DINUCLEAR ZINC COMPLEXES USING A SET OF TWO POLYTADENATE PHENOLATE LIGANDS AND APPLICATIONS IN POLYMERIZATION OF CATALYSIS OF *D,L*-LACTONE

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ABSTRACT

The synthesis and characterization of 9 dinuclear zinc complexes are reported, including the X-ray crystal structures of 5 complexes. The set of three ligand motif (R) -2,6-bis((E) -((2-(dimethylamino) ethyl) imino) methyl) phenol (where R is Cl, t-But and OMe) L_1, L_2, L_3, and a set of three related ligands has been synthesized; (R) -2,6-bis(((2-(dimethylamino) ethyl) amino) methyl) phenol (where R is Cl, t-But and OMe) L_4, L_5, L_6. Dizinc diacetate complexes have been synthesized ($[L^nZn_2(OAc)_2][PF_6]$) (n= 1, 2, 3) . Dizinc trihalide complexes have also been prepared $[L^nZn_2(\mu\text{-Cl}) Cl_2]$ (n= 1, 2, 3, 4, 5, 6) . The dizinc complexes were tested as initiators for *D,L*-lactide ring opening polymerization. Structural differences between complexes of the three ligands are discussed.

**KEYWORDS:** Ligands, Complexes, Catalysis (initiator), Polymerization.

INTRODUCTION
Over the past few decades, there has been much research into bimetallic complexes due to the interesting properties arising from the close proximity of the two metal centers.[1]

These include studies of bimetallic complexes magnetic, electronic, spectroscopic, and structural properties, as well as their reactivity.[1,2] Binuclear zinc complexes have attracted particular interest as important structural mimics of the active site of a range of metalloenzymes[3], such as zinc-dependent aminopeptidases, metallo-lactamases, and alkaline phosphatases.[4] Dizinc complexes have allowed new catalytic processes to be developed that are beyond the scope of natural enzymes. These processes include Mannich-type reactions[5], Aldol reactions[6], Friedel-Crafts alkylations[7], alkynylation reactions[8], as well as polymerization catalysis.[9] Phenol-based compartmental ligands are often used to stabilize dinuclear metal cores.[10-16]

A common motif in the design of dinucleating ligands L^n (1, 2, 3, 4, 5, 6), and the dizinc complexes C_n (1, 2, 3, 4, 5, 6) derived from L_1, L_2, L_3, L_4, L_5, L_6 (schema 1), will be the focus of this study. An important goal of this study was to synthesis of bi-nuclear zinc complexes (schema 2), The dizinc complexes were applied as initiators in the ring opening polymerization of DL-lactide. Zinc has very low toxicity and is present as ions in many human metabolisms.

We report here the synthesis and characterization of 9 complexes.
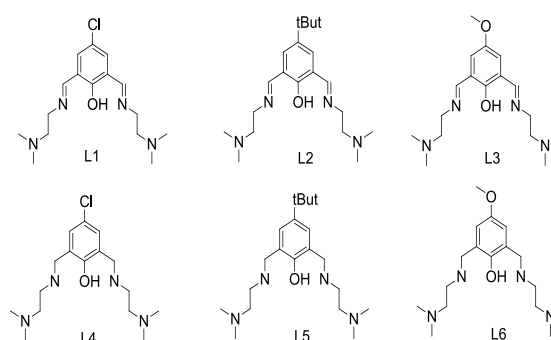
Scheme 1: Structures of L.[1-6]
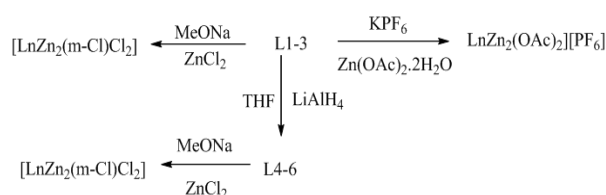
Scheme 2: Synthesis of the dizinc complexes.[a]

RESULTS AND DISCUSSION

To synthesize the ligands imines L_1, L_2, L_3, we carred out the condensation of N, N-dimethylethane-1,2-diamine respectively on the precursors diphormylphenol A01, A02, A03, in the presence of NH_4PF_6 in ethanol at reflux (80°C) (Schema 3). L_1, L_2, L_3 were prepared in good yield (78- 88%).

The IR spectrum of ligand L_1 shows a band at 1637 cm^{-1} attributed to the vibration ν (C = N) imine[17], and the absence of the frequency band ν (C = O) of the precursor (A01).

