; ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.15 (s, 1 H, C=C^{im}), 7.02 (s, 1 H, C=C^{im}), 6.24 (s, 1 H, CH^a), 6.02 (s, 1 H, CH^b), 5.31 (s, 2 H, H$^{4\text{-}4'}$), 3.57 (^{im}N-CH$_3$), 2.27 (s, 6 H, Me$^{5\text{-}5'}$), 1.96 (s, 3 H, Me$^{3'}$), 1.73 (s, 3 H, Me^3), 0.15 (s, 3H, Zn-CH$_3$). ^{13}C-$\{^1$H$\}$ NMR (C$_6$D$_6$, 297 K): δ 149.3, 148.9, 145.5, 141.0 (C$^{3\text{ or }5}$), 140.5 (C^{im}), 124.7, 121.7 (C=C^{im}), 106.5, 106.0 (C$^{4\text{-}4'}$), 70.4 (CH^a), 66.4 (CH^b), 33.5 (^{im}N-CH$_3$), 12.8, 12.7 (Me$^{3,3'}$), 10.0, 9.6 (Me$^{5\text{-}5'}$), −2.4 (Zn-Me).

Synthesis of [Zn(Et)(bpzime)] (11). The synthesis of **11** was carried out in an identical manner to **4**, using bpzimeH (1.0 g, 3.18 mmol), ZnEt$_2$ (1.0 M in hexane) (3.18 mL, 3.18 mmol). Yield: 87% (1.13 g, 2.77 mmol). Anal. Calcd. For C$_{18}$H$_{26}$N$_6$OZn: C, 53.01; H, 6.43; N, 20.61; Found: C, 52.91; H, 6.40; N, 20.83; ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.15 (s, 1 H, C=C^{im}), 7.07 (s, 1 H, C=C^{im}), 6.25 (s, 1 H, CH^a), 6.08 (s, 1 H, CH^b), 5.31 (s, 2 H, H$^{4\text{-}4'}$), 3.61 (^{im}N-CH$_3$), 2.23 (s, 6 H, Me$^{5\text{-}5'}$), 1.96, 1.73 (s, 3 H, Me$^{3\text{-}3'}$), 1.98 (t, 3H, Zn-CH$_2$<u>CH$_3$</u>), 1.07 (q, 2H, Zn-<u>CH$_2$</u>CH$_3$). ^{13}C-$\{^1$H$\}$ NMR (C$_6$D$_6$, 297 K): δ 149.3, 148.9, 145.5, 141.1 (C$^{3\text{ or }5}$), 140.4, (C^{im}), 123.9, 121.6 (C=C^{im}), 107.0, 105.9 (C$^{4\text{-}4'}$), 70.4 (CH^a), 66.4 (CH^b), 33.6 (^{im}N-CH$_3$), 12.9, 12.8 (Me$^{3,3'}$), 9.8, 9.5 (Me$^{5\text{-}5'}$), 13.5 (Zn-<u>CH$_2$</u>CH$_3$), 0.22 (Zn-CH$_2$<u>CH$_3$</u>).

Synthesis of [Zn(CH$_2$SiMe$_3$)(bpzime)] (12). The synthesis of **12** was carried out in an identical manner to **6**, using bpzimeH (1.0 g, 3.18 mmol), Li(CH$_2$SiMe$_3$) 0.7 M in hexane (9.1 mL, 6.36 mmol) and ZnCl$_2$ (0.43 g, 3.18 mmol). Yield: 87% (1.29 g, 2.77 mmol). Anal. Calcd. For C$_{20}$H$_{32}$N$_6$OSiZn: C, 51.55; H, 6.92; N, 18.04; Found: C, 51.66; H, 7.06; N, 18.11; ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.15 (s, 1 H, C=C^{im}), 7.08 (s, 1 H, C=C^{im}), 6.31 (s, 1 H, CH^a), 6.06 (s, 1 H, CH^b), 5.32 (s, 2 H, H$^{4\text{-}4'}$), 3.58 (^{im}N-CH$_3$), 2.25 (s, 6 H, Me$^{5\text{-}5'}$), 1.95, 1.71 (s, 6 H, Me$^{3\text{-}3'}$), 0.85 (s, 9H, Zn-CH$_2$<u>SiMe$_3$</u>), −0.10 (s, 2H, Zn-<u>CH$_2$</u>SiMe$_3$). ^{13}C-$\{^1$H$\}$ NMR (C$_6$D$_6$, 297 K): δ 149.4, 148.8, 145.5, 140.9 (C$^{3\text{ or }5}$), 140.3 (C^{im}), 124.1, 121.3 (C=C^{im}), 106.4, 105.8 (C$^{4\text{-}4'}$), 70.6 (CH^a), 66.5 (CH^b), 33.5 (^{im}N-CH$_3$), 12.8, 12.7 (Me$^{3,3'}$), 9.9, 9.6 (Me$^{5\text{-}5'}$), 3.36 (Zn-CH$_2$<u>SiMe$_3$</u>), −9.9 (Zn-<u>CH$_2$</u>SiMe$_3$).

