New Racemic and Single Enantiopure Hybrid Scorpionate/Cyclopentadienyl Magnesium and Zinc Initiators for the Stereoselective ROP of Lactides.

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ABSTRACT

The preparation of the first racemic bis(pyrazol-1-yl)methane-based NNCp-donor hybrid scorpionate/cyclopentadienyl magnesium and zinc complexes [Mg(R)(κ^2-η^5-NNCp)] (**1–6**) [NNCp = bpztcp, R = Me **1**, Et **2**, CH_2SiMe_3 **3**; bpzpcp, R = Me **4**, Et **5**, CH_2SiMe_3 **6**] and [Zn(R)(κ^2-η^1-NNCp)] (**7–12**) [NNCp = bpztcp, R = Me **7**, Et **8**, CH_2SiMe_3 **9**; bpzpcp, R = Me **10**, Et **11**, CH_2SiMe_3 **12**] has been carried out by the reaction of the corresponding racemic NNCp-H donor scorpionate pro-ligands with Grignard reagents RMgCl, after deprotonation with Bu^nLi, or directly with ZnR_2. The resulting alkyl magnesium complexes (**1–6**) have been employed in a protonolysis reaction with 2,6-dimethylphenol to yield the aryloxide magnesium complexes [Mg(OAr)(κ^2-η^5-NNCp)] (**13** and **14**) [NNCp = bpztcp **13**, bpzpcp **14**]. Subsequently, the enantiopure scorpionate pro-ligand (*R*,*R*)-bpmycpH (**16a**) {bpmycpH = 1-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*R*)-2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadiene} and (*R*,*R*)-bpmycp'H (**16b**) {bpmycp'H = 2-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*R*)-2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadiene} were obtained as a mixture of two scorpionate/cyclopentadiene regioisomers, both enantiopure compounds, with an excellent diastereomeric excess (>99% d.e.) in a one-pot process with the fulvene (1*R*)-(–)-myrtenal (**15**) as a chiral substrate to control the stereochemistry of the newly created asymmetric center. In a similar manner, this new enantiopure heteroscorpionate pro-ligand reacted with RMgCl (after addition of ^nBuLi) or with ZnR_2 to give the single enantiopure complexes [Mg(R)(κ^2-η^5-*R*,*S*-bpmycp)] (**17–19**) (R = Me **17**, Et **18**, CH_2SiMe_3 **19**) {*R*,*S*-bpmycp = 2-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*S*)-2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadienyl} and [Zn(R)(κ^2-η^1-*R*,*S*-bpmycp)] (**20–22**) (R = Me **20**, Et **21**, CH_2SiMe_3 **22**). The structures of these complexes were elucidated by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and the X-ray crystal structures of **2**, **3**, **7** and **21** were also established.

Interestingly, these racemic and single enantiopure alkyl- and aryloxide-containing magnesium and zinc hybrid scorpionate/cyclopentadienyl complexes **1–3**, **5–9**, **11–14**, **19** and **21** can act as single-component initiators for the ring-opening polymerization of *rac*-lactide under mild conditions. The polymerizations are living, as evidenced by the narrow polydispersities (M_w/M_n = 1.08) of the isolated polymers and the linear nature of the number average molecular weight versus conversion plot. More importantly, microstructural analysis of poly(*rac*-lactide)s revealed that, whereas the myrtenal substituent on the single enantiomerically pure initiator **21** exerts an appreciable influence on the degree of stereoselectivity to produce isotactic-enriched poly(lactide)s with a P_i value up to 0.77, the racemic mixtures of initiators impart more discrete levels of heteroselectivity in the production of PLAs, with a P_s value of 0.72.

INTRODUCTION

In recent years our research group[1] has made significant contributions in the preparation of efficient catalysts for the well-controlled ring-opening polymerization (ROP) of cyclic esters such as lactide, an inexpensive and annually renewable natural feedstock.[2] The biocompatible nature and the non-toxicity to living tissue of the bioassimilable polylactides (PLAs)[3,4] have attracted our attention to the use of biocompatible metals[5] for the design of catalysts bearing heteroscorpionte ligands derived from bis(pyrazol-1-yl)methane moieties.[6] Furthermore, a chiral version of this class of initiators with high enantiopurities has also been utilized in different catalytic chemistry.[1,7] In this context, whereas a large number of complexes (*i.e.*, with metals of groups 2, 12, 3, lanthanides, 4, 6, 8, 9 and 13)[1] containing [NNX] (X = N, O, S)-heteroscorpionate ligands have been prepared and employed as catalysts in the processes mentioned above, the [NNCp]-hybrid scorpionate/cyclopentadienyl compounds have been less widely studied. In addition, this type of compounds was unknown until we reported the first hybrid scorpionate/cyclopentadienyl ligand,[8,9] although related cyclopentadienyl/scorpionate hybrid ligands

derived from the hydrobis(3,5-dimethylpyrazol-1-yl)borate moiety had been reported previously.[10] In this sense, our group has actively contributed to the preparation of new magnesium,[11a] zinc,[11a] scandium,[11b,12] yttrium[11b,12] and lutetium[13] derivatives with this class of ligand. Many of these complexes have been employed as interesting initiators in the ring-opening polymerization of cyclic esters,[11] in the polymerization of styrene,[12] or in the hydroamination of aminoalkenes.[13] More recently, we reported the preparation of the first single enantiopure hybrid scorpionate/cyclopentadiene pro-ligand[14] through the highly diastereoselective nucleophilic addition of a lithium bis(3,5-dimethylpyrazol-1-yl)methanide derivative to a new enantiopure fulvene, which bears a chiral substrate to control the stereochemistry of the newly created asymmetric center. In addition, this ligand proved to be an excellent reagent to introduce chirality into metal complexes and a new enantiomerically pure alkyl zinc complex was prepared,[14] which represented the first such complex that was capable of producing isotactic-enriched poly(lactide)s ($P_i = 0.77$) from *rac*-LA.[15]

As a continuation of the work outlined above, we report here a full description of the preparation of families of magnesium and zinc metal complexes bearing both racemic and single enantiopure hybrid scorpionate/cyclopentadienyl ligands, their different structural arrangements, reactivity, and catalytic behavior as single-component initiators for the efficient and stereoselective ROP of *rac*-lactide in the production of heterotactic- and isotactic-enriched polylactides.

RESULTS AND DISCUSSION

Synthesis of the racemic compounds

Deprotonation with ^{n}BuLi at the cyclopentadiene group of the hybrid scorpionate/cyclopentadiene ligands bpztcpH[9] and bpzpcpH,[9] which were isolated as mixtures of two regioisomers, [bpztcpH = 1-

[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene and 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene] and [bpzpcpH = 1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethyl]-1,3-cyclopentadiene and 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethyl]-1,3-cyclopentadiene], followed by addition of commercially available Grignard reagents RMgCl in THF in a 1:1 molar ratio afforded, after the appropriate work-up, the mononuclear alkyl magnesium complexes [Mg(R)(κ^2-η^5-NNCp)] (**1–6**) [NNCp = bpztcp, R = Me **1**, Et **2**, CH_2SiMe_3 **3**; bpzpcp, R = Me **4**, Et **5**, CH_2SiMe_3 **6**]. These complexes were isolated as pale yellow solids in good yields (ca. 90%) (see Scheme 1a). Alternatively, reaction of the bpztcpH or bpzpcpH pro-ligands with ZnR_2 (1 equiv *vs* Zn) in toluene under reflux cleanly afforded the corresponding zinc complexes [Zn(R)(κ^2-η^1-NNCp)] (**7–12**) [NNCp = bpztcp, R = Me **7**, Et **8**, CH_2SiMe_3 **9**; bpzpcp, R = Me **10**, Et **11**, CH_2SiMe_3 **12**] in very good yield (*ca*. 90%) as white solids (see Scheme 1b). The reactivity of complexes **1–12** was explored and the alkyl magnesium complexes **1–6** were employed in a protonolysis reaction with 2,6-dimethyphenol in a 1:1 molar ratio to yield the aryloxide magnesium complexes [Mg(OAr)(κ^2-η^5-NNCp)] **13** and **14** [NNCp = bpztcp **13**, bpzpcp **14**] in *ca*. 85% isolated yield (see Scheme 1a). When these reactions were similarly carried out with the zinc complexes **7–12** a complex mixture of products was obtained and the appropriate aryloxide-containing complex could not be isolated. Complexes **1–14** constitute the first examples of magnesium and zinc metal complexes bearing a chiral hybrid scorpionate/cyclopentadienyl ligand.

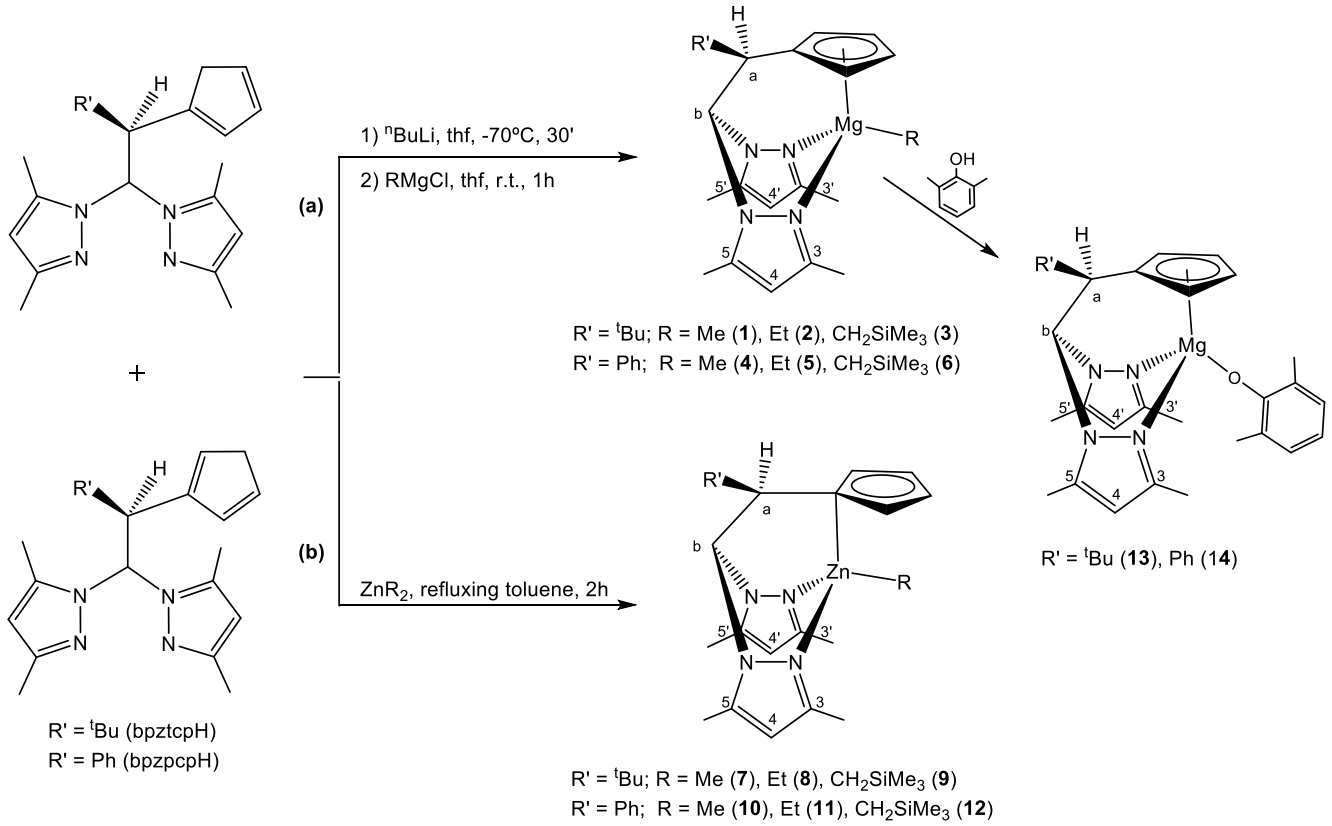
The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1–14** exhibit two distinct sets of pyrazole resonances, indicating the existence of two types of pyrazole ring. Furthermore, the ^{1}H NMR spectra contain signals due to the moiety bound at the methylene bridge (^{t}Bu or Ph) and the alkyl or aryloxide group in compounds **1–12** and **13** and **14**, respectively. The pattern corresponding to the cyclopentadienyl fragment shows four multiplets for all complexes, but in the zinc compounds these signals appear at

lower field. This observation is consistent with a η^1-Cp coordination mode for the cyclopentadienyl group.[11a] A tetrahedral environment can be proposed for the metal atom in all complexes, in which the two pyrazole rings are located in *cis* and *trans* positions with respect to the *tert*-butyl and *para*-tolyl group (see Scheme 1). The phase-sensitive ^{1}H NOESY-1D spectra were 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 **1–14** 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 ^{1}H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers.