The ^{1}H NMR spectrum of ligand L_1 reveals the presence of two signal at 2.63 ppm and 3.73 ppm assigned respectively to the protons –CH_2-N and = N-CH_2, and another signal at 8.50 ppm assigned to imine protons.

The band at 1637 cm^{-1} attributed to the vibration ν (C = N), the absence of the frequency band ν (C = O), the disappearance of the signal at 10.20 ppm of carbonyl protons (CH = O) appearance of a new signal at 8.50 ppm assigned to imine protons. Indicate that the ligand L_1 is in its imine form.

We observe the presence of a band at 1637 cm^{-1} for the ligand L_2 and at 1638 cm^{-1} for L_3 each attributed to the ν (C = N) imine vibration. The disappearance of the frequency band ν (C = O) is observed on the IR spectra of the precursors of ligands L_2 and L_3.

On the ^{1}H NMR spectrum of ligand L_2, two triplets at 2.64 ppm and at 3.74 ppm assigned respectively to the protons –CH_2-N and = N-CH_2 and a singlet at 8.57 ppm assigned to the imine protons are observed.

This information collected on IR and ^{1}H NMR spectra confirms the structures of ligands, L_2 and L_3.
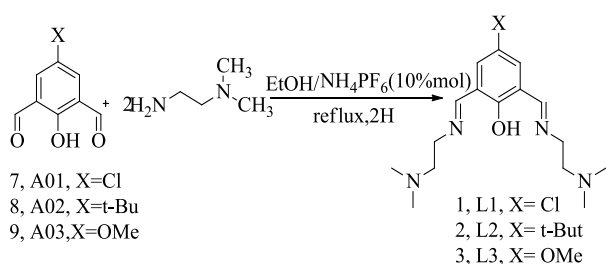
Scheme 3: Synthesis of ligands L_1, L_2, L_3.[a]

The action of $LiAlH_4$ on these ligands imines L_1, L_2, L_3 at room temperature in THF gaves ligands diamine L_4, L_5, L_6 in good overall yield (91-95%) (Scheme 4).

The IR spectrum of ligand L_4 obtained by reduction of ligand L_1 is different from the IR spectrum.

A band is observed at 1039 cm^{-1}, attributed to the ν (C-N) vibration.[18]

The band at 1637 cm^{-1} attributed to the ν (C = N) vibration has disappeared.

The ^{1}H NMR spectrum of ligand L_4 reveals the presence of two signal at 2,42 ppm and 2,67 ppm assigned respectively to the protons –CH_2-N and = N-CH_2, disappearance of the signal at 8.50 ppm, appearance of a new signal at 3.84 ppm assigned to Ar-CH_2 protons. The absence of the signal at 163.50 ppm (Carbon C = N) of the ligand L_1 on the ^{13}C NMR spectrum shows that the ligand L_1 is in its reduced form.

We observe the presence of a band at 1040 cm^{-1} for the ligand L_5 and at 1040 cm^{-1} for L_6 each attributed to the ν (C-N) vibration. The frequency band ν (C = N) observed on the IR spectra of ligands L_2 and L_3 has disappeared.

The ^{1}H NMR spectrum of the L_5 ligand reveals a new signal in the form of a singlet at 3.88 ppm attributed to the Ar-CH_2- protons, the disappearance of the signal at 8.57 ppm attributed to the imine protons. Likewise on the ^{1}H NMR spectrum of ligand L_6, a new signal at 3.73 ppm and the disappearance of the signal at 8.54 ppm are observed.

This information collected on IR and ^{1}H NMR spectra confirms the structures of ligands, L_5 and L_6.
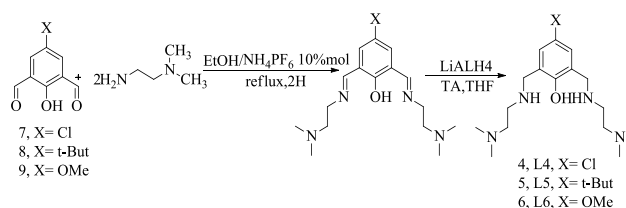
Scheme 4: Synthesis of ligands L_4, L_5, L_6.[a]

$[L^nZn2(\mu-Cl)Cl_2]$. The synthesis of the dizinc trihalide complexes $[L^nZn_2(\mu-Cl)Cl_2]$ C_4, C_5, C_6; was achieved; simply by mixing the ligands imines L_1, L_2, L_3 and zinc chloride in methanol by adding a base to this mixture. $[L^nZn2(\mu-Cl)Cl_2]$ were prepared in good yield (75- 81%) and yielded orange solids.