Synthesis of [Zn(Me)(bpzampe)Zn(Me)₂] (13). The synthesis of **13** was carried out in an identical manner to **4**, using bpzampe (1.0 g, 2.83 mmol) and ZnMe₂ (2.0 M in toluene) in a 1:2 molar ratio (2.83 mL, 5.66 mmol). Yield: 90% (1.34 g, 2.54 mmol). Anal. Calcd. For $C_{23}H_{35}N_5OZn_2$: C, 52.29; H, 6.68; N, 13.26; Found: C, 52.51; H, 6.72; N, 13.52; ^1H NMR (C_6D_6, 297 K), δ 7.20 (d, 2H, N-Ph^o), 6.53 (d, 2H, N-Ph^m), 5.78 (s, 2H, CH^b, CH^a), 5.38 (s, 1H, H$^{4'}$), 5.20 (s, 1H, H^4), 2.49 (s, 6H, NMe₂), 2.11 (s, 6H, Me$^{5-5'}$), 1.56 (s, 3H, Me$^{3'}$), 1.17 (s, 3H, Me^3), 0.16 (s, 3H, Zn-Me), −0.17 (s, 6H, Zn-Me₂). ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 149.9–137.5 (C$^{3\text{ or }5}$), 138.7, 124.4 (C^{Ph}), 128.9 (C^o), 122.1 (C^m), 105.5, 104.6 (C$^{4-4'}$), 80.4 (C^a), 70.2 (C^b), 39.8 (NCH₃), 12.4–9.4 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), −2.4 (Zn-Me), −15.3 (Zn-Me₂).

Synthesis of [Zn(Et)(bpzampe)Zn(Et)₂] (14). The synthesis of **14** was carried out in an identical manner to **4**, using bpzampeH (1.0 g, 2.83 mmol) and ZnEt₂ (1.0 M in hexane) in a 1:2 molar ratio (5.66 mL, 5.66 mmol). Yield: 89% (1.45 g, 2.51 mmol). Anal. Calcd. For $C_{26}H_{41}N_5OZn_2$: C, 54.75; H, 7.25; N, 12.28; Found: C, 54.59; H, 7.39; N, 12.42; ^1H NMR (C_6D_6, 297 K), δ 7.26 (d, 2H, N-Ph^o), 6.58 (d, 2H, N-Ph^m), 5.82 (s, 2H, CH^b, CH^a), 5.41 (s, 1H, H$^{4'}$), 5.25 (s, 1H, H^4), 2.51 (s, 6H, NMe₂), 2.15 (s, 6H, Me$^{5-5'}$), 1.80 (t, 3H, Zn-CH₂$\underline{CH_3}$), 1.95 (s, 3H, Me$^{3'}$), 1.40 (t, 6H, Zn-(CH₂$\underline{CH_3}$)₂), 1.22 (s, 3H, Me^3), 0.80 (q, 2H, Zn-$\underline{CH_2}$CH₃), 0.40 [q, 4H, Zn-($\underline{CH_2}$CH₃)₂]. ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 150.0–132.0 (C$^{3\text{ or }5}$), 138.8, 123.9 (C^{Ph}), 127.0 (C^o), 112.1 (C^m), 105.7, 104.7 (C$^{4-4'}$), 79.9 (C^a), 77.4 (C^b), 40.0 (NMe) 39.8, 14.0–12.6 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), 13.6 (Zn-CH₂$\underline{CH_3}$), 13.1 [Zn-(CH₂$\underline{CH_3}$)₂], 4.1 (Zn-$\underline{CH_2}$CH₃), −2.5 [Zn-($\underline{CH_2}$CH₃)₂].

