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DESIGNING CATIONIC ZINC AND MAGNESIUM CATALYSTS FOR COORDINATION–INSERTION POLYMERIZATION OF LACTIDE

CRAIG A. WHEATON and PAUL G. HAYES

Department of Chemistry and Biochemistry,
University of Lethbridge, Lethbridge, Alberta, Canada

This review presents a synopsis of the development of cationic zinc and magnesium metal complexes as catalysts for the polymerization of lactones, with the major focus being directed toward the polymerization of lactide. By utilizing an electron-rich, neutral bis(phosphinimine) pincer ligand, cationic complexes with high ambient temperature activity for polymerization of lactide were obtained for the first time. A number of important structure–activity relationships have been established for this new class of catalyst. Recent progress toward P-stereogenic analogues of these cationic catalysts is also summarized.

***Keywords*: catalysis, cation, lactide polymerization, magnesium, zinc**

1. INTRODUCTION

Polylactide (PLA), a biodegradable polymer prepared by the ring-opening polymerization (ROP) of lactide (LA), is increasingly being touted as a viable alternative to conventional, petrochemically derived plastics.[1] In fact, PLA is currently being produced and marketed by Natureworks LLC, a subsidiary of Cargill, in a process that uses corn as the feedstock for the production of LA monomers.[2] Currently, the

Address correspondence to Paul G. Hayes, Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, Alberta, Canada T1K 3M4. E-mail: p.hayes@uleth.ca

initiator used to prepare polylactide for commodity applications on an industrial scale is stannous octoate. This system, however, suffers from a number of drawbacks, including poor molecular weight and stereocontrol, and growing public concern regarding potential toxicity. Thus, enhanced interest in polylactide has stimulated intensive research efforts aimed at the development of new types of homogeneous metal catalysts for the ROP process.[3]

Vigorous activity in the development of homogeneous lactide polymerization catalysts began in the late 1990s with the seminal contributions of Coates et al.[4] and Chisholm and co-workers.[5] Their publication of well-defined zinc, magnesium, and calcium alkoxides stabilized by β-diketiminate and tris(pyrazolylborate) ancillary ligands (Figure 1), respectively, as well as Spassky[6] and Feijen's[7] reports of Al complexes capable of highly stereocontrolled polymerizations, revolutionized the field. Indeed, this work spawned a tremendous amount of progress, which continues today and has, for the most part, been extensively reviewed.[3] Catalysts based on Zn and alkaline earth metals,[8] rare earth metals,[9] and group 13 metals[10] have proven especially promising, and as such, have been thoroughly studied. Complexes of alkali metals,[11] group 4 metals,[12] and Fe[13] have also shown potential. As we have previously noted,[3d] such catalysts are typically metal alkoxides stabilized by a formally anionic ligand. The use of cationic metal complexes for this process, however, is rare. We therefore chose to pursue cationic complexes in an effort to open the field to a new class of lactide polymerization catalyst with unique electronic properties. The idea for this work was partly inspired by the revolutionary effect that cationic complexes had on olefin polymerization catalysis.[14]

Prior to initiating our work, there were virtually no examples of cationic single-site metal catalysts for lactide polymerization, although

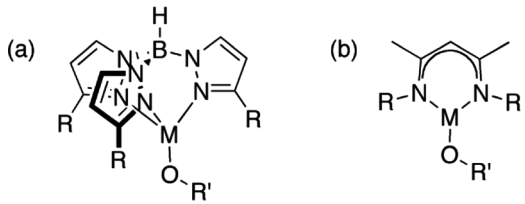


Figure 1. General structures of metal-alkoxide complexes of (a) tris(pyrazolylborate and (b) β-diketiminate ancillary ligands.