In addition, X-ray diffraction studies on **2**, **3×0.5C$_7$H$_8$** and **7** were carried out and the ORTEP diagrams are presented in Figures 1, 2 and 3, respectively. The most representative bond lengths and angles are presented in Table 1 and the crystallographic details are reported in Table S3 in the Supplementary Information (SI). In complex **3** there are two molecules in the asymmetric unit that only differ in the orientation of the $SiMe_3$ group and only one of these will be discussed here. X-ray diffraction studies confirmed that the presence in solution of the corresponding two enantiomers for these compounds (*R* + *S*) is maintained in the solid-state. All compounds have a monomeric structure in which the metal centers have a distorted tetrahedral geometry. In this arrangement the pyrazolic nitrogens N(1) and N(3) occupy two positions and the alkyl group and the cyclopentadienyl fragment the other two positions. The solid-state structures of **2** and **3×0.5C$_7$H$_8$** reveal that the C_5H_4 fragment is coordinated in a pentahapto fashion to the magnesium atom, a situation that has been previously observed in several other complexes[8,9,11-13] synthesized in our group with this type of hybrid ligand. Delocalization is also evident in the C_5H_4 ring, with the C–C bond lengths ranging on average from 1.387(4) Å to 1.417(3) Å for derivative **2** and from 1.398(5) Å to 1.413(2) Å for derivative **3** (Table 1). The C_5H_4 ring is

unsymmetrically bonded to the Mg atom, with Mg–C bond lengths ranging from 2.396(3) to 2.571(3) Å for **2** and from 2.429(1) to 2.523(1) Å for **3** (Table 1). These distances are consistent with those in other functionalized cyclopentadienylmagnesium complexes[16] and they are comparable to those previously observed in the magnesium[11a] and scandium and yttrium derivatives.[11b,12] The most notable feature in the X-ray molecular structure of complex **7** is the peripheral $\eta^1(\pi)$ coordination mode of the cyclopentadienyl ring. The difference (Δd) between the $C_{\alpha\beta}$ and $C_{\beta\beta}$ bonds (0.018 and 0.014 Å) and the distances between C_α and the zinc-bound carbon atom C(13) are somewhat smaller [(C(13)–C(14) 1.424(5) Å; C(14)–C(15) 1.373(5) Å] than expected for a single C–C bond, thus suggesting significant π-electron delocalization. These data, as well as the angle between the Zn–C bond and the plane of the cyclopentadienyl ring (91.9º), are in agreement with similar results for zinc complexes synthesized in our research group[11a] and also for zincocenes in which one of the two cyclopentadienyl moieties is in a similar $\eta^1(\pi)$-coordination mode.[17] Additionally, the Zn(1)–C(13) bond length of 2.191(3) Å is consistent with that previously observed in zincocenes with parallel [$\eta^5/\eta^1(\pi)$] and nonparallel [$\eta^5/\eta^1(\sigma)$] cyclopentadienyl rings.[17] The distances between Zn(1) and the carbon atoms C(14) [2.520(3) Å], C(15) [3.142(5) Å], C(16) [3.272(5) Å] and C(17) [2.773(4) Å] can be considered as nonbonding.[11a,17] To emphasize the coordination through C(13) to de Zn center in this complex, although it can not rule out an alternative coordination through C(14) in complexes (**10**-**12**), where R' = Ph, probably for steric reasons, as it was found in complex **21** (see below) or other related compounds.[(11a)]

Scheme 1. Synthesis of NNCp-scorpionate alkyl or aryloxide magnesium or zinc complexes (**1**–**14**).



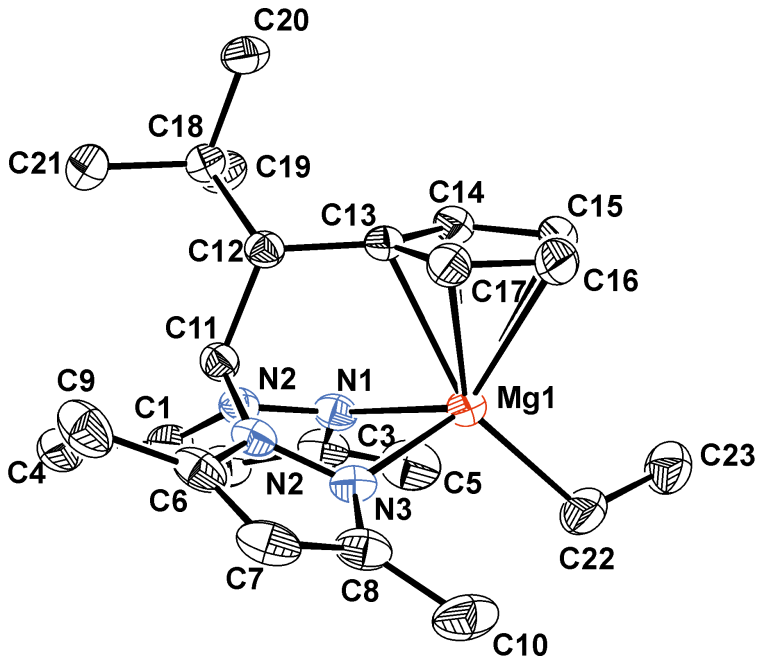


Figure 1. ORTEP view of the S enantiomer of the complex [Mg(Et)(κ^2-η^5-bpztcp)] (**2**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

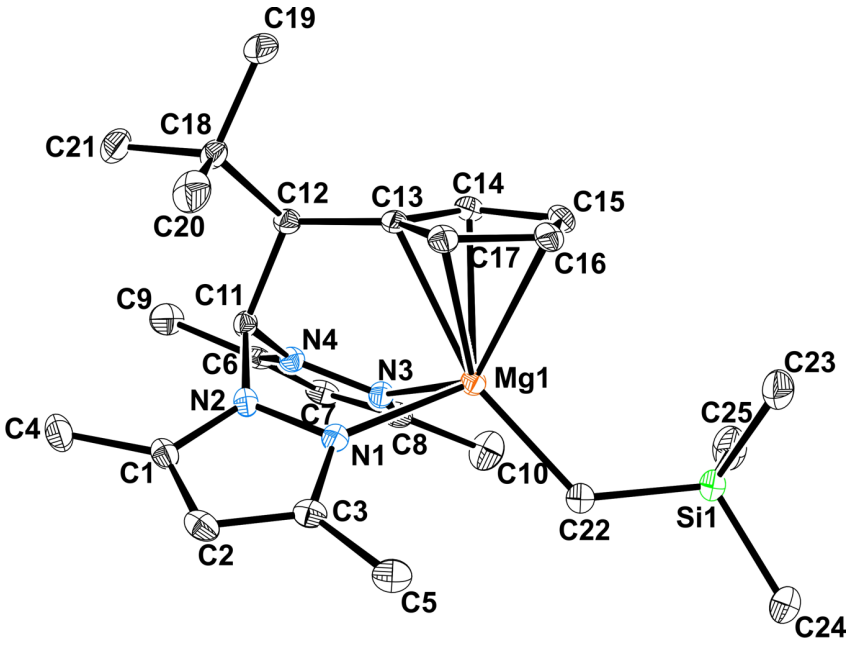


Figure 2. ORTEP view of the R enantiomer of the complex [Mg(CH_2SiMe_3)(κ^2-η^5-bpztcp)] (**3**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

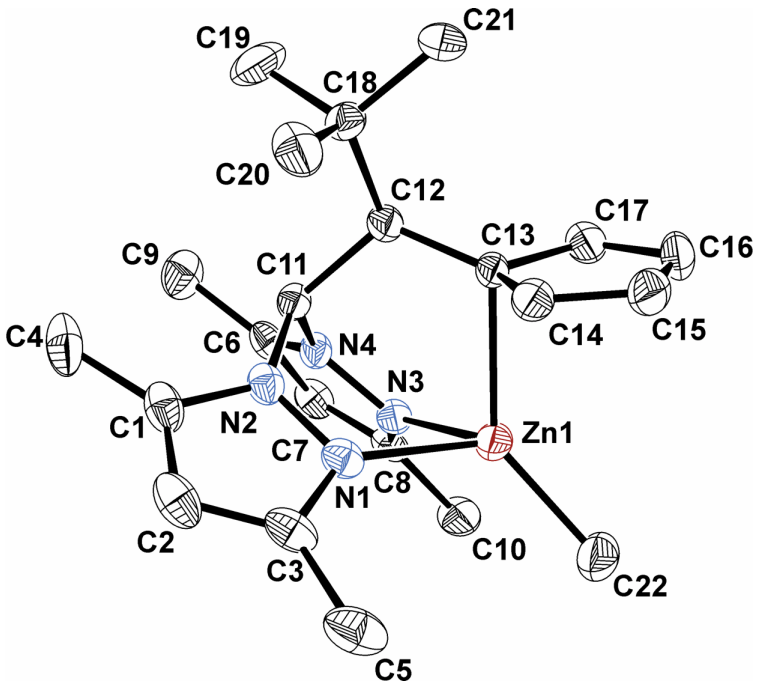


Figure 3. ORTEP view of the R enantiomer of the complex [Zn(Me)(κ^2-η^1(π)-bpztcp)] (**7**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

Table 1. Selected geometrical parameters from the X-ray studies of compounds **2**, **3×0.5C_7H_8**, **7** and **21**. Distances in Å, angles in degrees.

2		**3×0.5C_7H_8**				**7**		**21**	
		3a		**3b**					
Bond lengths									
Mg(1)–N(1)	2.189(2)	Mg(1)–N(1)	2.205(1)	Mg(2)–N(5)	2.199(1)	Zn(1)–N(1)	2.142(3)	Zn(1)–N(1)	2.136(5)
Mg(1)–N(3)	2.180(2)	Mg(1)–N(3)	2.198(1)	Mg(2)–N(7)	2.167(1)	Zn(1)–N(3)	2.169(3)	Zn(1)–N(3)	2.086(6)
Mg(1)–C(22)	2.113(3)	Mg(1)–C(22)	2.132(2)	Mg(2)–C(52)	2.139(2)	Zn(1)–C(13)	2.191(3)	Zn(1)–C(14)	2.137(6)
Mg(1)–C(13)	2.432(3)	Mg(1)–C(13)	2.429(1)	Mg(2)–C(43)	2.458(2)	Zn(1)–C(14)	2.520(3)	Zn(1)–C(13)	2.788(6)
Mg(1)–C(14)	2.396(3)	Mg(1)–C(14)	2.487(1)	Mg(2)–C(44)	2.472(2)	Zn(1)–C(15)	3.142(5)	Zn(1)–C(15)	2.734(8)
Mg(1)–C(15)	2.493(3)	Mg(1)–C(15)	2.523(1)	Mg(2)–C(45)	2.509(2)	Zn(1)–C(16)	3.272(5)	Zn(1)–C(16)	3.407(8)
Mg(1)–C(16)	2.571(3)	Mg(1)–C(16)	2.500(1)	Mg(2)–C(46)	2.508(1)	Zn(1)–C(17)	2.773(4)	Zn(1)–C(17)	3.445(7)
Mg(1)–C(17)	2.540(3)	Mg(1)–C(17)	2.440(2)	Mg(2)–C(47)	2.478(1)	Zn(1)–C(22)	1.953(4)	Zn(1)–C(27)	1.973(6)
C(13)–C(17)	1.407(4)	C(13)–C(14)	1.413(2)	C(43)–C(47)	1.416(2)	C(13)–C(14)	1.424(5)	C(13)–C(17)	1.379(9)
C(13)–C(14)	1.417(3)	C(13)–C(17)	1.424(2)	C(43)–C(44)	1.419(2)	C(13)–C(17)	1.440(5)	C(13)–C(14)	1.431(8)
C(14)–C(15)	1.415(4)	C(14)–C(15)	1.398(2)	C(44)–C(45)	1.402(2)	C(14)–C(15)	1.373(5)	C(14)–C(15)	1.44(1)
C(15)–C(16)	1.387(4)	C(15)–C(16)	1.411(2)	C(45)–C(46)	1.413(2)	C(15)–C(16)	1.386(6)	C(15)–C(16)	1.36(1)
C(16)–C(17)	1.395(4)	C(16)–C(17)	1.405(2)	C(46)–C(47)	1.395(2)	C(16)–C(17)	1.369(5)	C(16)–C(17)	1.36(1)
Angles									
C(22)–Mg(1)–N(3)	111.6(1)	N(3)–Mg(1)–N(1)	80.84(5)	N(7)–Mg(2)–N(5)	81.82(5)	C(22)–Zn(1)–N(1)	123.1(2)	C(27)–Zn(1)–N(3)	119.6(3)
C(22)–Mg(1)–N(1)	111.1(1)	C(22)–Mg(1)–N(3)	112.84(6)	C(52)–Mg(2)–N(7)	108.56(6)	C(22)–Zn(1)–N(3)	116.9(1)	C(27)–Zn(1)–N(1)	116.0(3)
N(3)–Mg(1)–N(1)	82.63(9)	C(22)–Mg(1)–N(1)	107.03(5)	C(52)–Mg(2)–N(5)	107.67(6)	N(1)–Zn(1)–N(3)	83.5(1)	N(3)–Zn(1)–N(1)	86.0(2)
N(2)–C(11)–N(4)	108.8(2)	N(2)–C(11)–N(4)	109(1)	Si(2)–C(52)–Mg(2)	125.27(9)	N(4)–C(11)–N(2)	109.2(3)	N(4)–C(11)–N(2)	110.7(5)
N(2)–C(11)–C(12)	117.2(2)	N(2)–C(11)–C(12)	117.6(1)	N(8)–C(41)–N(6)	109.6(1)	N(4)–C(11)–C(12)	110.9(3)	N(4)–C(11)–C(12)	113.7(5)

N(4)–C(11)–C(12)	111.3(2)	N(4)–C(11)–C(12)	110.6(1)	N(8)–C(41)–C(42)	116.9(1)	N(2)–C(11)–C(12)	116.5(3)	N(2)–C(11)–C(12)	115.5(5)
C(13)–C(12)–C(11)	114.6(2)	C(13)–C(12)–C(11)	114.4(1)	N(6)–C(41)–C(42)	110.8(1)	C(13)–C(12)–C(18)	115.0(3)	C(13)–C(12)–C(18)	115.6(6)
C(13)–C(12)–C(18)	117.0(2)	C(13)–C(12)–C(18)	116.2(1)	C(43)–C(42)–C(48)	117.5(1)	C(13)–C(12)–C(11)	117.7(3)	C(13)–C(12)–C(11)	114.7(5)
C(11)–C(12)–C(18)	113.6(2)	C(11)–C(12)–C(18)	113.6(1)	C(43)–C(42)–C(41)	113.8(1)	C(18)–C(12)–C(11)	112.9(3)	C(18)–C(12)–C(11)	111.6(5)
C(23)–C(22)–Mg(1)	117.9(2)	Si(1)–C(22)–Mg(1)	126.22(8)	C(48)–C(42)–C(41)	113.6(1)			C(28)–C(27)–Zn(1)	120.6(6)