Recrystallization of the crude material yielded a microcrystalline solid.

The ^{1}H NMR spectrum of $[L^2Zn2(\mu-Cl)Cl_2]$, in $CDCl_3$, shows a single aromatic peak at 7.32 ppm. The terminal NMe_2 groups are also observed at 2.59 ppm, The aromatic –CH=N protons resonate at 8.37 ppm; The remaining CH_2 protons in the ethylene diamine units are observed at 3.72 ppm and 1.,58 ppm.

The t-But Methyl groups are observed at 1.26 ppm.

The ^{1}H NMR spectrum of the C_5 complex is different from that of the ligand L_2.

The signals of the remaining CH_2 protons in the ethylene diamine units observed at 2.64 ppm and at 3.74 ppm for the free ligand underwent a shift of -1.06 and -0.02 respectively.

The protons of the imine respond to 8.37 ppm, ie -0.21 ppm of shift from their response on the free L_2 ligand.

The ^1H NMR spectrum of the C_4, C_6 complexes is very similar, and both complexes are symmetrical.

The ^{13}C NMR spectrum of C_5, in $CDCl_3$, shows 9 signals 169.81, 166.03, 138.45, 137.58, 121.44, 57.21, 51.89, 33.66, 31.19 ppm. Corresponding to the 9 types of carbon atoms of the C_5 complex.

The mass spectrometry were in agreement with the structural formula of $[L^2Zn_2(\mu\text{-Cl})Cl_2]$.

X-rayCrystallography

Themolecularstructureof $[L^2Zn2(\mu\text{-Cl})Cl_2]$ is shown in Fig. 1. The complex shows approximate C_2 symmetry about an axis coincident with the C-O vector. The two *N,N* five-membered chelate rings have the same configuration. Selected bond lengths and angles are listed in Table 1.
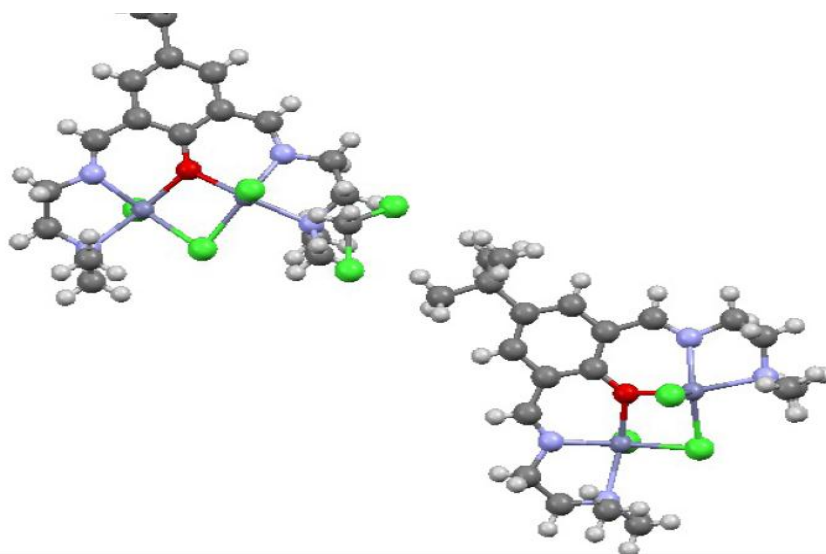

Figure 1: The molecular structure of $[L^2Zn2(\mu\text{-Cl})Cl2]$.

Table 1: Selected Bond Lengths (Å) and Angles (°) for $[L^2Zn_2(\mu\text{-Cl})Cl_2]^a$

Zn(1)-O(1)	2.034(3)	Zn(2)-O(1)	2.166(3)
Zn(1)-N(1)	2.084(3)	Zn(2)-N(2)	2.058(4)
Zn(1)-N(3)	2.155(3)	Zn(2)-N(4)	2.192(4)
Zn(1)-Cl(1)	2.273(1)	Zn(2)-Cl(2)	2.249(1)
Zn(1)-Cl(3)	2.439(1)	Zn(2)-Cl(3)	2.320(1)
Zn(1)- O(1)-Zn (2)	106.7(1)	Zn(1)- Cl(3)-Zn (2)	90.14(4)
Zn(1)…Zn(2)	3.370		

The zinc centers are both five coordinate with distorted square pyramidal geometries. The bond distances (Table 1) between the phenolate oxygen atom (O(1)) and the two zinc centers are somewhat different, with a shorter phenolate bond (**2.034 (3)** Å) to Zn(1).