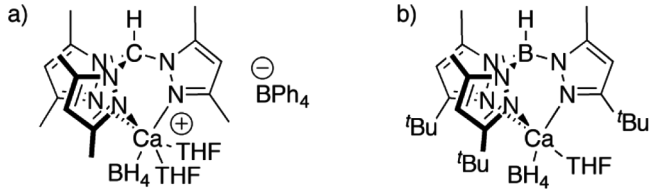
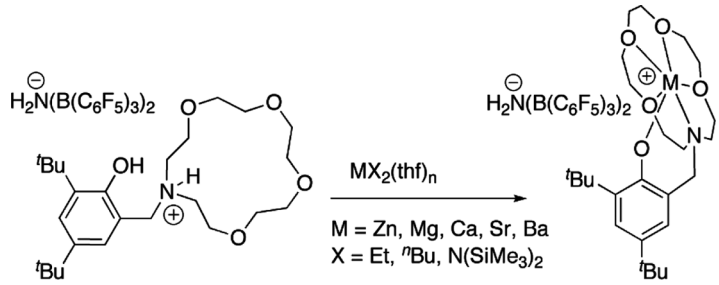


Figure 2. (a) A cationic calcium complex of a tris(pyrazolyl)methane ligand; (b) a directly analogous neutral calcium complex of a tris(pyrazolyl)borate ligand.

a few reports have appeared in recent years.[15,16] Specifically, Mountford et al. have studied a cationic calcium borohydride complex[15a] stabilized by a neutral tris(pyrazolyl)methane ligand (Figure 2a). The complex exhibited excellent lactide polymerization activity at ambient temperature, giving reasonable conversion of 250 equivalents of monomer to polymer in two hours. The polymer molecular weight, as determined by gel permeation chromatography (GPC) (43.2 kg mol^{-1}), agreed well with calculated values (32.8 kg mol^{-1}) and had a narrow polydispersity index (PDI = 1.2–1.4). Interestingly, an analogous neutral complex supported by an anionic tris(pyrazolyl)borate ligand (Figure 2b) was also investigated. This complex was found to be much more active, although molecular weight control was relatively poor at ambient temperature.

Carpentier and co-workers examined a variety of cationic zinc and alkaline earth metal complexes stabilized by a monoanionic phenolate ligand bearing a pendant crown-ether functionality (Scheme 1).[16b] Despite the absence of a traditional initiating group, these complexes, which operate via an activated monomer mechanism, displayed modest



Scheme 1. Preparation of cationic zinc and alkaline earth metal complexes of a doubly acidic phenol-based pro-ligand.

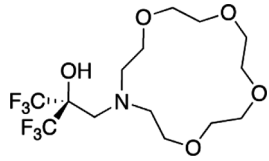


Figure 3. A modified alkoxide ligand used for the preparation of cationic zinc and alkaline earth metal complexes.

activity for the polymerization of L-lactide in the presence of ^{i}PrOH cocatalyst. While polymerization activity was generally found to correlate with the ionic radius of the metal, the calcium complex displayed the most desirable combination of activity and control. This complex achieved 90% conversion of 1000 equivalents of monomer in 11 hours at 60°C when 11 equivalents of ^{i}PrOH were employed. The polymerization proceeded in an immortal fashion, giving very narrow PDIs (1.05–1.08) and molecular weights (as determined by GPC) (13.0 kg mol^{-1}) remarkably close to that predicted (12.9 kg mol^{-1}).

More recently, the group published a study of zinc and alkaline earth complexes of a similar ligand in which the phenolate moiety was replaced by an alkoxide functionality containing electron withdrawing CF_3 groups (Figure 3).[16a] In this case, the Sr complex was most efficient, and when 5 equivalents of $PhCH_2OH$ cocatalyst were utilized, up to 85% of 2000 equivalents of lactide was polymerized in 24 hours at 100°C. Immortal polymerization characteristics were also evident for this family of catalysts. Overall, however, Ca, Sr, and Ba complexes of this new system were significantly less active than their phenolate analogues. The authors attributed this decreased activity to the presence of secondary metal $\cdots$ fluorine interactions, which were proposed to make monomer coordination less kinetically favorable.

Herein we describe our contribution to the progression of well-defined cationic zinc and magnesium complexes, from design and synthesis to highly active lactide polymerization catalysts.

1.1. Catalyst Design

Due to low toxicity and cost, as well as exceptional lactone polymerization properties,[8] the divalent metals zinc and magnesium were chosen as ideal initial candidates for our investigation of cationic metal