Synthesis of the single enantiopure compounds

Having prepared the new chiral heteroscorpionate compounds as racemic mixtures, it was of interest was to ascertain whether we could obtain a single enantiopure hybrid scorpionate/cyclopentadienyl ligand with this process in one step (addition of an organolithium to a fulvene).[11] This idea led us to focus our attention on (1*R*)-(–)-myrtenal as a possible chiral substrate to control the stereochemistry of a newly created asymmetric center.[18] The first step of our synthetic strategy was to design a one-pot procedure to synthesize a new enantiopure fulvene, containing this substrate, in good yield. It was found that reaction of the commercially available (1*R*)-(–)-myrtenal and cyclopentadiene in the presence of pyrrolidine gave, after the appropriate work up, a new enantiopure fulvene {2-(2,4-cyclopentadienylidenemethyl)-(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-heptene} (**15**), which was obtained as a red oil in good yield (*ca*. 90%) (Scheme 2). The ^{1}H NMR spectrum of **15** shows the corresponding four signals (H^2, H^3, H^4 and H^5) for the asymmetric cyclopentadiene in the fulvene. In addition, the spectrum exhibits five sets of resonances for H^b, H^d, H^e, H^f and *geminal*-H^h and three singlets for H^a and the methyl groups of the bicyclic substituent on the C^g atom. ^{1}H-^{13}C heteronuclear correlation (g-HSQC) experiments allowed us to assign the resonances corresponding to the ^{13}C{^{1}H} NMR spectrum of this compound. Once the new optically active fulvene had been synthesized, we focused our attention on the second step, *i.e.*, the preparation of the single enantiopure scorpionate ligand using the aforementioned methodology based on the asymmetric nucleophilic addition of organolithium reagents to C=C bonds.[19] Thus, a cold (0 ºC) THF solution of lithium bis(3,5-dimethylpyrazol-1-yl)methanide,[20] prepared *in situ* from ^{n}BuLi and bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[21] at –70 ºC, was added dropwise to a THF solution containing 1 equiv. of the new fulvene (**15**). The addition gave rise to a rapid color change from yellow to colorless. The reaction was complete after five minutes and the appropriate work-up gave a 1:1 mixture of two scorpionate/cyclopentadiene regioisomers, both of which were enantiopure compounds, (*R*,*R*)-bpmycpH (**16a**) {bpmycpH = 1-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*R*)-

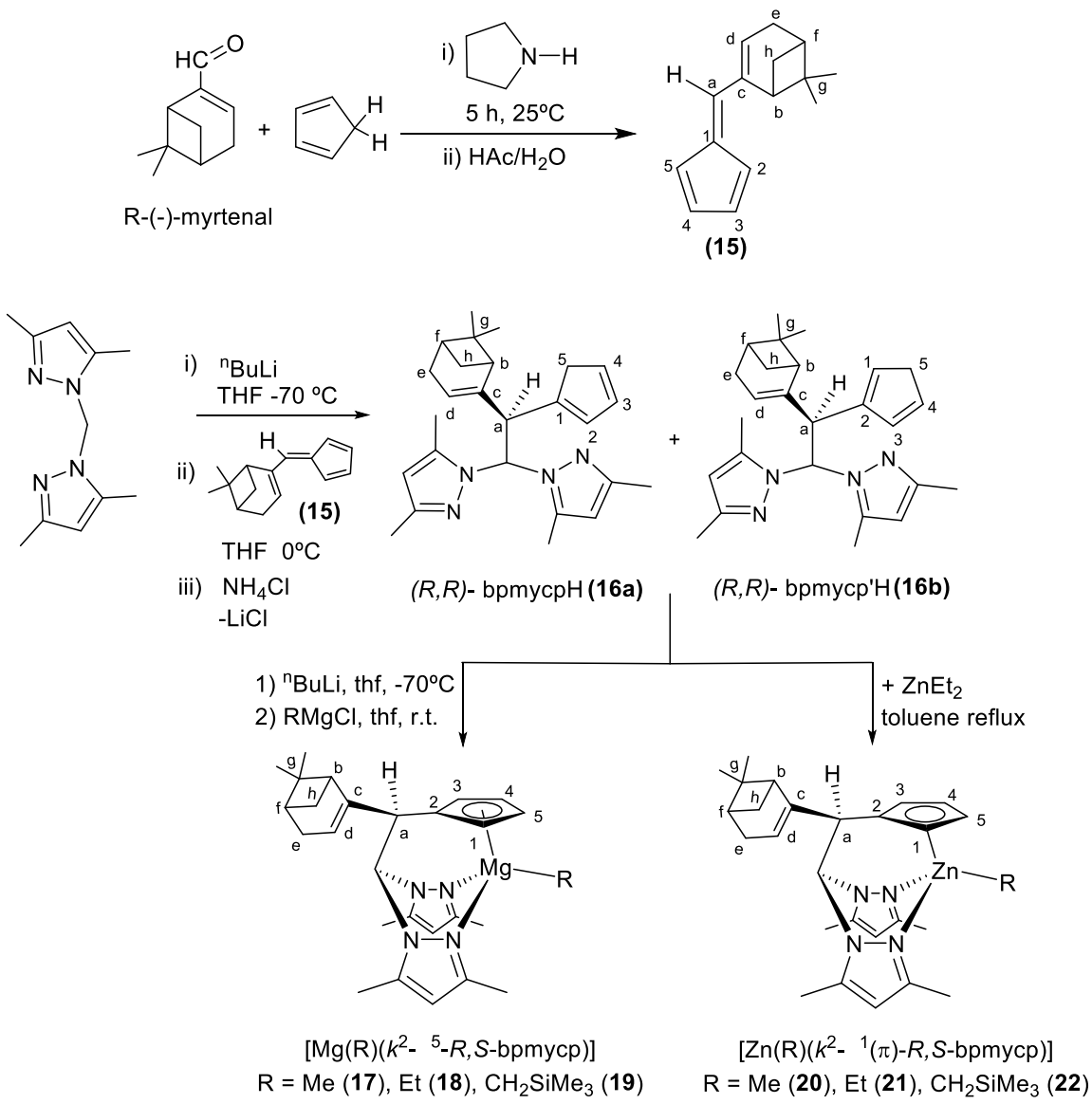
2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadiene} and (*R*,*R*)-bpmycp'H (**16b**) {bpmycp'H = 2-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*R*)-2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadiene} as colorless crystals in 63% yield and with an excellent diastereomeric excess (>99% *d.e.*) (Scheme 2). This procedure constitutes an efficient and highly diastereoselective method to prepare single enantiopure scorpionate ligands in a one-pot process.[18] Initial evidence for the stereochemical route was obtained by X-ray diffraction (see below), which showed that the newly formed chiral center has the *R* configuration.

The diastereoselectivity was assessed by considering the ^{1}H NMR spectrum and integrating the CH^a or Me signals of the bicycle, in the mixture of regioisomers, since the chemical shifts of these protons appear systematically at higher field for the *S* epimer. A diastereomeric ratio denoted as '>99:1' signifies that only the major diastereoisomer was detected. The ^{1}H NMR spectrum of **16** exhibits four singlets for each of the H^4, Me^3 and Me^5 pyrazole protons, indicating the presence of two tautomers because the two pyrazole rings are inequivalent. The spectrum also contains two doublets – one for the CH bridge to two pyrazole rings and one for CH^a. One set of signals for the cyclopentadiene group and the bicycle was observed for each tautomer. In both regioisomers (**16a** and **16b**) the H^5 signal in the ^{1}H NMR spectrum integrates for two protons, meaning that regioisomer **16c**, in which the cyclopentadiene group is bound by C^5 to the bis(pyrazol-1-yl)methane unit, can be ruled out.

The potential utility of this new enantiopure heteroscorpionate/cyclopentadiene pro-ligand was explored as a tridentate ligand in the preparation of single enantiopure magnesium and zinc metal complexes. Deprotonation of the cyclopentadiene group of **16** with Bu^nLi, followed by addition of commercially available Grignard reagents RMgCl in THF in a 1:1 molar ratio afforded, after the appropriate work-up, the single enantiopure mononuclear alkyl magnesium complexes [Mg(R)(κ^2-η^5-*R*,*S*-bpmycp)] (**17**–**19**) (R = Me **17**, Et **18**, CH_2SiMe_3 **19**) {*R*,*S*-bpmycp = 2-{2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(2*S*)-2-[(1*R*)-6,6-[3.1.1]-2-hepten-2-yl]ethyl}cyclopentadienyl}, which were isolated as pale yellow solids in good yield (*ca.* 90%) (see Scheme 2). Alternatively, the deprotonation

reaction with ZnR_2 in a 1:1 molar ratio yielded the single enantiopure zinc complexes [Zn(R)(κ^2-η^1-*R*,*S*-bpmycp)] (**20**–**22**) (R = Me **20**, Et **21**, CH_2SiMe_3 **22**), which were isolated as colorless solids in good yield (90%) (Scheme 2). It should be noted that the coordination of the cyclopentadienyl moiety to the metal center in both types of complexes produces a change in the configurational descriptor of the carbon C^a (*S*) with respect to that in compound **16** (*R*), but the spatial arrangement around this carbon atom is the same in both types of compounds. Complexes **17**–**22** constitute the first examples of metal complexes bearing an enantiopure hybrid scorpionate/cyclopentadienyl ligand.[14]

Scheme 2. Synthesis of single enantiopure compounds (**15**–**22**).



The ^{1}H NMR spectra of complexes **17–22** show two singlets for each of the H^4, Me^3 and Me^5 pyrazole protons, one doublet for each of the methine groups (CH bridge of the pyrazole rings and CH^a), four multiplets for protons H^b, H^d, H^e and H^f and two multiplets for the geminal-H^h bicycle protons. The ^{1}H NOESY-1D experiments allowed the unequivocal assignment of all ^{1}H resonances. Protons of the cyclopentadienyl group in the zinc complexes (**20–22**) showed significant deshielding with respect to the equivalent proton in the magnesium complexes (**17–19**) with η^5-Cp-coordination and this is consistent with a η^1-Cp-coordination, as observed previously in analogous hybrid scorpionate/cyclopentadienyl zinc complexes.[11a] In addition, the presence in solution of only one

enantiomer for complexes **17–22** was confirmed by the addition of a chiral shift reagent, as this addition did not modify the ^{1}H NMR spectra of these compounds. Furthermore, the specific rotations of these compounds were measured by polarimetry (see Experimental Section).

As mentioned above, the absolute configurations of **16–22** were verified by single crystal X-ray diffraction analysis of complex **21** (Figure 4).[14] Selected bond parameters and the crystallographic details are listed in Table 1 and Table S3, respectively, in the SI. The zinc atom has a distorted tetrahedral geometry in which the heteroscorpionate ligand acts in a tridentate fashion and is coordinated by the two nitrogens of the pyrazole rings and one carbon of the cyclopentadienyl group, with the ethyl ligand occupying the fourth site of the tetrahedron. The most notable feature in the X-ray molecular structure of complex **21** is the peripheral $\eta^1(\pi)$ coordination mode of the cyclopentadienyl ring discussed above. The X-ray diffraction studies also confirmed the presence in the solid state of one enantiomer.

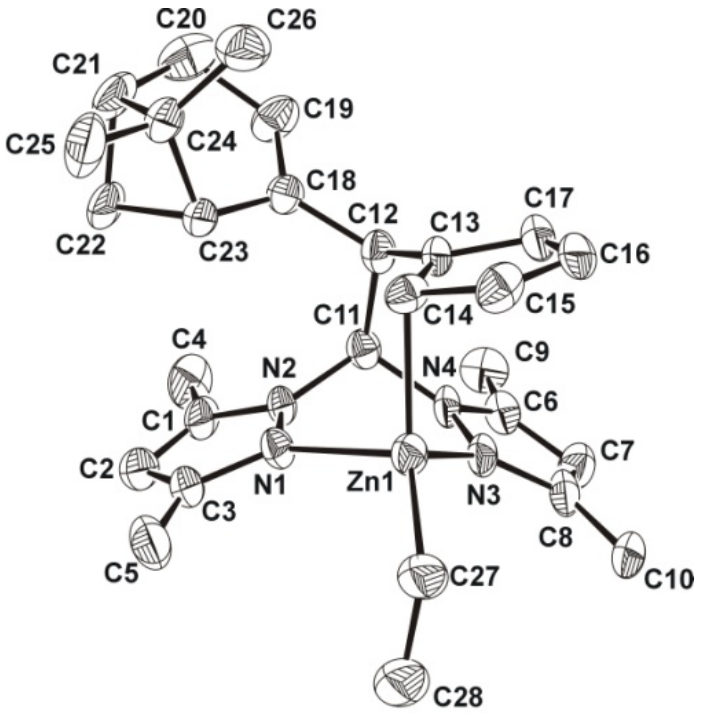


Figure 4. ORTEP diagram of the complex [Zn(Et)(κ^2-η^1-*R*,*S*-bpmycp)] (**21**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

Polymerization Studies

Complexes **1–3**, **5–9**, **11–14**, **19** and **21** were systematically assessed in the ring-opening polymerization of the polar monomer *rac*-lactide (LA) for the production of poly(lactide)s (PLAs). The reactions were carried out in tetrahydrofuran and toluene under mild conditions, 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 [NNCp]- hybrid scorpionate/cyclopentadienyl Mg- and Zn-alkyl complexes and other recently published related heteroscorpionate magnesium[11a,22] and zinc[11a,23]-alkyl,[23b,c,d]-amide[23a,e] and -alkoxide[23b] systems as initiating groups and also with other interesting and efficient systems reported to date.[14,15,24,25] Inspection of the experimental M_n values of the resulting PLAs revealed, as a common trend, that the molecular weights of the polymer samples closely approximated the expected theoretical calculated values for one growing polymer chain per catalyst molecule [M_n(calcd)PLA_{100} = 14 400 g·mol^{-1}]. Size exclusion chromatography (SEC) data for the resulting polyesters show a monomodal weight distribution (see Figure S1 in the SI) with polydispersities ranging from 1.07 to 1.21.