The bond distances between the chlorine (Cl(3)) and the two zinc centers are also different, Zn(1)-Cl(3) (2.439(1)Å); Zn(2)-Cl(3) (2.320(1)Å) $[L^nZn2(\mu\text{-Cl})Cl_2]$. The synthesis of the dizinc trihalide complexes $[L^nZn_2(\mu\text{-Cl})Cl_2]$ C_7, C_8, C_9; was achieved; simply by mixing the ligands imines L_4, L_5, L_6 and zinc chloride in methanol by adding a base to this mixture. $[L^nZn2(\mu\text{-Cl})Cl_2]$ were prepared in good yield (80-85%) and yielded orange solids (schema 4). Recrystallization of the crude material yielded a microcrystalline solid.

The ^1H NMR spectrum of **$[L^5Zn2(\mu\text{-Cl})Cl_2]$**, in $CDCl_3$, shows a single aromatic peak at 6,96 ppm.

The terminal NMe_2 groups are also observed at 2.61 ppm, The aromatic $-CH_2-N$ protons resonate at 3.60 ppm and 3.24 ppm The remaining CH_2 protons in the ethylene diamine units are observed at 2.85 ppm, 2.50 ppm and 2.23 ppm. The t-But Methyl groups are observed at 1.22 ppm.

We note a disappearance of the L_5 ligand signals observed at 3.84, 2.67 and 2.42 ppm attributed respectively to the protons Ar-CH2, CH2-N and-N-CH2 and an appearance of new signals at 4.19, 3.56, 3.20-3.25, 2.73–2.89, 2.54, 2.28 ppm [85] assigned respectively to the protons Ar-CH2, Ar-CH2, CH2-N, CH2-N, CH2-N, CH2-N.

The ^1H NMR spectrum of the C_7, C_9 complexes is very similar, and both complexes are symmetrical.

The ^{13}C NMR spectrum of C_8, in $CDCl_3$, shows 9 signals 159, 139.4, 127.11, 124.3, 57.7, 54.3, 44.70, 33.8, 31.6 ppm. Corresponding to the 9 types of carbon atoms of the C_8 complex.

The mass spectrometry were in agreement with the structural formula of **[L^5Zn2(μ-Cl)Cl$_2$]**.

However, the aromatic CH_2 protons resonate as a pair of AB doublets at 3.60 and 3.24 ppm; indicating that the complex is chiral.

X-rayCrystallography Themolecularstructure of **[L^5Zn$_2$(μ-Cl)Cl$_2$]** is shown in **Fig. 2**. The complex shows approximate C_2 symmetry about an axis coincident with the C-O vector. The two *N,N* five-membered chelate rings have the same configuration. Selected bond lengths and angles are listed in Table 2.
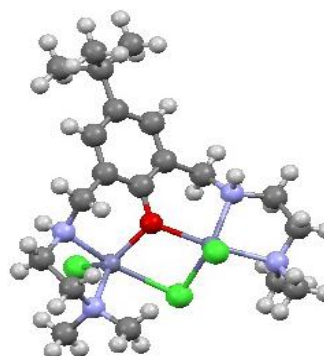

Figure 2: The molecular structure of [L^5Zn2(μ-Cl)Cl$_2$]

Table 2: Selected Bond Lengths (Å) and Angles (°) for [L^5Zn2(μ-Cl)Cl$_2$]^a

Zn(1)-O(1)	1.977(2)	Zn(2)-O(1)	2.056 (2)
Zn(1)-N(1)	2.136(3)	Zn(2)-N(2)	2.127 (3)
Zn(1)-N(3)	2.160(3)	Zn(2)-N(4)	2.195 (3)
Zn(1)-Cl(1)	2.245(9)	Zn(2)-Cl(3)	2.275 (9)
Zn(1)-Cl(2)	2.5637(8)	Zn(2)-Cl(2)	2.383(8)
Zn(1)- O(1)-Zn (2)	111,49 (9)	Zn(2)- Cl(2)-Zn (1)	84,66 (3)
Zn(1)…Zn(2)	3.334		

The zinc centers are both five coordinate with distorted square pyramidal geometries. The bond distances (Table 1) between the phenolate oxygen atom (O(1)) and the two zinc centers are somewhat different, with a shorter phenolate bond (1.977 (2) Å) to Zn(1).