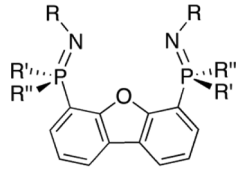


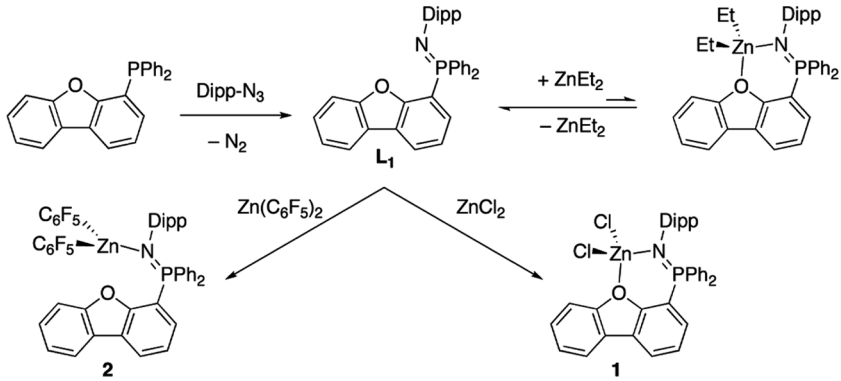
Figure 4. General structure of a dibenzofuran-based bis(phosphinimine) pincer ligand.

complexes. It was envisioned that by coupling these metals with a suitable initiating group and ancillary ligand set, ambient temperature polymerization of lactide via a coordination–insertion mechanism could, for the first time, be achieved at a formally cationic metal center.

In order to prepare a cationic complex of zinc or magnesium bearing an appropriate initiating group, it was necessary to first design and prepare a strongly donating, neutral ancillary ligand. Ligand neutrality was required so that a single anionic initiating group could be installed at the remaining valence of the cationic metal where the coordination–insertion process would take place. Phosphinimine donors were targeted, as they are known to be strongly electron donating,[17] chemically robust, highly modular, and conveniently studied by ^{31}P NMR spectroscopy. A chelating scaffold was then conceived whereby phosphinimine groups were placed at the 4 and/or 6 positions of a dibenzofuran (dbf) backbone (Figure 4), which was crucial for ensuring ligand rigidity and chemical robustness, as well as providing an additional hemilabile oxygen donor.

2. MONO(PHOSPHINIMINE) LIGAND

For a variety of reasons, including simplicity of synthesis and preliminary scoping studies, a monophosphinimine ligand was first chosen as an appropriate ancillary to support cationic zinc[18] and magnesium complexes. Installation of one phosphinimine functionality on dibenzofuran was readily achieved by a Staudinger[19] reaction between 4-(PPh_2)-dibenzofuran[20] and 2,6-di*iso*propylphenylazide (Dipp-azide),[21] giving L_1 in high yield and purity (Scheme 2). Initial experiments were aimed at exploring the reactivity of this neutral bidentate ligand with commercially available zinc species in order to assess its binding properties (Scheme 2). It was hoped that formation of neutral complexes with the general formula LMR_2 would be useful precursors for the generation of cationic complexes via alkide abstraction, upon reaction with



Scheme 2. Synthesis of a neutral bidentate monophosphinimine ligand and neutral zinc complexes thereof.

Brønsted (e.g., $[H(OEt_2)_2][B(C_6F_5)_4]$) or Lewis acids (e.g., $B(C_6F_5)_3$).[14a,22]

2.1. Complexation Studies

Surprisingly, it was found that diethylzinc does not bind irreversibly to $\mathbf{L_1}$, but rather the two molecules exist in equilibrium that favors the free starting materials.[23] Therefore, the more electron-deficient zinc species $ZnCl_2$ and $Zn(C_6F_5)_2$ were employed to determine if increased Lewis acidity would promote the formation of tightly bound complexes. This was indeed determined to be the case, and in this way, complexes **1** and **2** were prepared. Crystallographic studies (Figure 5) revealed strong binding of the zinc center by the phosphinimine nitrogen in both compounds, although coordination of the dbf oxygen only occurred to a significant degree with $ZnCl_2$, and even in this complex the Zn–O contact was relatively long [Zn(1)–O(1) = 2.381(1) Å]. In contrast, the Zn–O bond of a typical zinc-alkoxide is closer to 2.0 Å in the case of a bridging oxygen (e.g., average of 2.109 Å for the ^{t}BuZnO^{t}Bu tetramer),[24] and often much less than 2.0 Å for a terminal alkoxide (e.g., 1.800(5) Å for a β-diketiminate–ZnO^{t}Bu complex).[25]

Due to the lack of success in preparing cationic zinc complexes through a traditional route, alternate synthetic strategies were pursued. Ultimately, it was established that cationic zinc complexes are most effectively prepared by the straightforward path outlined in Scheme 3,