The aforementioned complexes acted as active single-component catalysts for the well-controlled polymerization of *rac*-LA. A variety of polymerization conditions were explored and the results of these experiments are collected in Table 2. The polymerizations were well controlled and gave low-medium molecular weight polymers with low polydispersity indexes. For instance, the racemic magnesium alkyl derivative **3** polymerized 32% of the monomer at 50 ºC after 14.5 hours (entry 4) to yield a low molecular weight polymer with a narrow molecular weight distribution (M_n = 4 900, M_w/M_n = 1.14). Unexpectedly, the racemic zinc counterparts proved to be much more active, in contrast to results previously obtained in our group with analogs zinc[11a,23d,e] versus magnesium[11a,22b,c] alkyls. For instance, after 5 hours 68% of the monomer was converted by the zinc alkyl analog **9** under otherwise identical conditions (entry 14). The characteristics and the molecular weight distributions remained unchanged. A decrease in the reaction temperature to 25 ºC led to a marked

reduction in the productivity (entries 2 and 11) and only traces of polymer were obtained when both metal catalysts were employed. Additionally, when toluene was used as solvent, a dramatic reduction in the catalytic activity was observed for all racemic magnesium and zinc initiators (entries 5, 7 and 13). This change probably occurs due to the complexation of magnesium and zinc ions by the coordinating tetrahydrofuran solvent, which in these cases would enhance the nucleophilicity of the alkyl initiating group and the alkoxide propagating chains. Not surprisingly, the trend in the metal activity observed for the single enantiopure magnesium *versus* zinc complexes, **19** and **21**, respectively, parallels that observed previously for the racemic counterparts **1–3**, **5–9** and **11–14**. More interestingly, the solvent dependence observed for the enantiopure initiators was opposite to that previously described for the related racemic mixtures of initiators, possibly due to the antagonist effect of the tetrahydrofuran coordination to the metal center, in this particular case. Consistently, for **19** and **21** all polymerizations were carried out using toluene as solvent because polymeric materials were not recovered when reactions were performed in tetrahydrofuran, even after several days of reaction time. In addition, it was also found that the nature of the racemic NNCp heteroscorpionate and the leaving alkyl/aryloxide metal substituents (Scheme 1) affects the catalytic activity for both families of metal initiators, with bpztcp > bpzpcp, possibly due to the higher steric hindrance of the latter, and OAr > alkyl, as a result of the electron-withdrawing effect of the oxygen atom in the former.

The high level of control afforded by these initiators in the polymerization of *rac*-lactide is further exemplified by the narrow molecular weight distributions in conjunction with the linear correlation between M_n and percentage conversion ($R^2 = 0.991$) (see Figure S2). These results are characteristic of well-controlled living propagations and the existence of a single type of reaction site, a situation similar to the living behavior previously observed in the hybrid scorpionate/cyclopentadienyl-based alkyl magnesium[11a] analogs for L-lactide. Kinetic studies conducted on the ROP of *rac*-LA with **8** at 50 ºC in tetrahydorfuran established that the reaction order with respect to monomer and catalyst concentration follows a first-order dependence (square correlation coefficients ≥ 0.975) (see Figures

S3, S4 and Table S1 in the SI). In addition, the experimentally obtained pseudo-first-order rate constant, k_{app}, values for initiator **8** are lower than those determined in our group for the recently reported dinuclear single enantiopure bisalkyl/aryloxide mixed ligands complex [$(ZnEt)_2$(*R*,*R*-bpzmm)(μ-OAr)][23b] (Ar = 2,6-$C_6H_3Me_2$) at each [catalyst]$_0$ studied ($k_{app,50°C}$ = 49 ± 3 × 10^{-4} s^{-1} *vs* $k_{app,50°C}$ = 14.3 ± 0.4 × 10^{-4} s^{-1} for **8**, at a [Zn]$_0$ = 20 mM). This difference is probably due to the presence of the aryloxide group in the dinuclear complex,[23b] which is a more suitable mimic of the putative propagating alkoxide species, in addition to the higher steric hindrance of the cyclopentadienyl group on **8**, which permanently delays the coordination of the incoming lactide monomer to the zinc center. However, the data for **8** compare well with those measured in our group under identical conditions for the related racemic monoalkyl [$Zn(CH_2SiMe_3)$(bpzte)]$_2$[23c] ($k_{app,50°C}$ = 8.3 ± 0.3 × 10^{-4} s^{-1}) and the racemic monoamide [$Zn\{N(SiMe_3)_2\}$(bpzte)][23a] ($k_{app,50°C}$ = 13.8 ± 0.2 × 10^{-4} s^{-1}) – in both cases the data relate to the ring-opening of L-LA. Furthermore, low molecular weight materials produced by initiators **8** and **14** were studied by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS)[26] (see Figure S5 and S6 in the SI). This technique provided evidence that the ring-opening of *rac*-LA occurs by the initial addition of the alkyl (for **8**) or the aryloxide (for **14**) fragment to the monomer in the materials produced, with cleavage of the acyl-oxygen bond[27] followed by further monomer additions to the (macro)alcohols.

As a comparison, the new [NNCp]-hybrid scorpionate/cyclopentadienyl Mg and Zn-alkyl/aryloxide complexes proved to be more active for the ROP of *rac*-LA than the previously described related alkyls [Mg(R)(κ^2-η^5-bpzcp)][11a] and [Zn(R){κ^2-η^1(π)-bpzcp}][11a] (Table 2, entries 9 and 17; only traces of product were obtained for both initiators at 50 ºC), 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.

Poly(*rac*-lactide) Microstructure Analysis

Microstructural analysis by homonuclear decoupled ^{1}H NMR spectroscopy of the poly(*rac*-lactide)s revealed that both families of racemic mixtures of magnesium and zinc initiators **1–3**, **5–9** and **11–14** lead to a moderate level of heterotacticity. In this respect, the zinc counterparts reach higher levels, as for catalyst **9**, with $P_s = 0.72$ (Table 2, entry 14, Figure S7 in the SI), possibly through a chain-end control mechanism.[30] In contrast, both families of single enantiopure initiators impart a significant preference for isotactic dyad enchainment, with higher values determined for the zinc analogs once again. In fact, the most selective initiator **21** reached a P_i value of 0.77 (Table 2, entry 23, Figure S8 and Table S2 in the SI), which indicates that the polymer contained an average of 9 units (Ł ≈ 9) of enantiomerically pure L-lactide {Ł = $2/(1 - P_i)$},[31] as determined by the method of Coudane *et al.*[31] This is a remarkable result considering the very scarce number of zinc catalysts bearing chiral auxiliaries that have succeeded in the isoselective ROP of *rac*-LA.[14,15] Additionally, analysis of the tetrads resulting from stereoerrors (*i.e.*, tetrads other than *iii*) of the isotactic PLA produced by **21** indicated that an enantiomorphic site control mechanism[32] is dominant ([*sis*]/[*sii*]/[*iis*]/[*isi*] = 1/1/1/2 ratio, Figure S8 and Table S2 in the SI). This behavior for catalyst **21** is most probably the result of the high homosteric control caused by the single enantiopure hybrid scorpionate/cyclopentadienyl ligand synthesized in this work.

Table 2. Polymerization of *rac*-Lactide Catalyzed by 1–3, 5–9, 11–14, 19 and 21.[a]

entry	initiator	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**	50	14.5	0.12	9	1 300	2 100	1.19	0.63
2	**2**	25	24	traces	-	-	-	-	-
3	**2**	50	14.5	0.38	29	4 200	5 100	1.21	0.59
4	**3**	50	14.5	0.42	32	4 700	4 900	1.14	0.64
5	**3**[g]	50	14.5	0.19	15	2 100	2 800	1.18	0.62
6	**5**	50	14.5	0.23	18	2 600	2 100	1.19	0.65
7	**5**[g]	50	14.5	traces	-	-	-	-	-
8	**6**	50	14.5	0.26	20	2 900	3 300	1.16	0.68
9	**[Mg(CH_2SiMe_3) (κ^2-η^5-bpzcp)]**	90	4	0.82	32	9 200	8 800	1.07	
10	**7**	50	5	1.08	83	12 000	12 800		0.66
11	**8**	25	24	traces	-	-	-	-	-
12	**8**	50	5	1.14	88	12 700	13 100	1.13	0.69
13	**8**[g]	50	5	0.68	52	7 600	7 000	1.14	0.66
14	**9**	50	5	0.88	68	9 800	10 300	1.18	0.72
15	**11**	50	5	0.93	72	10 400	10 800	1.09	0.67
16	**12**	50	5	0.76	59	8 400	9 300	1.10	0.69
17	**[Zn(CH_2SiMe_3) {κ^2-η^1(π)-bpzcp}]**	90	4	traces	-	-	-	-	-
18	**13**	25	24	traces	-	-	-	-	-

19	**13**	50	5	0.72	56	8 000	7 600	1.09	0.68
20	**13**[g]	50	5	0.51	39	5 700	6 000	1.13	0.70
21	**14**	50	5	0.22	17	2 400	2 500	1.08	0.69
22	**19**[g]	50	14.5	0.32	25	3 600	3 100	1.16	0.71[f]
23	**21**[g]	20	15	0.41	32	4 600	4 800	1.08	0.77[f]
24	**21**[g]	50	4	0.61	47	6 800	6 600	1.13	0.73[f]

[a] Polymerization conditions: 90 μmol of catalyst, 20 mL of tetrahydrofuran as solvent, [*rac*-lactide]$_0$/[M]$_0$ = 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[33] 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.[34] [f] The parameter P_i (i = isotactic) is the probability of forming a new *i*-dyad. The P_i and the P_s ~~(s = syndiotactic)~~ values were calculated from the following tetrad probabilities based on enantiomorphic site control statistics[35] in the polymerization of *rac*-lactide: *sis, sii, iis* = $[P_i^2(1-P_i)+P_i(1-P_i)^2]/2$; *iii* = $[P_i^2(1-P_i)^2+P_i^3+(1-P_i)^3]/2$; *isi* = $[P_i(1-P_i)+P_i(1-P_i)]/2$. [g] 25 mL of toluene as solvent.

CONCLUSIONS

In conclusion, we present here a complete study of two families of magnesium and zinc complexes based on our initial results in the search for a single enantiopure hybrid scorpionate/cyclopentadienyl ligand. In this respect, we describe here the first examples of mononuclear magnesium and zinc metal alkyls bearing these racemic NNCp-donor hybrid ligands of the type [Mg(R)(κ^2-η^5-NNCp)] and [Zn(R)(κ^2-η^1-NNCp)], respectively, which were prepared easily. In addition, the efficient preparation of an unprecedented enantiopure scorpionate ligand with an excellent diastereomeric excess (>99% d.e.) in a one-pot process is reported. The potential utility of this ligand as a valuable scaffold was verified through the preparation of new single enantiopure magnesium and zinc complexes. Moreover, whereas the protonolysis reaction of the magnesium monoalkyls with 2,6-dimethyphenol afforded the corresponding aryloxides [Mg(OAr)(κ^2-η^5-NNCp)], complex mixtures of products were obtained in the case of the zinc analogs. Single-crystal X-ray diffraction studies on derivatives **2**, **3**, **7** and **21** confirmed that in the structures the hybrid scorpionate/cyclopentadienyl ligands are arranged in a tridentate fashion with a κ^2-η^5-NNCp and κ^2-η^1-NNCp coordination mode for the magnesium and zinc alkyls, respectively.

Interestingly, the chiral alkyl-/aryloxide-containing magnesium and zinc complexes prepared behave as single-component living initiators for the ROP of *rac*-LA under mild conditions. These reactions afford medium/low molecular weight polymers with narrow molecular weight distributions in a few hours for the zinc-based initiators. The MALDI-ToF mass spectrum suggests that the initiation process is mediated by alkyl/aryloxide transfer to the monomer and inspection of the kinetic parameters showed that propagations present the usual pseudo-first order dependence on monomer and catalyst concentrations. More importantly, the evaluation of the influence of the chiral centers on these new NNCp-donor heteroscorpionates in the stereoselective production of PLAs revealed that, whereas the myrtenal substituent on the enantiomerically pure initiator **21** exerts an appreciable influence to afford

isotactic-enriched poly(lactide)s (P_i = 0.77), the racemic mixtures impart more discrete levels of heteroselectivity (P_s = 0.72).

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 or on a Varian 400/54/ASC spectrometer and are referenced to the residual deuterated solvent. ^{1}H NMR homodecoupled and NOESY-1D spectra were recorded on the same instruments 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 specific rotation $[\alpha]_D^{25}$ was measured at a concentration of 0.1% w/v in toluene at 25 ºC on a JASCO P2000 Polarimeter equipped with a sodium lamp operating at 589 nm with a light path length of 10 cm. Gel Permeation Chromatography (GPC) measurements were performed on a Polymer Laboratories PL size exclusion chromatography-220 instrument equipped with a TSK-GEL G3000H column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 40 ºC 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. Before 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). 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. Reagents RMgCl, anhydrous MeOH, pyrrolidine, anhydrous $ZnCl_2$, $ZnMe_2$, $ZnEt_2$ and $LiCH_2SiMe_3$ were used as purchased (Aldrich). Cyclopentadiene was purchased from Aldrich and cracked prior to use. $Zn(CH_2SiMe_3)_2$ was prepared according to literature procedures.[23d,36] The ligands bpztcpH and bpzpcpH were prepared according to the literature procedure.[9] 2,6-Dimethylphenol was sublimed twice under reduced pressure and stored in a glovebox. *rac*-Lactide was sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Synthesis of [Mg(Me)(κ^2-η^5-bpztcp)] (1). In a 250 mL Schlenk tube, bpztcpH (1.00 g, 2.95 mmol) was dissolved in dry THF (50 mL) and cooled to –70 ºC. Bu^{n}Li (1.6 M in *n*-hexane) (1.84 mL, 2.95 mmol) was added dropwise and the mixture was stirred for 30 min maintaining the temperature at –70 ºC. A solution of MeMgCl (3.0 M in THF) (0.98 mL, 2.95 mmol) was added and the mixture was allowed to warm up to room temperature and stirred for 1 h, after which the solvent was evaporated under reduced pressure and the product was extracted with toluene (50 mL) and filtered. The solvent was evaporated and a sticky yellow solid was obtained. The solid was washed with *n*-hexane (20 mL) to yield compound **1** as a pale yellow solid. Yield 95% (1.05 g, 2.79 mmol). Anal. Calcd for $C_{22}H_{32}MgN_4$: C, 70.12; H, 8.56; N, 14.87. Found: C, 70.15; H, 8.51; N, 14.82. ^{1}H NMR (C_6D_6, 297 K): δ 6.82 (m, 1H, H^{Cp}), 6.71 (m, 1 H, H^{Cp}), 6.30 (bs, 1 H, CH^b), 6.16 (m, 1 H, H^{Cp}), 5.94 (m, 1 H, H^{Cp}), 5.29 (s, 1 H, H^4), 5.26 (s, 1 H, H$^{4'}$), 2.82 (bs, 1 H, CH^a), 2.19 (s, 3 H, Me^3), 2.18 (s, 3 H, Me$^{3'}$), 1.76 (s, 3 H, Me^5), 1.67 (s, 3 H, Me$^{5'}$), 0.96 (s, 9 H, ^{t}Bu), –0.8 (s, 3 H, Mg-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 148.6–137.0 (C$^{3,3',5,5'}$), 112.6, 107.5, 106.7, 105.5, 104.4 (C^{Cp}), 106.2 (C^4), 105.6 (C$^{4'}$), 64.7 (C^b), 59.8 (C^a), 34.8, 28.71 (^{t}Bu), 13.5 (Me^3), 12.5 (Me$^{3'}$), 11.0 (Me^5), 10.2 (Me$^{5'}$), –5.01 (Mg-Me).