The bond distances between the chlorine (Cl(2)) and the two zinc centers are also different, Zn(1)-Cl(2) (2.5637(8) Å) ; Zn(2)-Cl(2) (2.3830 (8) Å).

The distances between the zinc center (3.370 Å in complexe[L^2Zn$_2$(μ-Cl)Cl$_2$] is significantly longer than those observed for [L^5Zn$_2$(μ-Cl)Cl$_2$].

This effect probably relates to the improved donation from the imine versus amine groups, supported by the reduction in the length of the Zn-N(imine) bonds (between 2.084(3) and 2.058(3) Å) c.f. the Zn-N(amine) counterparts in [L^5Zn$_2$(μ-Cl)Cl$_2$] 2.127 (3) and 2.136(3), and the associated 4.79° widening of the Zn(1)-O(1)-Zn(2) angle.

Zn-O(1) bonds, differ between the complexes in [L^2Zn$_2$(μ-Cl)Cl$_2$] (2.034(3) and 2.166(3) Å) longer than those in [L^5Zn$_2$(μ-Cl)Cl$_2$] 1.977(2) and 2.056 (2) Å), This is accompanied by a much longer Zn(1)-N(1) (2.136 (3) Å) distance in L_5, compared to the Zn(1)-N(1) (2.084(3) Å) distance of L_2, and due to the increased constraint and coordinating strength of the imine units.

[L^nZn$_2$(OAc)$_2$][PF$_6$] (n=1,2,3). The synthesis of the dizinc acetate complexes **[L^nZn$_2$(OAc)$_2$][PF$_6$]. C$_1$, C$_2$, C$_3$** ; was achieved; simply by mixing the ligands imines **L$_1$, L$_2$, L$_3$** and zinc acetate dihydrate in the presence of KPF$_6$ in methanol. **[L^nZn$_2$(OAc)$_2$][PF$_6$]** were prepared in good yield (91-94%)and yielded orange solids. Recrystallization of the crude material yielded a microcrystalline solid.

The ^1H NMR spectrum of **[L^2Zn$_2$(OAc)$_2$][PF$_6$]**, in $CDCl_3$, shows a single aromatic peak at 7.5 ppm. The terminal NMe$_2$ groups are also observed at 2.45 ppm, The protons acetate are observed at 2.02 ppm; The aromatic –CH=N protons resonate at 8.55 ppm; The remaining CH_2 protons in the ethylene diamine units are observed at 3.83 ppm and 2.80 ppm. The t-But Methyl groups are observed at 1.28 ppm.

The ^1H NMR spectrum of the **C$_2$** complex is different from that of the ligand **L$_2$**.

The signals of the remaining CH_2 protons in the ethylene diamine units observed at 2.64 ppm and at 3.74 ppm for the free ligand underwent a shift of + 0.23 and + 0.17 respectively.

The protons of the imine respond to 8.67ppm, ie - 0.12 ppm of shift from their response on the free L_2 ligand.

The ^1H NMR spectrum of the **C$_1$, C$_3$** complexes is very similar, and both complexes are symmetrical.

The ^{13}C NMR spectrum of **C$_2$**, in CDCl$_3$, shows 12 signals at 178.78 ppm (CAr-O), 172.75 ppm (OAc), 166.53 ppm (C = N), 140.24 ppm (Ar), 139.07 ppm (Ar), 120.48 ppm (Ar), 57.61 ppm (NCH2), 52.42 ppm (NCH2), 45.47 ppm (NMe2) 33.69 ppm (C-tBut) 31.07 ppm(tBu) and 22.96 ppm (OAc).[19] corresponding to the 12 types of carbon atoms of the **C$_2$** complex.

The mass spectrometry were in agreement with the structural formula of **[L^{2}Zn$_2$(OAc)$_2$][PF$_6$]**.

The complex was symmetrical, and the singlet observed for the acetate methyl protons suggests the differing acetate groups are in rapid exchange. **[L^{n}Zn$_2$(OAc)$_2$][PF$_6$].** It was relevant to determine whether an acetate group could be exchanged with a noncoordinating counterion, and for these studies the hexafluorophosphate anion was selected as it allows monitoring of the complexation by 1H NMR spectroscopy.

X-rayCrystallography.
Themolecularstructureof **[L^{2}Zn$_2$(OAc)$_2$][PF$_6$]** is shown in **Fig. 3**.

The complex shows approximate **C$_2$** symmetry about an axis coincident with the C-O vector. The two *N,N* five-membered chelate rings have the same configuration. Selected bond lengths and angles are listed in **Table 3**.