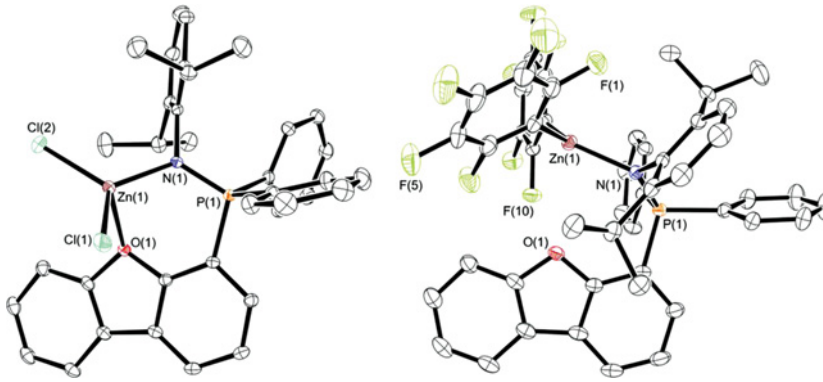
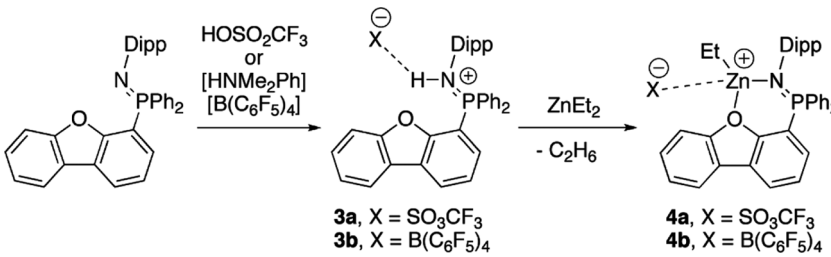


Figure 5. Displacement ellipsoid plots (30% probability) of complexes **1** (left) and **2** (right), with hydrogen atoms omitted for clarity. (Color figure available online.)

which is similar to that previously exploited by Bochmann et al. for the generation of cationic zinc complexes of an α-diimine ligand (Figure 6).[26] The ligand was first reacted with a suitable Brønsted acid, giving the N-protonated aminophosphonium salts **3a**/**3b**. Isolation of these salts provided access to an alkane elimination complexation route. In this way, **3a** and **3b** were reacted with diethylzinc to afford the corresponding cationic complexes **4a** and **4b** in excellent yield and purity.[18] The triflate counterion imparted sufficient crystallinity in **3a** and **4a** to render X-ray crystal structure determination of both compounds possible (Figure 7). The structure of **3a** verified the location of the acidic proton, while the structure of **4a** confirmed the formation of a ligand-bound metal complex. Despite the fact that the triflate moiety was coordinated to the zinc center in the solid-state structure of **4a**,



Scheme 3. Synthesis of cationic zinc-alkyl complexes of a chelating monophosphinimine ligand.

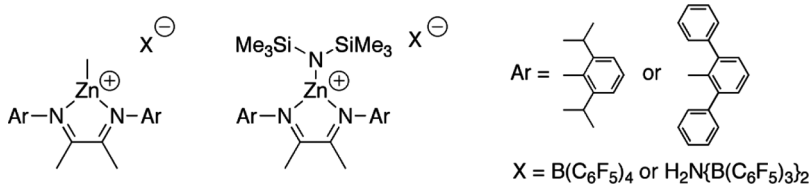


Figure 6. Cationic zinc complexes of an α-diimine ligand prepared by Bochmann et al.

the compound can still be regarded as "activated" due to the possibility of displacement of the anion by small molecules such as lactide. Furthermore, examination of **4b** by multinuclear NMR spectroscopy argued against the presence of a contact ion pair in solution.[27]

2.2. Polymerization Studies Using Cationic/Activated Species

It has been well established that alkyls are poor initiating groups for lactide polymerization, and alkoxides generally lead to much higher activities.[3] However, zinc-alkoxide analogues of **4a** and **4b** could not be obtained. For this reason, the efficacy of the zinc-alkyl complexes **4a** and **4b** as lactide polymerization catalysts was investigated.[18] Disappointingly, preliminary polymerization experiments demonstrated that both species displayed relatively poor activity. Under the conditions employed ($[LA]_0/[\mathbf{4}] = 100$, $[LA]_0 = 0.5$ M, C_6H_6/C_6H_5Br solvent), **4a** required 9 hours to reach 85% conversion to PLA, while **4b** took only 6 hours to achieve 90% conversion