Synthesis of [Mg(Et)(κ^2-η^5-bpztcp)] (2). The synthesis of **2** was carried out in an identical manner to **1** using bpztcpH (1.00 g, 2.95 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.84 mL, 2.95 mmol) and EtMgCl (2.00 M in Et_2O) (1.48 mL, 2.95 mmol) to yield complex **2** as pale yellow solid. Yield 92% (1.06 g, 2.71 mmol). Crystals suitable for X-ray diffraction studies were obtained by crystallization from toluene at –26 ºC. Anal. Calcd for $C_{23}H_{34}MgN_4$: C, 70.68; H, 8.77; N, 14.33. Found: C, 70.69; H, 8.73; N, 14.32. ^{1}H NMR (C_6D_6, 297 K): δ 6.83 (m, 1 H, H^{Cp}), 6.72 (m, 1 H, H^{Cp}), 6.29 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.13 (m, 1 H, H^{Cp}), 5.90 (m, 1 H, H^{Cp}), 5.31 (s, 1 H, H^4), 5.27 (s, 1 H, $H^{4'}$), 2.79 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.20 (s, 3 H, Me^3), 2.19 (s, 3 H, $Me^{3'}$), 1.95 (t, 3 H, J_{HH} = 10 Hz, Mg-CH_2-$\underline{CH_3}$), 1.76 (s, 3 H, Me^5), 1.67 (s, 3 H, $Me^{5'}$), 0.95 (s, 9 H, ^{t}Bu), 0.04 (q, 2 H, J_{HH} = 10 Hz, Mg-$\underline{CH_2}$-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 148.6–137.3 ($C^{3,3',5,5'}$), 112.7, 107.5, 106.8, 105.5, 104.3 (C^{Cp}), 106.3 (C^4), 105.8 ($C^{4'}$), 64.7 (C^b), 59.7 (C^a), 34.6, 28.7 (^{t}Bu), 13.5 (Me^3), 13.3 ($Me^{3'}$), 13.2 (Mg-CH_2-$\underline{CH_3}$), 11.2 (Me^5), 10.1 ($Me^{5'}$), 0.5 (Mg-$\underline{CH_2}$-CH_3).

Synthesis of [Mg(CH_2SiMe_3)(κ^2-η^5-bpztcp)] (3). The synthesis of **3** was carried out in an identical manner to **1** using bpztcpH (1.00 g, 2.95 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.84 mL, 2.95 mmol) and Me_3SiCH_2MgCl (1.00 M in Et_2O) (2.95 mL, 2.95 mmol) to yield complex **3** as pale yellow solid. Yield 88% (1.16 g, 2.59 mmol). Crystals suitable for X-ray diffraction studies were obtained by crystallization from toluene at –26 ºC. Anal. Calcd for $C_{25}H_{40}MgN_4Si$: C, 66.87; H, 8.98; N, 12.48. Found: C, 66.90; H, 8.95; N, 12.50. ^{1}H NMR (C_6D_6, 297 K): δ 6.77 (m, 1 H, H^{Cp}), 6.67 (m, 1 H, H^{Cp}), 6.25 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.09 (m, 1 H, H^{Cp}), 5.86 (m, 1 H, H^{Cp}), 5.29 (s, 1 H, H^4), 5.25 (s, 1 H, $H^{4'}$), 2.74 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.18 (s, 3 H, Me^3), 2.17 (s, 3 H, $Me^{3'}$), 1.75 (s, 3 H, Me^5), 1.74 (s, 3 H, $Me^{5'}$), 0.91 (s, 9 H, ^{t}Bu), 0.59 (s, 9 H, Mg-CH_2-Si$\underline{Me_3}$), –1.29 (s, 2 H, Mg-$\underline{CH_2}$-$SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 148.6–137.0 ($C^{3,3',5,5'}$), 112.6, 107.6, 107.4, 105.4, 104.8 (C^{Cp}), 106.4 (C^4), 105.7 ($C^{4'}$), 64.6 (C^b), 59.6 (C^a), 34.7, 28.6 (^{t}Bu), 13.3 ($Me^{3,3'}$), 11.1 (Me^5), 10.2 ($Me^{5'}$), 4.8 (Mg-CH_2-Si$\underline{Me_3}$), –5.2 (Mg-$\underline{CH_2}$-$SiMe_3$).

Synthesis of [Mg(Me)(κ^2-η^5-bpzpcp)] (4). The synthesis of **4** was carried out in an identical manner to **1** using bpzpcpH (1.00 g, 2.78 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.74 mL, 2.78 mmol) and MeMgCl (3.00 M in thf) (0.93 mL, 2.78 mmol) to yield complex **4** as pale yellow solid. Yield 96% (1.06 g, 2.67 mmol). Anal. Calcd for $C_{24}H_{28}MgN_4$: C, 72.64; H, 7.11; N, 14.12. Found: C, 72.68; H, 7.15; N, 14.20. ^{1}H NMR (C_6D_6, 297 K): δ 7.07–6.97 (m, 5 H, Ph), 6.83 (m, 1 H, H^{Cp}), 6.72 (m, 1 H, H^{Cp}), 6.31 (m, 1 H, H^{Cp}), 5.99 (m, 1 H, H^{Cp}), 5.94 (bs, 1 H, CH^b), 5.35 (s, 1 H, H^4), 5.27 (s, 1 H, $H^{4'}$), 4.44 (bs, 1 H, CH^a), 2.25 (s, 3 H, Me^3), 2.24 (s, 3 H, $Me^{3'}$), 1.58 (s, 3 H, Me^5), 1.17 (s, 3 H, $Me^{5'}$), –0.72 (s, 3 H, Mg-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.6–137.4 ($C^{3,3',5,5'}$), 141.2, 128.9, 128.8, 125.2 (C^{Ph}), 111.3, 108.0, 107.3, 105.3, 104.6 (C^{Cp}), 105.9 (C^4), 105.5 ($C^{4'}$), 69.3 (C^b), 55.3 (C^a), 12.7 (Me^3), 12.6 ($Me^{3'}$), 10.0 (Me^5), 9.9 ($Me^{5'}$), –11.9 (Mg-Me).

Synthesis of [Mg(Et)(κ^2-η^5-bpzpcp)] (5). The synthesis of **5** was carried out in an identical manner to **1** using bpzpcpH (1.00 g, 2.78 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.74 mL, 2.78 mmol) and EtMgCl (2.00 M in Et_2O) (1.39 mL, 2.78 mmol) to yield complex **5** as pale yellow solid. Yield 90% (1.03 g, 2.50 mmol). Anal. Calcd for $C_{25}H_{30}MgN_4$: C, 73.09; H, 7.36; N, 13.64. Found: C, 73.10; H, 7.39; N, 13.70. ^{1}H NMR (C_6D_6, 297 K): δ 7.06–6.94 (m, 5 H, Ph), 6.82 (m, 1 H, H^{Cp}), 6.71 (m, 1 H, H^{Cp}), 6.27 (m, 1 H, H^{Cp}), 5.95 (m, 1 H, H^{Cp}), 5.92 (bs, 1 H, CH^b), 5.36 (s, 1 H, H^4), 5.28 (s, 1 H, $H^{4'}$), 4.43 (bs, 1 H, CH^a), 2.26 (s, 3 H, Me^3), 2.25 (s, 3 H, $Me^{3'}$), 1.98 (t, 3 H, J_{HH} = 10 Hz, Mg-CH_2-$\underline{CH_3}$), 1.59 (s, 3 H, Me^5), 1.16 (s, 3 H, $Me^{5'}$), 0.03 (q, 2 H, J_{HH} = 10 Hz, Mg-$\underline{CH_2}$-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 148.9–138.7 ($C^{3,3',5,5'}$), 141.2, 128.8, 128.7, 125.2 (C^{Ph}), 111.3, 107.5, 107.4, 104.8, 104.3 (C^{Cp}), 105.9 (C^4), 105.5 ($C^{4'}$), 69.3 (C^b), 55.3 (C^a), 13.5 (Me^3), 12.5 ($Me^{3'}$), 12.5 (Mg-CH_2-$\underline{CH_3}$), 10.0 (Me^5), 9.8 ($Me^{5'}$), 0.6 (Mg-$\underline{CH_2}$-CH_3).

Synthesis of [Mg(CH_2SiMe_3)(κ^2-η^5-bpzpcp)] (6). The synthesis of **6** was carried out in an identical manner to **1** using bpzpcpH (1.00 g, 2.78 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.74 mL, 2.78 mmol) and Me_3SiCH_2MgCl (1.00 M in Et_2O) (2.78 mL, 2.78 mmol) to yield complex **6** as pale yellow solid. Yield 91% (1.19 g, 2.53 mmol). Anal. Calcd for $C_{27}H_{36}MgN_4Si$: C, 69.15; H, 7.74; N, 11.95. Found: C, 69.13; H, 7.76; N, 11.90. ^{1}H NMR (C_6D_6, 297 K): δ 7.06–6.90 (m, 5 H, Ph), 6.78 (m, 1 H, H^{Cp}), 6.68 (m, 1 H, H^{Cp}), 6.24 (m, 1 H, H^{Cp}), 5.92 (m, 1 H, H^{Cp}), 5.89 (bs, 1 H, CH^b), 5.34 (s, 1 H, H^4), 5.25 (s, 1 H, $H^{4'}$), 4.38 (bs, 1 H, CH^a), 2.24 (s, 6 H, $Me^{3,3'}$), 1.55 (s, 3 H, Me^5), 1.12 (s, 3 H, $Me^{5'}$), 0.63 (s, 9 H, Mg-CH_2-Si$\underline{Me_3}$), –1.19 (s, 2 H, Mg-$\underline{CH_2}$-$SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.5–137.4 ($C^{3,3',5,5'}$), 141.2, 128.9, 128.5, 125.2 (C^{Ph}), 111.4, 108.4, 107.4, 105.6, 104.3 (C^{Cp}), 106.1 (C^4), 105.7 ($C^{4'}$), 69.3 (C^b), 55.2 (C^a), 13.3 (Me^3), 13.2 ($Me^{3'}$), 10.0 (Me^5), 9.9 ($Me^{5'}$), 4.8 (Mg-CH_2-Si$\underline{Me_3}$), –5.0 (Mg-$\underline{CH_2}$-$SiMe_3$).

Synthesis of [Zn(Me)(κ^2-η^1(π)-bpztcp)] (7). In a 250 mL Schlenk tube bpztcpH (1.00 g, 2.95 mmol) was dissolved in dry toluene (50 mL). $ZnMe_2$ (2.00 M in toluene) (1.47 mL, 2.95 mmol) was added and the mixture was heated under reflux for 2 h. The crude reaction mixture was dried under reduced pressure and the resulting sticky pale white solid was washed with cold *n*-hexane to yield compound **7** as a white solid. Yield 90% (1.10 g, 2.65 mmol). Crystals suitable for X-ray diffraction studies were obtained by crystallization from toluene at –26 ºC. Anal. Calcd for $C_{22}H_{32}N_4Zn$: C, 63.23; H, 7.72; N, 13.41. Found: C, 63.23; H, 7.76; N, 13.39. ^{1}H NMR (C_6D_6, 297 K): δ 7.04 (m, 1 H, H^{Cp}), 6.79 (m, 1 H, H^{Cp}), 6.25 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.09 (m, 1 H, H^{Cp}), 5.97 (m, 1 H, H^{Cp}), 5.34 (s, 1 H, H^4), 5.33 (s, 1 H, $H^{4'}$), 2.98 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.10 (s, 3 H, Me^3), 2.04 (s, 3 H, $Me^{3'}$), 1.77 (s, 3 H, Me^5), 1.77 (s, 3 H, $Me^{5'}$), 0.84 (s, 9 H, ^{t}Bu), –0.28 (s, 3 H, Zn-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.2–137.1 ($C^{3,3',5,5'}$), 116.6, 115.4, 111.7, 105.1, 99.1 (C^{Cp}), 106.1 (C^4), 105.0 ($C^{4'}$), 64.7 (C^b), 60.4 (C^a), 34.5, 28.5 (^{t}Bu), 12.6 (Me^3), 12.5 ($Me^{3'}$), 10.8 (Me^5), 9.9 ($Me^{5'}$), –2.0 (Zn-Me).

Synthesis of [Zn(Et)(κ^2-η^1(π)-bpztcp)] (8). The synthesis of **8** was carried out in an identical manner to **7** using bpztcpH (1.00 g, 2.95 mmol) and $ZnEt_2$ (1.00 M in *n*-hexane) (2.95 mL, 2.95 mmol) to yield complex **8** as a white solid. Yield 89% (1.13 g, 2.63 mmol). Anal. Calcd for $C_{23}H_{34}N_4Zn$: C, 63.96; H, 7.93; N, 12.97. Found: C, 64.00; H, 7.96; N, 13.02. ^{1}H NMR (C_6D_6, 297 K): δ 7.09 (m, 1 H, H^{Cp}), 6.80 (m, 1 H, H^{Cp}), 6.21 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.09 (m, 1 H, H^{Cp}), 5.97 (m, 1 H, H^{Cp}), 5.33 (s, 1 H, H^4), 5.32 (s, 1 H, $H^{4'}$), 2.96 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.14 (s, 3 H, Me^3), 2.07 (s, 3 H, $Me^{3'}$), 1.76 (t, 3 H, J_{HH} = 10 Hz, Zn-CH_2-$\underline{CH_3}$), 1.73 (s, 3 H, Me^5), 1.68 (s, 3 H, $Me^{5'}$), 0.82 (s, 9 H, ^{t}Bu), 0.59 (q, 2 H, J_{HH} = 10 Hz, Zn-$\underline{CH_2}$-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.0–137.3 ($C^{3,3',5,5'}$), 116.0, 115.6, 111.4, 105.6, 99.2 (C^{Cp}), 106.2 (C^4), 105.4 ($C^{4'}$), 64.8 (C^b), 60.4 (C^a), 35.4, 28.5 (^{t}Bu), 13.6 (Zn-CH_2-$\underline{CH_3}$), 12.6 (Me^3), 12.5 ($Me^{3'}$), 10.7 (Me^5), 9.9 ($Me^{5'}$), –0.9 (Zn-$\underline{CH_2}$-CH_3).