Synthesis of [Zn(Me)(bpzaepe)Zn(Me)₂] (15). The synthesis of **15** was carried out in an identical manner to **4**, using bpzaepeH (1.0 g, 2.62 mmol) and ZnMe₂ (2.0 M in toluene) in a 1:2 molar ratio (2.62 mL, 5.24 mmol). Yield: 90% (1.31 g, 2.35 mmol). Anal. Calcd. For $C_{25}H_{39}N_5OZn_2$: C, 53.97; H, 7.07; N, 12.59; Found: C, 54.03; H, 7.22; N, 12.62; ^1H NMR (C_6D_6, 297 K), δ 7.19 (d, 2H, N-Ph^o), 6.54 (d, 2H, N-Ph^m), 5.81 (s, 1H, CH^b), 5.79 (s, 1H, CH^a), 5.40, (s, 1H, H$^{4'}$), 5.23 (s, 1H, H^4), 2.98 [q, 4H, N-($\underline{CH_2}$CH₃)₂], 2.10 (s, 6H, Me$^{5-5'}$), 1.65 (s, 3H, Me$^{3'}$), 1.21 (s, 3H, Me^3), 0.89 [t, 6H, N-(CH₂$\underline{CH_3}$)₂], 0.22 (s, 3H, Zn-Me), −0.16 (s, 6H, Zn-Me₂). ^{13}C {^1H} NMR (C_6D_6, 297 K), δ 149.9–

137.5 ($C^{3\ or\ 5}$), 138.8, 124.6 (C^{Ph}), 128.9 (C^o), 122.1 (C^m), 105.5, 104.6 ($C^{4-4'}$), 80.4 (C^a), 70.2 (C^b), 44.2 (N$\underline{C}H_2CH_3$), 12.3 (NCH$_2\underline{C}H_3$), 12.4–9.4 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), −2.4 (Zn-Me), −15.4 (Zn-Me$_2$).

Synthesis of [Zn(Et)(bpzaepe)Zn(Et)$_2$] (16). The synthesis of **16** was carried out in an identical manner to **4**, using bpzaepeH (1.0 g, 2.62 mmol) and ZnEt$_2$ (1.0 M in hexane) in a 1:2 molar ratio (5.24 mL, 5.24 mmol). Yield: 90% (1.41 g, 2.36 mmol). Anal. Calcd. For C$_{28}$H$_{45}$N$_5$OZn$_2$: C, 56.20; H, 7.58; N, 11.70; Found: C, 56.29; H, 7.72; N, 11.62; ^{1}H NMR (C$_6$D$_6$, 297 K), δ 7.18 (d, 2H, N-Ph^o), 6.55 (d, 2H, N-Ph^m), 5.80 (s, 1H, CH^b), 5.77 (s, 1H, CH^a), 5.41 (s, 1H, H$^{4'}$), 5.26 (s, 1H, H^4), 2.97 (q, 4H, N-($\underline{C}H_2CH_3)_2$), 2.15 (s, 6H, Me$^{5-5'}$), 1.96 (s, 3H, Me$^{3'}$), 1.80 (t, 3H, Zn-CH$_2\underline{C}H_3$), 1.40 [t, 6H, Zn-(CH$_2\underline{C}H_3)_2$], 1.21 (s, 3H, Me^3), 0.89 (t, 6H, N-(CH$_2\underline{C}H_3)_2$), 0.80 (q, 2H, Zn-$\underline{C}H_2CH_3$), 0.4 (q, 4H, Zn-($\underline{C}H_2CH_3)_2$). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 297 K), δ 149.9–132.0 ($C^{3,3'}$, $C^{5,5'}$, C^{Ph}), 127.9 (C^o), 111.9 (C^m), 105.7, 104.7 ($C^{4-4'}$), 79.9 (C^a), 77.4 (C^b), 44.2 (N-$\underline{C}H_2CH_3$), 12.3 (N-CH$_2\underline{C}H_3$), 39.8, 14.0–12.6 (Me^3, Me$^{3'}$, Me$^{5'}$, Me^5), 13.51 (Zn-CH$_2\underline{C}H_3$), 13.2 [Zn-(CH$_2\underline{C}H_3)_2$], 4.1 (Zn-$\underline{C}H_2CH_3$), −2.7 [Zn-($\underline{C}H_2CH_3)_2$].