Figure 3: The molecular structure of [L^{2}Zn$_2$(OAc)$_2$][PF$_6$].

Table 3: Selected Bond Lengths (Å) and Angles (°) for [L^{2}Zn$_2$(OAc)$_2$][PF$_6$][a]

Zn(1)-O(5)	1.9746 (16)	Zn(2)-O(2)	1.9691(15)
Zn(1)-O(3)	1.9861 (15)	Zn(2)-O(4)	1.9841(16)
Zn(1)-N(1)	2.0298 (19)	Zn(2)-N(3)	2.0253 (18)
Zn(1)-O(1)	2.0862 (14)	Zn(2)-O(1)	2.1062 (14)
Zn(1)-N(2)	2.2023 (18)	Zn(2)-N(4)	2.2154 (18)
Zn(1)- O(1)-Zn (2)	101.71(1)	Zn(1)…Zn (2)	3.246

The zinc centers are both five coordinate with distorted square pyramidal geometries. The bond distances (Table 2) between the phenolate oxygen atom (O(1)) and the two zinc centers are somewhat different, with a shorter phenolate bond (2.0862 (14) Å) to Zn(1).

The distances between the zinc center (3.370Å in complexe [L^{2}Zn$_2$(μ-Cl)Cl$_2$] is longer than those observed for [L^{2}Zn$_2$(OAc)$_2$][PF$_6$] (3.246 Å), may be due to the increased constraint and coordinating strength of the imine units, and presumably due to the presence from acetate groups.

Lactide Ring Opening Polymerization
Lactide zinc initiators have shown some of the fastest rates as well as excellent stereocontrol in lactide polymerization.[12]

[L^{1}Zn$_2$(μ-OEt)Cl$_2$] was shown to be a rapid and controlled initiator, and the Mg(II) and Co(II) analogues were less effective.[9]

With the improved synthesis of **[LnZn$_2$(μ-OEt)X$_2$]** complexes in hand, it was of interest to test the new complexes **[L^{n}Zn$_2$(μ-OAc)$_2$][PF$_6$]** et **[L^{n}Zn$_2$(μ-Cl)Cl$_2$]** as initiators for lactide polymerization (tableau).

The polymerizations of DL-lactide initiated by the zinc complexes were carried out for three hours, at 110 ° C., in dichloromethane in the presence of benzyl alcohol (BnOH) **Schéma 5**.

Schéma 5: Polymerization of DL-lactide initiated by zinc complexes in the presence of BnOH.

Table 4: Polymerization of DL-lactide.[a]

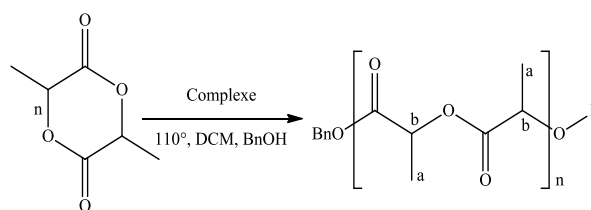| Initiators	[LA]/[I]	(BnOH/[I]	Time (h)	Conv. (%)	$M_{n,calc}$ (g.mol^{-1})	M_n (g.mol^{-1})	M_w/M_n
$([L^2Zn_2(\mu\text{-}Ac)_2][PF_6])$	200	10	3	98	2822	6559	1.36
$[L^1Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	97	2793	6172	1.24
$[L^2Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	97	2793	6080	1.33
$[L^4Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	99	2851	4704	1.34
$[L^5Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	99	2851	2167	1.49
$[L^2Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	95	2736	3136	1.31
$[L^1Zn_2(\mu\text{-}Cl)Cl_2]$	200	10	3	97	2793	3472	1.36

- The conversion is calculated by integration of the signal corresponding to the CH of the lactide (around 5 ppm) with respect to the signals of the CH of the polymer.
- The values of the Mnexp masses (g.mol^{-1}) are determined by calibration with standard samples of polystyrene, corrected by the correction coefficient proposed by Duda and Penczek [5] Mnexp CES = MnCES / PS.0,58

CONCLUSION
We have synthesized and characterized by various spectroscopic methods, including X-ray crystal structures, eight dinuclear zinc complexes (C1, C2, C3, C4, C5, C6, C7 and C8).