Synthesis of [Zn(CH_2SiMe_3)(κ^2-η^1(π)-bpztcp)] (9). In a 250 mL Schlenk tube anhydrous $ZnCl_2$ (0.40 g, 2.95 mmol) was dissolved in dry Et_2O (20 mL) and cooled to –70 ºC. A solution of $LiCH_2SiMe_3$ (1.00 M in pentane) (5.90 mL, 5.90 mmol) was added dropwise and the resulting mixture was stirred for 2 h. The resulting suspension was filtered and the colorless solution was added to a previously prepared solution of bpztcpH (1.00 g, 2.95 mmol) in toluene (50 mL). The resulting mixture was heated under reflux and stirred for 2 h. The solvent was evaporated under reduced pressure and the resulting sticky pale red solid was washed with *n*-hexane (15 mL) to yield compound **9** as a white solid. Yield 86% (1.24 g, 2.54 mmol). Anal. Calcd for $C_{25}H_{40}N_4SiZn$: C, 61.27; H, 8.23; N, 11.43. Found: C, 61.24; H, 8.19; N, 11.44. ^{1}H NMR (C_6D_6, 297 K): δ 7.09 (m, 1 H, H^{Cp}), 6.80 (m, 1 H, H^{Cp}), 6.23 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.09 (m, 1 H, H^{Cp}), 5.95 (m, 1 H, H^{Cp}), 5.34 (s, 1 H, H^4), 5.33 (s, 1 H, $H^{4'}$), 2.96 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.10 (s, 3 H, Me^3), 2.06 (s, 3 H, $Me^{3'}$), 1.77 (s, 3 H, Me^5), 1.73 (s, 3 H, $Me^{5'}$), 0.82 (s, 9 H, ^{t}Bu), 0.63 (s, 9 H, Zn-CH_2-Si$\underline{Me_3}$), –0.30 (s, 2 H, Zn-$\underline{CH_2}$-$SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.0–137.2

($C^{3,3',5,5'}$), 115.9, 115.1, 111.5, 105.7, 99.2 (C^{Cp}), 106.5 (C^4), 105.3 ($C^{4'}$), 64.8 (C^b), 60.4 (C^a), 35.5, 28.5 (^{t}Bu), 12.7 (Me^3), 12.5 ($Me^{3'}$), 10.7 (Me^5), 9.9 ($Me^{5'}$), 3.2 (Zn-CH_2-Si$\underline{Me_3}$), –3.8 (Zn-$\underline{CH_2}$-$SiMe_3$).

Synthesis of [Zn(Me)(κ^2-η^1(π)-bpzpcp)] (10). The synthesis of **10** was carried out in an identical manner to **7** using bpzpcpH (1.00 g, 2.79 mmol) and $ZnMe_2$ (2.00 M in toluene) (1.39 mL, 2.79 mmol) to yield complex **10** as a white solid. Yield 95% (1.16 g, 2.65 mmol). Anal. Calcd for $C_{24}H_{28}N_4Zn$: C, 65.83; H, 6.45; N, 12.79. Found: C, 65.90; H, 6.45; N, 12.78. ^{1}H NMR (C_6D_6, 297 K): δ 7.26 (m, 1 H, H^{Cp}), 7.06–6.95 (m, 5 H, Ph), 6.80 (m, 1 H, H^{Cp}), 6.03 (m, 1 H, H^{Cp}), 5.98 (d, 1 H, J_{HH} = 5 Hz, CH^b), 5.88 (m, 1 H, H^{Cp}), 5.32 (s, 1 H, H^4), 5.29 (s, 1 H, $H^{4'}$), 4.55 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.14 (s, 3 H, Me^3), 2.07 (s, 3 H, $Me^{3'}$), 1.61 (s, 3 H, Me^5), 1.10 (s, 3 H, $Me^{5'}$), –0.04 (s, 3 H, Zn-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.4–138.2 ($C^{3,3',5,5'}$), 141.0, 128.8, 127.5, 126.6 (C^{Ph}), 125.1, 118.2, 116.9, 114.2, 111.9 (C^{Cp}), 106.1 (C^4), 105.3 ($C^{4'}$), 69.4 (C^b), 56.8 (C^a), 13.1 (Me^3), 12.6 ($Me^{3'}$), 9.9 (Me^5), 9.8 ($Me^{5'}$), –5.3 (Zn-Me).

Synthesis of [Zn(Et)(κ^2-η^1(π)-bpzpcp)] (11). The synthesis of **11** was carried out in an identical manner to **7** using bpzpcpH (1.00 g, 2.79 mmol) and $ZnEt_2$ (1.00 M in *n*-hexane) (2.79 mL, 2.79 mmol) to yield complex **11** as a white solid. Yield 91% (1.15 g, 2.54 mmol). Anal. Calcd for $C_{25}H_{30}N_4Zn$: C, 66.44; H, 6.69; N, 12.40. Found: C, 66.40; H, 6.66; N, 12.44. ^{1}H NMR (C_6D_6, 297 K): δ 7.22 (m, 1 H, H^{Cp}), 7.06–6.99 (m, 5 H, Ph), 6.75 (m, 1 H, H^{Cp}), 6.01 (m, 1 H, H^{Cp}), 5.96 (d, 1 H, J_{HH} = 5 Hz, CH^b), 5.87 (m, 1 H, H^{Cp}), 5.37 (s, 1 H, H^4), 5.26 (s, 1 H, $H^{4'}$), 4.53 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.23 (s, 3 H, Me^3), 2.08 (s, 3 H, $Me^{3'}$), 1.85 (t, 3 H, J_{HH} = 10 Hz, Zn-CH_2-$\underline{CH_3}$), 1.63 (s, 3 H, Me^5), 1.10 (s, 3 H, $Me^{5'}$), 0.75 (q, 2 H, J_{HH} = 10 Hz, Zn-$\underline{CH_2}$-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.4–138.5 ($C^{3,3',5,5'}$), 141.0, 128.9, 127.6, 126.5 (C^{Ph}), 125.7, 118.1, 116.9, 114.2, 112.0 (C^{Cp}), 105.7 (C^4), 105.3 ($C^{4'}$), 69.2 (C^b), 56.7 (C^a), 13.9 (Zn-CH_2-$\underline{CH_3}$), 12.7 (Me^3), 12.5 ($Me^{3'}$), 10.0 (Me^5), 9.8 ($Me^{5'}$), 1.1 (Zn-$\underline{CH_2}$-CH_3).

Synthesis of [Zn(CH_2SiMe_3)(κ^2-η^1(π)-bpzpcp)] (12). The synthesis of **12** was carried out in an identical manner to **9** using bpzpcpH (1.00 g, 2.79 mmol), $ZnCl_2$ (0.38 g, 2.79 mmol) and $LiCH_2SiMe_3$ (1.00 M in pentane) (5.58 mL, 5.58 mmol) to yield complex **12** as pale white solid. Yield 89% (1.27 g, 2.48 mmol). Anal. Calcd for $C_{27}H_{36}N_4SiZn$: C, 63.58; H, 7.11; N, 10.98. Found: C, 63.54; H, 7.07; N, 10.96. ^{1}H NMR (C_6D_6, 297 K): δ 7.21 (m, 1 H, H^{Cp}), 7.07–6.92 (m, 5 H, Ph), 6.83 (m, 1 H, H^{Cp}), 6.05 (m, 1 H, H^{Cp}), 5.96 (d, 1 H, J_{HH} = 5 Hz, CH^b), 5.90 (m, 1 H, H^{Cp}), 5.32 (s, 1 H, H^4), 5.21 (s, 1 H, $H^{4'}$), 4.56 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.18 (s, 3 H, Me^3), 2.08 (s, 3 H, $Me^{3'}$), 1.62 (s, 3 H, Me^5), 1.12 (s, 3H, $Me^{5'}$), 0.58 (s, 9 H, Zn-CH_2-Si$\underline{Me_3}$), –0.22 (s, 2 H, Zn-$\underline{CH_2}$-$SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.6–138.3 ($C^{3,3',5,5'}$), 141.3, 129.0, 127.5, 126.3 (C^{Ph}), 125.6, 118.3, 117.0, 114.1, 111.8 (C^{Cp}), 105.6 (C^4), 105.2 ($C^{4'}$), 69.3 (C^b), 56.7 (C^a), 12.8 (Me^3), 12.5 ($Me^{3'}$), 10.0 (Me^5), 9.9 ($Me^{5'}$), 4.2 (Zn-CH_2-Si$\underline{Me_3}$), –2.8 (Zn-$\underline{CH_2}$-$SiMe_3$).

Synthesis of [Mg(OAr)(κ^2-η^5-bpztcp)] (13). In a 250 mL Schlenk tube [Mg(Me)(κ^2-η^5-bpztcp)] (**1**) (1.00 g, 2.65 mmol) was dissolved in dry toluene (50 mL) and cooled to –70 ºC. A cooled (–20 ºC) solution of 2,6-dimethylphenol (0.31 g, 2.65 mmol) in toluene (15 mL) was added and the resulting mixture was stirred at 0 ºC during 30 min. The solvent was evaporated under reduced pressure at and a sticky white product was obtained. The solid was washed with *n*-hexane (20 mL) to yield compound **13** as a white solid. Yield 85% (1.09 g, 2.26 mmol). Anal. Calcd for $C_{29}H_{38}MgN_4O$: C, 72.12; H, 7.93; N, 11.60. Found: C, 72.13; H, 7.98; N, 11.69. ^{1}H NMR (C_6D_6, 297 K): δ 7.30 (d, 2 H, J_{HH} = 10 Hz, $H^{m,(Me_2\text{-}OAr)}$), 6.87 (m, 1 H, H^{Cp}), 6.82 (t, 1 H, J_{HH} = 10 Hz, $H^{p,(Me_2\text{-}OAr)}$), 6.76 (m, 1 H, H^{Cp}), 6.21 (d, 1 H, J_{HH} = 5 Hz, CH^b), 6.11 (m, 1 H, H^{Cp}), 5.78 (m, 1 H, H^{Cp}), 5.29 (s, 1 H, H^4), 5.28 (s, 1 H, $H^{4'}$), 2.71 (bs, 1 H, CH^a), 2.43 (s, 6 H, $\underline{Me}_2$-OAr), 2.03 (s, 3 H, Me^3), 2.01 (s, 3 H, $Me^{3'}$), 1.62 (s, 3 H, Me^5), 1.55 (s, 3 H, $Me^{5'}$), 0.92 (s, 9 H, ^{t}Bu). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 149.2–137.6 ($C^{3,3',5,5'}$), 162.1, 128.9, 125.6, 113.4

($C^{Me_2\text{-}OAr}$), 113.8, 109.1, 106.2, 105.0, 103.2 (C^{Cp}), 105.7 (C^4), 105.4 ($C^{4'}$), 65.0 (C^b), 59.9 (C^a), 34.5, 28.7 (^{t}Bu), 18.1 (Me$_2$-OAr) 12.7 (Me^3), 12.6 ($Me^{3'}$), 11.0 (Me^5), 10.2 ($Me^{5'}$).

Synthesis of [Mg(OAr)(κ^2-η^5-bpzpcp)] (14). The synthesis of **14** was carried out in an identical manner to **13** using [Mg(Me)(κ^2-η^5-bpzpcp)] (**4**) (1.00 g, 2.52 mmol) and 2,6-dimethylphenol (0.31 g, 2.52 mmol) to yield compound **14** as a white solid. Yield 88% (1.11 g, 2.22 mmol). Anal. Calcd for $C_{31}H_{34}MgN_4O$: C, 74.03; H, 6.81; N, 11.14. Found: C, 74.10; H, 6.79; N, 11.21. ^{1}H NMR (C_6D_6, 297 K): δ 7.33 (d, 2 H, J_{HH} = 10 Hz, $H^{m,(Me_2\text{-}OAr)}$), 7.12–6.92 (m, 5 H, Ph), 6.89 (t, 1 H, J_{HH} = 10 Hz, $H^{p,(Me_2\text{-}OAr)}$), 6.83 (m, 1 H, H^{Cp}), 6.75 (m, 1 H, H^{Cp}), 6.21 (m, 1 H, H^{Cp}), 5.82 (m, 1 H, H^{Cp}), 5.81 (d, 1 H, J_{HH} = 5 Hz, CH^b), 5.37 (s, 1 H, H^4), 5.29 (s, 1 H, $H^{4'}$), 4.32 (d, 1 H, J_{HH} = 5 Hz, CH^a), 2.35 (s, 6 H, Me$_2$-OAr), 2.12 (s, 3 H, Me^3), 2.09 (s, 3 H, $Me^{3'}$), 1.45 (s, 3 H, Me^5), 1.19 (s, 3 H, $Me^{5'}$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 148.9–138.3 ($C^{3,3',5,5'}$), 161.7, 128.8, 125.3, 112.6 ($C^{Me_2\text{-}OAr}$), 141.3, 130.7, 128.7, 128.5 (C^{Ph}), 114.0, 108.3, 107.2, 105.1, 104.0 (C^{Cp}), 105.6 (C^4), 105.3 ($C^{4'}$), 69.5 (C^b), 55.5 (C^a), 18.3 (Me$_2$-OAr) 12.8 (Me^3), 12.0 ($Me^{3'}$), 9.7 (Me^5), 9.6 ($Me^{5'}$).