Synthesis of [Zn(Me)(bpzime)Zn(Me)$_2$] (17). The synthesis of **17** was carried out in an identical manner to **4**, using bpzimeH (1.0 g, 3.18 mmol) and ZnMe$_2$ (2.0 M in toluene) in a 1:2 molar ratio (3.18 mL, 6.36 mmol). Yield: 87% (1.35 g, 2.76 mmol). Anal. Calcd. for C$_{19}$H$_{30}$N$_6$OZn$_2$: C, 46.64; H, 6.18; N, 17.18; Found: C, 46.49; H, 6.32; N, 17.32; ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.15 (s, 1 H, C=C^{im}), 7.04 (s, 1 H, C=C^{im}), 6.27 (s, 1 H, CH^a), 6.01 (s, 1 H, CH^b), 5.33 (s, 2 H, H$^{4-4'}$), 3.56 (^{im}N-CH$_3$), 2.29 (s, 6 H, Me$^{5-5'}$), 1.95 (s, 3 H, Me$^{3'}$), 1.71 (s, 3 H, Me^3), 0.16 (s, 3H, Zn-$\underline{C}H_3$), −0.17 (s, 6H, Zn-$\underline{C}H_3)_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 149.3, 148.8, 145.4, 141.0 ($C^{3\ or\ 5}$), 140.3 (C^{im}), 125.0, 121.3 (C=C^{im}), 106.5, 105.9 ($C^{4-4'}$), 70.4 (CH^a), 66.4 (CH^b), 33.6 (^{im}N-CH$_3$), 12.9, 12.5 (Me$^{3,3'}$), 9.8, 9.4 (Me$^{5-5'}$), −2.4 (Zn-Me), −15.4 (Zn-Me$_2$).

Synthesis of [Zn(Et)(bpzime)Zn(Et)$_2$] (18). The synthesis of **18** was carried out in an identical manner to **4**, using bpzimeH (1.0 g, 3.18 mmol) and ZnEt$_2$ (1.0 M in hexane) in a 1:2 molar ratio (6.36 mL, 6.36 mmol). Yield: 77% (1.30 g, 2.45 mmol). Anal. Calcd. for C$_{22}$H$_{36}$N$_6$OZn$_2$: C, 49.73; H, 6.83; N, 15.82; Found: C, 49.59; H, 6.82; N, 15.62; ^{1}H NMR (C$_6$D$_6$, 297 K): δ 7.17 (s, 1 H, C=C^{im}), 7.10 (s, 1 H, C=C^{im}), 6.33 (s, 1 H, CH^a), 6.06 (s, 1 H, CH^b), 5.31 (s, 2 H, H$^{4-4'}$), 3.57 (^{im}N-CH$_3$), 2.27 (s, 3

H, Me$^{5-5'}$), 1.95, 1.72 (s, 3 H, Me$^{3-3'}$), 1.80 (t, 3H, Zn-CH$_2$CH$_3$), 1.40 [t, 6H, Zn-(CH$_2$CH$_3$)$_2$], 0.80 (q,

2H, Zn-CH$_2$CH$_3$), 0.40 [q, 4H, Zn-(CH$_2$CH$_3$)$_2$]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 297 K): δ 149.3, 148.6, 145.4,

141.0 (C$^{3 \text{ or } 5}$), 140.2 (C^{im}), 124.7, 121.6 (C=C^{im}), 106.4, 105.9 (C$^{4-4}$), 70.5 (CH^a), 66.3 (CH^b), 33.5

(^{im}N-CH$_3$), 12.9, 12.7 (Me$^{3,3'}$), 9.9, 9.6 (Me$^{5-5'}$), 13.5 (Zn-CH$_2$CH$_3$), 13.2 [Zn-(CH$_2$CH$_3$)$_2$], 4.1 (Zn-

CH$_2$CH$_3$), −2.7 [Zn-(CH$_2$CH$_3$)$_2$].