Zinc dinuclear trichloride complexes $[L^nZn_2 (\mu\text{-}Cl) Cl_2]$ (C4, C5, C6, C7 and C8) were treated with sodium methanolate. This quantitatively results in the substitution of the chloride-based bridging group to give $[L^nZn_2 (\mu\text{-}OMe) Cl_2]$.

zinc dinuclear complexes have been involved in the lactide ring-opening polymerization reaction.

They all showed good activity and good efficiency in controlling the properties of the polymer.

PLA is characterized by proton nuclear magnetic resonance. The number-average molar masses Mn, the weight-average molar masses Mw, and the polymolecularity indices (Mw / Mn) are measured by size exclusion chromatography (SEC) at 35°C.

Experimental Section
Full experimental details for ligand, complex and polymer syntheses can be found in the Supporting Information; however, some examples of our ligand, complex and polymer syntheses are given here.

L$_1$. In a flask with stir bar was charged with 5-chloro-2-hydroxyisophthalaldehyde (100 mg; 0.543 mmol), N, N-dimethylethylene-1,2-diamine (0.12 mL; 1.196 mmol), 20 mL of absolute ethanol, and 10 mol% NH$_4$PF$_6$.

The mixture is heated to reflux (80 ° C.) and stirred for 2 h. After cooling, the solvent is evaporated on a rotary evaporator.

The product obtained is dissolved in ether. After concentration and drying under vacuum yielded a yellow paste (78%).

RMN ^{1}H (400MHz, CDCl$_3$): δ 8.51 (s, 2H, -CH=N) 7.59 (s, 2H, Ar-H), 3.73 (t, J= 6,6Hz, 2H), 2.63 (t, J=6.7Hz, 2H), 2.30 (s, 12H, -N-(CH$_3$)$_4$) ppm.

RMN ^{13}C (400MHz, CDCl$_3$) : δ 163.5, 159.5, 130.3, 122.1, 121.6, 58.8, 57.3, 44.7 ppm.
IR (v, cm^{-1}) : 2941, 2818, 2768, 2117, 1637, 1444, 1361, 1361, 1252, 1213, 1184, 1155, 1040, 992, 872, 843,781, 758, 701cm^{-1}.

HRMS (m/z): [M+H]$^+$ calculée C$_{16}$H$_{26}$N$_4$OCl: 325.1795; trouvée: 325.1785.

L4. In a flask with stir bar was charged with **L$_1$** (127 mg, 0.391 mmol), 10 ml de THF, LiAlH$_4$ (32.64 mg, 0.860 mmol, 2.2 equiv.) Is gradually added to the flask at 0°C. The mixture is stirred at room temperature for 1 hour, 10mL of dichloromethane are added at the end of the reaction.

Saturated solution of NaSO$_4$ is added dropwise until a precipitate of aluminum and lithium salts is formedAfter filtration and concentration, the product is dried under vacuum and a yellow paste is obtained with a yield of 92%.

RMN ^{1}H (400MHz, CDCl$_3$): δ 6.98 (s, 2H, Ar-H), 3.81 (s, 4H, Ar-CH$_2$), 2.67 (t, J= 5,8Hz, 2H), 2.42 (t, J= 5,9Hz, 2H), 2.19 (s, 12H,-N-(CH$_3$)$_4$) ppm.

RMN ^{13}C (400MHz, CDCl$_3$): δ 155.3, 127.5, 126.2, 122.9, 58.6, 50.4, 46.2, 45.7 ppm.
IR (v, cm^{-1}): 2941, 2818, 2768, 2344, 2116, 1635, 1455, 1401, 1268, 1233, 1156, 1117, 1098, 1040, 990, 970, 937, 867,774, 731 cm^{-1}.

HRMS (m/z): [M+H]$^+$ calculée C$_{16}$H$_{30}$N$_4$OCl: 329.2108; trouvée: 329.2099.

[L^{1}Zn$_2$(OAc)$_2$][PF$_6$]. In a flask with stir bar was charged with 4-chloro-2,6-bis((*E*)-((2-(diméthylamino) éthyl) imino) phénol (50 mg, 0.154 mmol) (**L$_1$**), zinc acétate dihydrate (Zn(OAc)$_2$·2H$_2$O) (67 mg, 0,308 mmol), and KPF$_6$ (53 mg, 0.154 mmol) in 5 mL de méthanol. The

mixture is stirred at room temperature for 2 hour. After concentrating the solution by half, diethyl ether is added until a precipitate forms. After filtration, orange solid is obtained with a yield of 92% and then recrystallized by slow diffusion in a chloroform pentane mixture.