Synthesis of fulvene (15). In a 250 cm^3 Schlenk tube containing MeOH (20 mL) was dissolved in the following order: *R*-(–)-myrtenal (5.63 mL, 37.00 mmol), freshly cracked cyclopentadiene (6.15 mL, 92.00 mmol) and pyrrolidine (4.63 mL, 55.50 mmol). The red-colored mixture was allowed to react for 5 h under N_2, after which was added Et_2O (45 mL), HOAc (3.33 mL, 59.00 mmol) and water (15 mL). Fulvene was extracted into the organic phase and this was washed with 10% aqueous $NaHCO_3$ w/v (2 × 10 mL) and dried first with $CaCl_2$ (1 h) and then with anhydrous $MgSO_4$. The resulting mixture was dried under reduced pressure to yield compound **15** as a red oil. Yield: 90% (6.60 g, 33.3 mmol). Anal. Calcd. for $C_{15}H_{18}$: C, 90.90; H, 9.09. Found: C, 90.85; H, 9.98. ^{1}H NMR (C_6D_6, 297 K), δ 6.70 (m, 1 H, H^3), 6.58 (bs, 2 H, $H^{a,4}$), 6.48 (m, 1 H, H^2), 6.28 (m, 1 H, H^5), 5.75 (s, 1 H, H^d), 2.91 (m, 1 H, H^f), 2.29 (m, 1 H, H^h), 2.17 (m, 2 H,

H^e), 1.87 (bs, 1 H, H^b), 1.20 (s, 3 H, Me^g), 1.11 (d, 1H, J_{HH} = 8.9 Hz, H^h), 0.79 (s, 3 H, Me^g). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 148.1 (C^c), 143.0 (C^1), 139.3 (C^a), 134.7 (C^d), 134.4 (C^4), 129.8 (C^2), 128.4 (C^5), 119.7 (C^3), 45.1 (C^f), 40.3 (C^b), 32.9 (C^e), 31.4 (C^h), 26.1 (Me^g), 20.8 (Me^g). $[\alpha]_D^{25}$ = +20.5 (*c* 1.00, toluene).

Synthesis of [(*R*,*R*)-bpmycpH and (*R*,*R*)-bpmycp'H] (16a and 16b). In a 250 cm^3 Schlenk tube bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) (1.0 g, 4.89 mmol) was dissolved in dry THF (50 mL) and cooled to around –70 ºC (acetone/liquid nitrogen). Bu^nLi (1.6 M in *n*-hexane) (3.6 mL, 4.89 mmol) was added dropwise, maintaining the reaction temperature at –70 °C for 1 h to give a yellow suspension. After this time the reaction mixture was warmed to 0 ºC (salt/ice) and added dropwise to a solution of compound **15** (0.97 g, 4.89 mmol) in THF (20 mL). The resulting mixture was maintained at 0 ° C for 5 min. A solution of NH_4Cl was added and the reaction mixture was added to a separating funnel. The resulting organic phase was dried over $MgSO_4$ and under reduced pressure to give a colorless oil. The product was purified using a plug of silica, eluting with a mixture of AcOEt/hexane (1:9) and recrystallized from Et_2O to give compound **16** as colorless crystals. Yield: 63% (1.24 g, 3.08 mmol). Anal. Calcd. for $C_{26}H_{34}N_4$: C, 77.61; H, 8.46; N, 13.85. Found: C, 77.50; H, 8.41; N, 13.75. ^1H NMR (two tautomers) (C_6D_6, 297 K), δ 6.95 (d, 1 H, J_{HH} = 11.8 Hz, CH^b), 6.89 (d, 1 H, J_{HH} = 11.8 Hz, CH^b), 6.52 (m, 1 H, H^{Cp}), 6.28 (bs, 1 H, H^{Cp}), 6.23 (m, 1 H, H^{Cp}), 6.13 (m, 1 H, H^{Cp}), 6.09 (m, 1 H, H^{Cp}), 6.01 (bs, 1 H, H^{Cp}), 5.62 (s, 1 H, H^4), 5.61 (s, 1 H, H^4), 5.50 (s, 1 H, $H^{4'}$), 5.48(s, 1 H, $H^{4'}$), 5.40 (bs, 2 H, H^d), 5.33 (d, 1 H, J_{HH} = 11.8 Hz, CH^a), 5.29 (d, 1 H, J_{HH} = 11.8 Hz, CH^a), 2.96 (dd, 1 H, J_{HH} = 23.4, 1.4 Hz, H^f), 2.81 (dd, 1 H, J_{HH} = 23.4, 1.4 Hz, H^f), 2.56 (bs, 2 H, H^{5Cp}), 2.54 (s, 3 H, Me^5), 2.49 (s, 3 H, Me^5), 2.43 (m, 2 H, H^{5Cp}), 2.41 (s, 3 H, $Me^{5'}$), 2.35 (s, 3 H, $Me^{5'}$), 2.26 (m, 4 H, H^e), 2.21 (s, 3 H, Me^3), 2.20 (s, 3 H, Me^3), 2.14 (s, 3 H, $Me^{3'}$), 2.12 (s, 3 H, $Me^{3'}$), 2.05 (m, 2 H, H^h), 1.85 (bs, 2 H, $H^{b,(myr)}$), 1.18 (s, 6 H, Me^g), 0.76 (d, 1 H, J_{HH} = 8.6 Hz, H^h), 0.72 (d, 1 H, J_{HH} = 8.6 Hz, H^h), 0.63 (s, 3 H, Me^g), 0.61 (s, 3 H, Me^g). ^{13}C-{^1H} NMR (two tautomers) (C_6D_6, 297 K), 147.1–145.2 ($C^{3,3'}$), 145.8, 143.9 (C^c), 140.0–131.5 ($C^{5,5'}$),

134.4–127.4 (C^{Cp}), 120.1, 119.0 (C^{d}), 106.8–105.9 ($C^{4,4'}$), 73.9, 73.5 (C^{b}), 50.0, 49.7 (C^{a}), 44.0(C^{Cp}), 43.6, 43.1 ($C^{b,(myr)}$), 41.5 (C^{Cp}), 40.5 (C^{f}), 37.8 (C^{g}), 31.7, 31.6 (C^{h}), 31.6, 31.5 (C^{e}), 26.3, 26.2 (Me^{g}), 21.2, 20.8 (Me^{g}), 13.7–11.4 ($Me^{3,3',5,5'}$). $[\alpha]_D^{25}$ = +37.7 (*c* 1.00, toluene).

Synthesis of [Mg(Me)(κ^2-η^5-*R,S*-bpzmycp)] (17). The synthesis of **17** was carried out in an identical manner to **1** using *R,R*-bpzmycpH (**16**) (1.00 g, 2.48 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.55 mL, 2.48 mmol) and MeMgCl (3.00 M in THF) (0.83 mL, 2.48 mmol) to yield complex **17** as a pale yellow solid. Yield: 91% (0.99 g, 2.26 mmol). Anal. Calcd for $C_{27}H_{36}MgN_4$: C, 73.55; H, 8.23; N, 12.71. Found: C, 73.62; H, 8.22; N, 12.75. ^{1}H NMR (C_6D_6, 297 K), δ 6.81 (m, 1 H, H^{Cp}), 6.69 (m, 1 H, H^{Cp}), 6.31 (m, 1 H, H^{Cp}), 6.12 (bs, 1 H, CH^{b}), 5.79 (m, 1 H, H^{Cp}), 5.35 (s, 1 H, H^{4}), 5.28 (s, 1 H, $H^{4'}$), 4.97 (bs, 1 H, H^{d}), 3.75 (bs, 1 H, CH^{a}), 2.19 (s, 6 H, $Me^{3,3'}$), 2.15 (m, 3 H, $H^{h,e}$), 2.02 (m, 1 H, H^{f}), 1.93 (m, 1 H, $H^{b,(myr)}$), 1.75 (s, 3 H, Me^{5}), 1.68 (s, 3 H, $Me^{5'}$), 1.22 (m, 1 H, H^{h}), 1.17 (s, 3 H, Me^{g}), 0.91 (s, 3 H, Me^{g}), –0.73 (s, 3 H, Mg-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), 149.4–137.5 ($C^{3,3',5,5'}$), 149.4 (C^{d}), 128.5 (C^{c}), 115.6, 110.7, 108.5, 107.6, 103.9 (C^{Cp}), 106.3 (C^{4}), 106.0 ($C^{4'}$), 67.5 (C^{b}), 54.8 (C^{a}), 46.5 ($C^{b,(myr)}$), 40.6 (C^{f}), 37.6 (C^{g}), 32.7 (C^{h}), 31.9 (C^{e}), 26.1 (Me^{g}), 21.2 (Me^{g}), 13.0 (Me^{3}), 12.7 ($Me^{3'}$), 10.8 (Me^{5}), 10.0 ($Me^{5'}$), –1.2 (Mg-CH_3). $[\alpha]_D^{25}$ = + 30.0 (*c* 1.00, toluene).

Synthesis of [Mg(Et)(κ^2-η^5-*R,S*-bpzmycp)] (18). The synthesis of **18** was carried out in an identical manner to **1** using *R,R*-bpzmycpH (**16**) (1.00 g, 2.48 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.55 mL, 2.48 mmol) and EtMgCl (2.00 M in Et_2O) (1.24 mL, 2.48 mmol) to yield complex **18** as a pale yellow solid. Yield: 89% (1.00 g, 2.20 mmol). Anal. Calcd for $C_{28}H_{38}MgN_4$: C, 73.92; H, 8.42; N, 12.32. Found: C, 74.00; H, 8.38; N, 12.35. ^{1}H NMR (C_6D_6, 297 K), δ 6.80 (m, 1 H, H^{Cp}), 6.67 (m, 1 H, H^{Cp}), 6.28 (m, 1 H, H^{Cp}), 6.11 (bs, 1 H, CH^{b}), 5.79 (m, 1 H, H^{Cp}), 5.37 (s, 1 H, H^{4}), 5.30 (s, 1 H, $H^{4'}$), 4.95 (bs, 1 H, H^{d}), 3.73 (bs, 1 H, CH^{a}), 2.15 (m, 3 H, $H^{h,e}$), 2.21 (s, 3 H, Me^{3}), 2.20 (s, 3 H, $Me^{3'}$), 2.00 (m, 1 H, H^{f}), 1.93 (m, 1 H, $H^{b,(myr)}$),

1.93 (t, 3 H, J_{HH} = 8.1 Hz, Mg-CH_2-$\underline{CH_3}$), 1.76 (s, 3 H, Me^5), 1.69 (s, 3 H, $Me^{5'}$), 1.21 (d, 1 H, J_{HH} = 8.4 Hz, H^h), 1.19 (s, 3 H, Me^g), 0.90 (s, 3 H, Me^g), –0.06 (q, 2 H, J_{HH} = 8.1 Hz, Mg-$\underline{CH_2}$-CH_3). ^{13}C-{^1H} NMR (C_6D_6, 297 K), 149.3–137.7 ($C^{3,3',5,5'}$), 149.3 (C^d), 129.1 (C^c), 116.0, 110.8, 108.9, 106.3, 103.8 (C^{Cp}), 106.1 (C^4), 105.4 ($C^{4'}$), 67.6 (C^b), 54.8 (C^a), 46.7 ($C^{b,(myr)}$), 40.7 (C^f), 37.7 (C^g), 32.7 (C^h), 31.9 (C^e), 26.2 (Me^g), 21.2 (Me^g), 13.8 (Mg-CH_2-$\underline{CH_3}$), 12.8 (Me^3), 12.7 ($Me^{3'}$), 10.8 (Me^5), 10.1 ($Me^{5'}$), 0.7 (Mg-$\underline{CH_2}$-CH_3). $[\alpha]_D^{25}$ = + 29.2 (*c* 1.00, toluene).

Synthesis of [Mg(CH_2SiMe_3)(κ^2-η^5-*R,S*-bpzmycp)] (19). The synthesis of **19** was carried out in an identical manner to **1** using *R,R*-bpzmycpH (**16**) (1.00 g, 2.48 mmol), Bu^nLi (1.60 M in *n*-hexane) (1.55 mL, 2.48 mmol) and Me_3SiCH_2MgCl (1.00 M in Et_2O) (2.48 mL, 2.48 mmol) to yield complex **19** as pale yellow solid. Yield: 93% (1.18 g, 2.31 mmol). Anal. Calcd for $C_{30}H_{44}MgN_4Si$: C, 70.23; H, 8.64; N, 10.92. Found: C, 70.29; H, 8.61; N, 11.00. ^1H NMR (C_6D_6, 297 K), δ 6.78 (m, 1 H, H^{Cp}), 6.65 (m, 1 H, H^{Cp}), 6.26 (m, 1 H, H^{Cp}), 6.06 (bs, 1 H, CH^b), 5.72 (m, 1 H, H^{Cp}), 5.34 (s, 1 H, H^4), 5.27 (s, 1 H, $H^{4'}$), 4.89 (bs, 1 H, H^d), 3.67 (bs, 1 H, CH^a), 2.14 (m, 3 H, $H^{h,e}$), 2.19 (s, 6 H, $Me^{3,3'}$), 1.95 (m, 1 H, H^f), 1.92 (m, 1 H, $H^{b,(myr)}$), 1.75 (s, 3 H, Me^5), 1.68 (s, 3 H, $Me^{5'}$), 1.23 (m, 1 H, H^h), 1.16 (s, 3 H, Me^g), 0.88 (s, 3 H, Me^g), 0.60 (s, 9 H, Mg-CH_2-Si$\underline{Me_3}$), –1.26 (s, 2 H, Mg-$\underline{CH_2}$-$SiMe_3$). ^{13}C-{^1H} NMR (C_6D_6, 297 K), 149.1–137.3 ($C^{3,3',5,5'}$), 149.0 (C^d), 128.9 (C^c), 115.8, 110.6, 108.3, 107.7, 103.7 (C^{Cp}), 106.1 (C^4), 106.0 ($C^{4'}$), 67.2 (C^b), 54.4 (C^a), 46.5 ($C^{b,(myr)}$), 40.4 (C^f), 37.4 (C^g), 32.4 (C^h), 31.6 (C^e), 25.9 (Me^g), 21.0 (Me^g), 13.4 (Me^3), 13.2 ($Me^{3'}$), 10.6 (Me^5), 9.9 ($Me^{5'}$), 4.8 (Mg-CH_2-Si$\underline{Me_3}$), –5.2 (Mg-$\underline{CH_2}$-$SiMe_3$). $[\alpha]_D^{25}$ = + 27.1 (*c* 1.00, toluene).