Typical Polymerization Procedures

Polymerizations of *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 a glovebox with

the required amount of LA and initiator, separately, and then attached to the vacuum line. The initiator

and LA were dissolved in the appropriate amount of tetrahydrofuran and temperature equilibration

was ensured in both Schlenk flasks by stirring the solutions for 15 min in a 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 acetic acid in water (0.35 M). Polymers were

precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo

to constant weight.

Typical Kinetic Procedure

A solution of catalyst in tetrahydrofuran (1.25 mL) was added to a solution of monomer (10 mL) in

the same solvent to give [*rac*-LA]$_0$ = 0.80 M. The initial monomer/catalyst ratio was [*rac*-

LA]$_0$/[catalyst]$_0$ = 100 and the initial [catalyst]$_0$ = 8 mM was adjusted to 20 mM. The resulting mixture

was stirred at 20 ºC 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 for Complexes 4 and 5

Suitable crystals of **4** and **5** were grown from a toluene/pentane mixture. Intensity data were collected at 240 K on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromated MoKα radiation source (λ = 0.71073 Å). Data were integrated using SAINT[31] and an absorption correction was performed with the program SADABS.[32] The structures were solved by direct methods using the WINGX package[33] and refined by full-matrix least-squares methods based on F^2. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Conflict of interest

The authors declare no competing financial interests.

†Electronic supplementary information (ESI) available: Details of the ring opening polymerization of *rac*-lactide and crystal data and structure refinement for **4** and **5**. CCDC 1562872-1562873.

References

(1)   M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486-494.

(2)   (*a*) P. Van Wouwe, M. Dusselier, E. Vanleeuw and B. Sels, *ChemSusChem*, 2016, **9**, 907-921; (*b*) J. A. Galbis, M. d. G. García-Martín, M. V. de Paz and E. Galbis, *Chem. Rev.*, 2016, **116**, 1600-1636; (*c*) S. M. Guillaume, E. Kirillov, Y. Sarazin and J.-F. Carpentier, *Chem. - Eur. J.*, 2015, **21**, 7988-8003; (*d*) D. J. A. Cameron and M. P. Shaver, *Chem. Soc. Rev.*, 2011, **40**, 1761-

1776; (*e*) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2010, **43**, 2093-2107.

(3)   (*a*) A. Jiménez, M. Peltzer and R. Ruseckaite, *Poly(lactic acid) Science and Technology : Processing, Properties, Additives and Applications*, RSC Polymer Chemistry Series, 2014; (*b*) R. Auras, L-T. Lim, S.E.M. Selke, H. Tsuji *Poly(lactic acid) synthesis, structures, properties, processing, and applications*, John-Wiley & Sons, Inc. Hoboken, New Jersey, USA, 2010; (*c*) P. Dubois, O. Coulembier and J.-M. Raquez, *Handbook of ring-opening polymerization*, Wiley-VCH, Weinheim, 2009; (*d*) M. H. Chisholm and Z. Zhou, in *Stereoselective polymerization with single-site catalysts*, eds. L. S. Baugh and J. A. M. Canich, CRC Press, Taylor & Francis, Boca Raton, Florida, 2008, ch. 25, pp. 645-660.

(4)   A. P. Pêgo, B. Siebum, M. J. A. Van Luyn, X. J. Gallego y Van Seijen, A. A. Poot, D. W. Grijpma and J. Feijen, *Tissue Eng.*, 2003, **9**, 981-994.

(5)   M. Penco, R. Donetti, R. Mendichi and P. Ferruti, *Macromol. Chem. Phys.*, 1998, **199**, 1737-1745.

(6)   (*a*) S. Inkinen, M. Hakkarainen, A.-C. Albertsson and A. Södergård, *Biomacromolecules*, 2011, **12**, 523-532; (*b*) D. J. Darensbourg, W. Choi and C. P. Richers, *Macromolecules*, 2007, **40**, 3521-3523.

(7)   P. Gruber and M. O'Brien, in *Biopolymers in 10 Volumes, Volume 4, Polyesters III, Applications and Commercial Products*, eds. Y. Doi and A. Steinbuchel, Weinheim: Wiley-VCH, 2002:235–249.