RMN ^{1}**H** (400MHz, CDCl$_3$): δ 8.45 (s, 2H, -CH=N), 7.30 (s, 2H, Ar-H), 3.87 (t, 4H, =N-CH$_2$-), 2.81 (t, 4H, -CH$_2$-N), 2.5 (s, 12H, -N-(CH$_3$)$_4$), 2.02 (s, 6H, OA$_C$) ppm.

RMN ^{13}**C** (400MHz, CDCl$_3$): δ 180.1, 1715, 167.0, 141.2, 122.3, 120.0, 57, 60, 52.5, 45.5, 23.5 ppm.

HRMS (m/z): [M+H]$^+$ calculée C$_{20}$H$_{30}$N$_4$O$_5$Zn$_2$: 569.0488; trouvée : 569.0469.

[L^{1}Zn$_2$(µ-Cl)Cl$_2$]. In a flask with stir bar was charged with 4-chloro-2,6-bis((E)-((2-(diméthylamino) éthyl) imino) phénol (80 mg, 0.246 mmol) (**L$_1$**) and méthanolate de sodium (14.6 mg, 0.271 mmol) in 5mL de méthanol. After 15 min of stirring, zinc chloride (74 mg, 0.543 mmol) is added. A yellow solid precipitated, Stirring is maintained for 1 hour, the the mixture was filtered and the precipitate dissolved in dichloromethane and filtered through Celite to remove the potassium salts yielded a yellow solid (75%).

RMN ^{1}**H** (400MHz, CDCl$_3$): δ 8.29 (s, 2H, -CH=N), 7.35 (s, 2H, Ar-H), 3.73 (t, 8H, -CH$_2$-N and =N-CH$_2$-), 2.59 (s, 12H, -N-(CH$_3$)$_4$) ppm.

RMN ^{13}**C** (400MHz, CDCl$_3$): δ 168.31, 139.07, 163.20 (C=N), 149.02 (Ar), 127.63 (Ar), 120.94 (Ar), 57.16, 52.20 ppm.

IR (v, cm^{-1}): 3563, 2968, 2887, 2322, 1645, 1547, 1455, 1440, 1403, 1328, 1257, 1223, 1165, 1071, 1023, 952, 889, 778,762, 735, 697cm^{-1}.

[L^{5}Zn2(µ-Cl)Cl$_2$]. The complex was synthesized according to the same operating mode as **[L^{1}Zn$_2$(µ-Cl)Cl$_2$]**, yellow solid is obtained with a yield of 80%.

RMN ^{1}**H** (400MHz, CDCl$_3$): δ 6.96 (s, 2H, Ar-H), 3.60 (m, 2H, ArCH$_2$), 3.24 (m, 2H, ArCH$_2$), 2.85 (m, 4H, NCH$_2$), 2.61 (s, 12H, N-(CH$_3$)$_4$), 2.50 (m, 2H, NCH$_2$), 2.23 (m, 2H, NCH$_2$), 1.22 (s, 9H, C-tBu) ppm.

RMN ^{13}**C** (400MHz, CDCl$_3$): δ 159, 139.4, 127.11, 124.3, 57.7, 54.3, 44.70, 33.8, 31.6 ppm.

IR (v, cm^{-1}): 3207, 2963, 2867, 2101, 1653, 1609, 1479, 1455, 1364, 1310, 1271, 1221, 1088, 1029, 930, 891, 872, 829, 775, 764 cm^{-1}.

Polymer: To a DCM (0.5 mL) solution of complex [LnZn$_2$ (µ-Cl) Cl$_2$] (0.003 mmol), was added sodium methoxide (0.25 mg, 0.004 mmol) under an argon atmosphere. The resulting mixture was stirred for 30 min.

Benzyl alcohol (0.0036mL, 0.034mmol) and DL-lactide (0.100mg, 0.69mmol) were added, The resulting mixture was heated at reflux (110°C) for 3 h.

Then the resulting mixture was stopped by cooling at 0°C. The conversion is determined by 1 H NMR analysis of the crude mixture.

The crude mixture was dissolved in DCM (0.5 mL), the polymer was precipitated in of ice-cold ethanol (2.5 mL). The recovered product by drying under vacuum, was precipitated again from a suitable mixture of diethyl ether and pentane.

Then the polymer was analyzed by exclusion chromatography.

Conversion (97%)
RMN ^{1}**H** (400MHz, CDCl$_3$) : δ 7.35 (m, BnOH), 5.17 (m, 1H, H^a), 4.34 (q, 1H, H^c), 1.57(m, 3H, H^b) ppm.

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