Synthesis of [Zn(Me)(κ^2-η^1(π)-*R,S*-bpzmycp)] (20). The synthesis of **20** was carried out in an identical manner to **7** using *R,R*-bpzmycpH (**16**) (1.00 g, 2.48 mmol) and $ZnMe_2$ (2.00 M in toluene) (1.24 mL, 2.48 mmol) to yield complex **20** as a white solid. Yield: 92% (1.10 g, 2.28 mmol). Anal. Calcd for $C_{27}H_{36}N_4Zn$: C, 67.28; H, 7.53; N, 11.62. Found: C, 67.48; H, 7.31; N, 11.67. ^1H NMR (C_6D_6, 297 K), δ

7.04 (m, 1 H, H^{Cp}), 6.81 (m, 1 H, H^{Cp}), 6.11 (d, 1 H, J_{HH} = 3.7 Hz, CH^{b}), 5.83 (m, 2 H, H^{Cp}), 5.35 (s, 1 H, H^{4}), 5.32 (s, 1 H, $H^{4'}$), 5.20 (bs, 1 H, H^{d}), 3.94 (d, 1 H, J_{HH} = 3.7 Hz, CH^{a}), 2.19 (m, 3 H, $H^{h,e}$), 2.14 (s, 3 H, Me^{3}), 2.08 (s, 3 H, $Me^{3'}$), 1.98 (m, 1 H, H^{f}), 1.92 (m, 1 H, $H^{b,(myr)}$), 1.76 (s, 3 H, Me^{5}), 1.69 (s, 3 H, $Me^{5'}$), 1.17 (s, 3 H, Me^{g}), 1.05 (d, 1 H, J_{HH} = 8.7 Hz, H^{h}), 0.77 (s, 3 H, Me^{g}), –0.14 (s, 3 H, Zn-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), 149.7–137.9 ($C^{3,3',5,5'}$), 149.0 (C^{d}), 129.3 (C^{c}), 118.0, 117.3, 114.0, 108.6, 93.8 (C^{Cp}), 106.1 (C^{4}), 105.8 ($C^{4'}$), 67.8 (C^{b}), 56.6 (C^{a}), 45.0 ($C^{b,(myr)}$), 40.7 (C^{f}), 37.9 (C^{g}), 32.5 (C^{h}), 31.9 (C^{e}), 26.1 (Me^{g}), 20.9 (Me^{g}), 12.3 (Me^{3}), 12.9 ($Me^{3'}$), 10.9 (Me^{5}), 10.0 ($Me^{5'}$), 1.2 (Zn-CH_3). $[\alpha]_D^{25}$ = + 31.3 (*c* 1.00, toluene).

Synthesis of [Zn(Et)(κ^2-η^1(π)-*R,S*-bpzmycp)] (21). The synthesis of **21** was carried out in an identical manner to **7** using *R,R*-bpzmycpH (**16**) (1.00 g, 2.48 mmol) and $ZnEt_2$ (1.00 M in *n*-hexane) (2.48 mL, 2.48 mmol) to yield complex **21** as a white solid. Crystals suitable for X-ray diffraction were obtained by crystallization from toluene at –26 ºC. Yield: 90% (1.10 g, 2.21 mmol). Anal. Calcd. for $C_{28}H_{38}N_4Zn$: C, 67.80; H, 7.72; N, 11.29. Found: C, 67.95; H, 7.61; N, 11.35. ^{1}H NMR (C_6D_6, 297 K), δ 7.09 (m, 1 H, H^{Cp}), 6.82 (m, 1 H, H^{Cp}), 6.08 (d, 1 H, J_{HH} = 3.7 Hz, CH^{b}), 5.82 (m, 2 H, H^{Cp}), 5.35 (s, 1 H, H^{4}), 5.34 (s, 1 H, $H^{4'}$), 5.19 (m, 1 H, H^{d}), 3.92 (d, 1 H, J_{HH} = 3.7 Hz, CH^{a}), 2.17 (m, 3 H, $H^{h,e}$), 2.17 (s, 3 H, Me^{3}), 2.08 (s, 3 H, $Me^{3'}$), 1.97 (m, 1 H, H^{f}), 1.92 (m, 1 H, $H^{b,(myr)}$), 1.80 (t, 3 H, J_{HH} = 8 Hz, Zn-CH_2-$\underline{CH_3}$), 1.73 (s, 3 H, Me^{5}), 1.67 (s, 3 H, $Me^{5'}$), 1.16 (s, 3 H, Me^{g}), 1.05 (d, 1 H, J_{HH} = 8.7 Hz, H^{h}), 0.76 (s, 3 H, Me^{g}), 0.69 (q, 2 H, J_{HH} = 8 Hz, Zn-$\underline{CH_2}$-CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), 149.3–137.8 ($C^{3,3',5,5'}$), 149.1 (C^{d}), 117.1 (C^{c}), 116.7, 114.4, 113.2, 108.28, 93.14 (C^{Cp}), 105.9 (C^{4}), 105.6 ($C^{4'}$), 67.8 (C^{b}), 56.4 (C^{a}), 44.7 ($C^{b,(myr)}$), 40.5 (C^{f}), 37.7 (C^{g}), 32.2 (C^{h}), 31.7 (C^{e}), 25.8 (Me^{g}), 20.6 (Me^{g}), 13.4 (Zn-CH_2-$\underline{CH_3}$), 12.5 ($Me^{3,3'}$), 10.6 (Me^{5}), 9.7 ($Me^{5'}$), 0.7 (Zn-$\underline{CH_2}$-CH_3). $[\alpha]_D^{25}$ = + 29.2 (*c* 1.00, toluene).

Synthesis of [Zn(CH_2SiMe_3)(κ^2-η^1(π)-*R,S*-bpzmycp)] (22). The synthesis of **22** was carried out in an identical manner to **9** using *R,R*-bpzmycpH **(16)** (1.00 g, 2.48 mmol), $ZnCl_2$ (0.34 g, 2.48 mmol) and

$LiCH_2SiMe_3$ (4.96 mL, 4.96 mmol) to yield complex **22** as a white solid. Yield: 86% (1.18 g, 2.13 mmol). Anal. Calcd for $C_{30}H_{44}N_4SiZn$: C, 65.02; H, 8.00; N, 10.11. Found: C, 65.02; H, 7.88; N, 10.21. ^{1}H NMR (C_6D_6, 297 K), δ 7.06 (m, 1 H, H^{Cp}), 6.83 (m, 1 H, H^{Cp}), 6.09 (d, 1 H, J_{HH} = 3.7 Hz, CH^b), 5.85 (m, 2 H, H^{Cp}), 5.35 (s, 1 H, H^4), 5.33 (s, 1 H, $H^{4'}$), 5.21 (m, 1 H, H^d), 3.87 (d, 1 H, J_{HH} = 3.7 Hz, CH^a), 2.18 (m, 3 H, $H^{h,e}$), 2.15 (s, 3 H, Me^3), 2.03 (s, 3 H, $Me^{3'}$), 1.97 (m, 1 H, H^f), 1.95 (m, 1 H, $H^{b,(myr)}$), 1.69 (s, 3 H, Me^5), 1.67 (s, 3 H, $Me^{5'}$), 1.13 (s, 3 H, Me^g), 1.01 (d, 1 H, J_{HH} = 8.7 Hz, H^h), 0.76 (s, 3 H, Me^g), 0.56 (s, 9 H, Zn-CH_2-Si$\underline{Me_3}$), –0.25 (s, 9 H, Zn-CH_2-Si$\underline{Me_3}$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), 149.5–137.3 ($C^{3,3',5,5'}$), 148.9 (C^d), 129.6 (C^c), 118.7, 114.5, 113.7, 108.4, 94.2 (C^{Cp}), 105.4 (C^4), 105.0 ($C^{4'}$), 66.8 (C^b), 56.0 (C^a), 44.2 ($C^{b,(myr)}$), 41.2 (C^f), 37.7 (C^g), 32.4 (C^h), 31.3 (C^e), 25.7 (Me^g), 20.8 (Me^g), 12.7 ($Me^{3,3'}$), 12.5 (Me^5), 10.8 ($Me^{5'}$), 10.2 (Zn-CH_2-Si$\underline{Me_3}$), –3.7 (Zn-$\underline{CH_2}$-$SiMe_3$). $[\alpha]_D^{25}$ = + 33.6 (*c* 1.00, toluene).

General 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 the glovebox with the required amount of *rac*-LA 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 tetrahydrofuran (2.5 mL) was added to a solution of *rac*-lactide (10 mL) in the same solvent to give an $[rac\text{-LA}]_0$ = 0.72 M. The initial ratio

monomer/catalyst was [*rac*-LA]$_0$/[catalyst]$_0$ = 90, and the initial [catalyst]$_0$ = 8 mM was gradually increased up to 20 mM. The resulting mixture was stirred at 50 ºC under a 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 Structure Determination for 2, 3×0.5C_7H_8 and 7. The crystal evaluation and data collection were performed on a Bruker X8 APEX2 CCD area detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å, sealed X-ray tube).

Data were integrated using SAINT[37] and an absorption correction was performed with the program SADABS.[38] For all structures, a successful solution by direct methods provided most non-hydrogen atoms from the E-map.[39] The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps using the program SHELXL.[39]

All non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms were included in the structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

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Supporting Information Available: Ring-opening polymerization of *rac*-lactide experimental details and X-ray diffraction experimental information for data collection, refinement, atom coordinates and anisotropic displacement parameters for complexes **2**, **3**, **7** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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New Racemic and Single Enantiopure Hybrid Scorpionate/Cyclopentadienyl Magnesium and Zinc Initiators for the Stereoselective ROP of Lactides.

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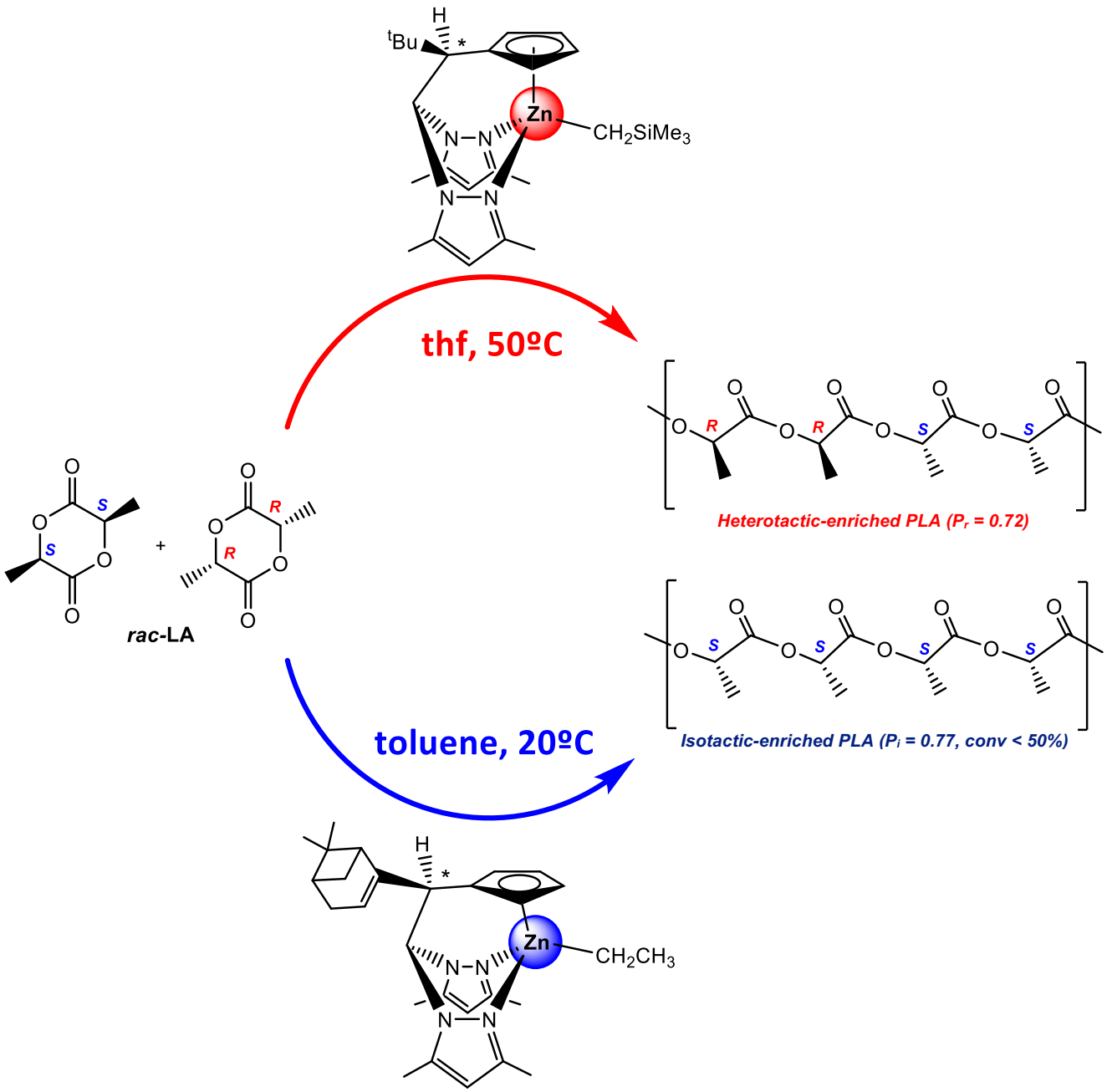
A novel enantiopure hybrid scorpionate/cyclopentadiene ligand was obtained in a one-pot procedure by an efficient and highly diastereoselective nucleophilic addition of an organolithium reagent to an electrophilically activated olefin in a new fulvene with a chiral substrate. In addition, the first racemic and single enantiopure bis(pyrazol-1-yl)methane-based NNCp-donor magnesium and zinc monoalkyls/aryloxides of the type [Mg(R)(κ^2-η^5-NNCp)]/[Mg(OAr)(κ^2-η^5-NNCp)] and [Zn(R)(κ^2-η^1-NNCp)], respectively, were synthesized in high yields. These complexes act as single-component living initiators for the well-controlled ROP of *rac*-LA. An inspection of the degree of stereoselectivity in the poly(lactide)s produced revealed that the myrtenal substituent on the enantiomerically pure initiators exerts an appreciable influence and affords isotactic-enriched materials (P_i = 0.77), while the racemic mixtures impart more discrete levels of heteroselectivity (P_s = 0.72).



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