(8)   (*a*) M. Carus and F. Aeschelmann, *Bio-based Building Blocks and Polymers –Global Capacities and Trends 2016 – 2021*, nova-Institute, 2017; (*b*) http://www.european-bioplastics.org/market/, (accessed 31/05/2017, 2017).

(9)   (*a*) G. Parkin, *Chem. Commun.*, 2000, 1971-1985; (*b*) C. F. Mills, *Zinc in human biology*, Springer-Verlag, New York, 1989.

(10)   (*a*) J. A. Cowan, *The Biological Chemistry of Magnesium*, Wiley-VCH, New York, 1995; (*b*) N. A. Campbell, *Biology, 3rd ed.*, Benjamin/Cummings Publishing Company, Redwood City, CA, 1993.

(11)   (*a*) M. J. Berridge, *The Journal of Physiology*, 1997, **499**, 291-306; (*b*) R. P. Rubin, G. B. Weiss and J. W. J. Putney, *Calcium in Biological Systems*, Plenum Press, New York, 1985.

(12)   (*a*) Y. Yang, H. Wang and H. Ma, *Inorg. Chem.*, 2015, **54**, 5839-5854; (*b*) C. Romain and C. K. Williams, in *Green Polymer Chemistry: Biobased Materials and Biocatalysis*, American Chemical Society, 2015, vol. 1192, ch. 9, pp. 135-146; (*c*) M. J. L. Tschan, J. Guo, S. K. Raman, E. Brule, T. Roisnel, M.-N. Rager, R. Legay, G. Durieux, B. Rigaud and C. M. Thomas, *Dalton Trans.*, 2014, **43**, 4550-4564; (*d*) X.-F. Yu, C. Zhang and Z.-X. Wang, *Organometallics*, 2013, **32**, 3262-3268; (*e*) Y. Wang, W. Zhao, D. Liu, S. Li, X. Liu, D. Cui and X. Chen, *Organometallics*, 2012, **31**, 4182-4190; (*f*) E. Piedra-Arroni, P. Brignou, A. Amgoune, S. M. Guillaume, J.-F. Carpentier and D. Bourissou, *Chem. Commun.*, 2011, **47**, 9828-9830; (*g*) M. H. Chisholm, *Pure Appl. Chem.*, 2010, **82**, 15; (*h*) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba and Ana M. Rodríguez, *Eur. J. Inorg. Chem.*, 2004, 260-266; (*i*) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **125**, 11350-11359; (*j*) M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583-11584.

(13)   (*a*) D. J. Darensbourg and O. Karroonnirun, *Inorg. Chem.*, 2010, **49**, 2360-2371; (*b*) F. Drouin, P. O. Oguadinma, T. J. J. Whitehorne, R. E. Prud'homme and F. Schaper, *Organometallics*, 2010, **29**, 2139-2147.

(14)   (*a*) S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689-692; (*b*) H. Wang and H. Ma, *Chem. Commun.*, 2013, **49**, 8686-8688.

(15)   A. Otero, J. Fernández-Baeza, A. Lara-Sánchez and L. F. Sánchez-Barba, *Coord. Chem. Rev.*, 2013, **257**, 1806-1868.

(16)   A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, J. Tejeda, M. Honrado, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Organometallics*, 2012, **31**, 4191-4202.

(17)   M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez, J. Martínez-Ferrer, S. Sobrino and A. M. Rodríguez, *Organometallics*, 2015, **34**, 3196-3208.

(18)   M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Eur. J. Inorg. Chem.*, 2016, 2562-2572.

(19)   M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Dalton Trans.*, 2014, **43**, 17090-17100.

(20)   M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Organometallics*, 2014, **33**, 1859-1866.

(21)   (*a*) M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, *Organometallics*, 2016, **35**, 189-197; (*b*) J. Martinez, J. A. Castro-Osma, A. Lara-Sánchez, A. Otero, J. Fernández-Baeza, J. Tejeda, L. F. Sánchez-Barba and A. Rodríguez-Dieguez, *Polym. Chem.*, 2016, **7**, 6475-6484.

(22)   (*a*) A. Otero, J. Fernández-Baeza, J. Tejeda, A. Lara-Sánchez, M. Sánchez-Molina, S. Franco, I. López-Solera, A. M. Rodríguez, L. F. Sánchez-Barba, S. Morante-Zarcero and A. Garcés, *Inorg. Chem.*, 2009, **48**, 5540-5554; (*b*) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. F. Sánchez-Barba, M. Sánchez-Molina, S. Franco, M. I. López-Solera and A. M. Rodríguez, *Inorg. Chem.*, 2007, **46**, 8475-8477.

(23)   (*a*) F. Isnard, M. Lamberti, L. Lettieri, I. D'Auria, K. Press, R. Troiano and M. Mazzeo, *Dalton Trans.*, 2016, **45**, 16001-16010; (*b*) A. Thevenon, C. Romain, M. S. Bennington, A. J. P. White, H. J. Davidson, S. Brooker and C. K. Williams, *Angew. Chem., Int. Ed.*, 2016, **55**, 8680-8685; (*c*) H.-C. Tseng, H.-Y. Chen, Y.-T. Huang, W.-Y. Lu, Y.-L. Chang, M. Y. Chiang, Y.-C. Lai and H.-Y. Chen, *Inorg. Chem.*, 2016, **55**, 1642-1650; (*d*) L. Chen, W. Li, D. Yuan, Y. Zhang, Q. Shen and Y. Yao, *Inorg. Chem.*, 2015, **54**, 4699-4708.

(24)   A. D. Schofield, M. L. Barros, M. G. Cushion, A. D. Schwarz and P. Mountford, *Dalton Trans.*, 2009, 85-96.

(25)   B. Gao, R. Duan, X. Pang, X. Li, Z. Qu, H. Shao, X. Wang and X. Chen, *Dalton Trans.*, 2013, **42**, 16334-16342.

(26)   Z. Mou, B. Liu, M. Wang, H. Xie, P. Li, L. Li, S. Li and D. Cui, *Chem. Commun.*, 2014, **50**, 11411-11414.

(27)   (*a*) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2006, **25**, 1012-1020; (*b*) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 5329-5334.

(28)   (*a*) J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.*, 1997, **18**, 325-333; (*b*) I. Barakat, P. Dubois, R. Jérôme and P. Teyssié, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 505-514.

(29)   (*a*) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2005, **44**, 8004-8010; (*b*) C.-X. Cai, A. Amgoune, C. W. Lehmann and J.-F. Carpentier, *Chem. Commun.*, 2004, 330-331.

(30)   S. Juliá, P. Sala, J. Del Mazo, M. Sancho, C. Ochoa, J. Elguero, J.-P. Fayet and M.-C. Vertut, *J. Heterocycl. Chem.*, 1982, **19**, 1141-1145.

(31)   SAINT v8.37, Bruker-AXS (2016), APEX3 v2016.1.0. Madison, Wisconsin, USA.

(32)   SADABS, Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D.. *J. Appl. Crystallogr.* (2015) **48**, 3.

(33)   L. J. Farrugia, J. Appl. Cryst., (2012), 45, 849 (b). G. M. Sheldrick, SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.

GRAPHICAL TABLE OF CONTENTS ENTRY

Mono- and Binuclear Chiral N,N,O-Scorpionate Zinc Alkyls as Efficient Initiators for the ROP of *rac*-Lactide

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The new chiral bis(pyrazol-1-yl)methane-based N,N,O-donor scorpionate ligands bpzampeH, bpzaepeH and bpzimeH react with $[ZnR_2]$ in 1:1 and 1:2 stoichiometries to yield the mononuclear monoalkyls $[Zn(R)(\kappa^3\text{-NNO})]$ and the binuclear trisalkyls $[Zn(R)(\kappa^2\text{-NN}\mu\text{-O})Zn(R)_2]$, respectively. The mononuclear and binuclear alkyl-containing zinc complexes act as effective single-component living initiators for the well-controlled ROP of *rac*-LA in only very few hours at 20 ºC, with the binuclear species showing higher activity, suggesting a cooperative effect of the two remote metals. Propagations follow a pseudo-first-order dependence on monomer and catalyst concentration. More importantly, the more sterically demanding mononuclear alkyls moderately promote the formation heterotactic poly(*rac*-lactide)s, with P_s values up to 0.68.

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