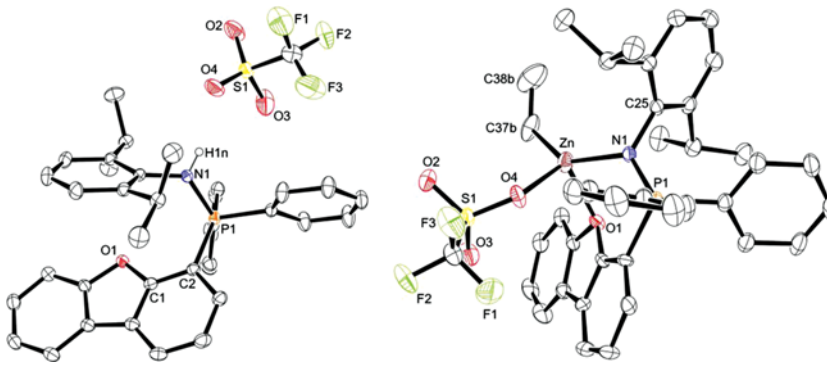


Figure 7. Displacement ellipsoid plots (30% probability) of the aminophosphonium salt **3a** (left) and the activated zinc complex **4a** (right), with hydrogen atoms and disordered atomic positions omitted for clarity. (Color figure available online.)

Table 1. Polymerization of L-lactide using **4a** and **4b** (Conditions: $T_{rxn} = 100°C$; $[LA]_0/[4] = 200$, $[LA]_0 = 0.50$ M, 1:1 C_6H_6/C_6H_5Br solvent)

Catalyst	Time (h)	Conversion (%)
4a	9	85
4b	6	90

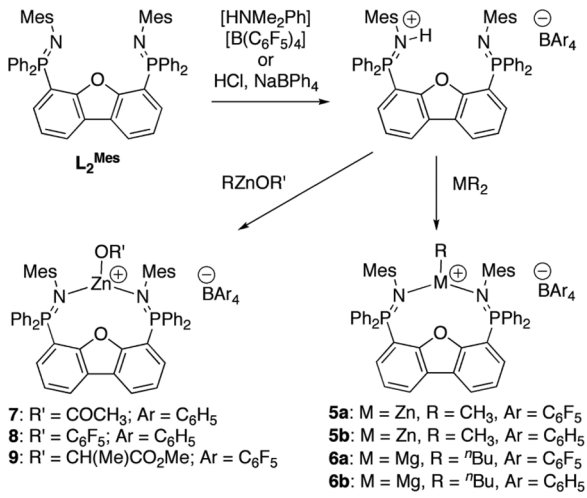
under the same conditions (Table 1). The resultant polymers were analyzed by gel-permeation chromatography, which indicated a maximum molecular weight of 5000 g mol^{-1} and a bimodal molecular weight distribution. These results were suggestive of relatively high rates of numerous unwanted reactions, such as inter- and intramolecular transesterification and chain-transfer. It is, however, interesting to note the comparatively low activity of **4a**, which suggests that competitive coordination of the triflate anion has a negative impact on catalytic activity. Overall, the results led us to further pursue the development of cationic zinc complexes incorporating more suitable initiating groups and the more strongly donating bis(phosphinimine) ancillary ligand.

3. BIS(PHOSPHINIMINE) LIGAND

Due to the poor properties of cationic zinc complexes of the monophosphinimine framework, the related bis(phosphinimine) scaffold ($\mathbf{L_2}$) was pursued. It was expected that this modification would alleviate low polymerization activity while allowing alkoxide initiating groups to be installed with greater ease. Such ligands were readily prepared by reaction of 4,6-$(PPh_2)_2$-dibenzofuran[20] with two equivalents of an aryl azide.[28] Initial investigation focused on the derivative $\mathbf{L_2^{Mes}}$, which bears 2,4,6-trimethylphenyl (Mes) N-aryl groups.

3.1. Complexation Studies of Zn and Mg

The previously described protonation–alkane elimination strategy was applied to the synthesis of cationic zinc and magnesium complexes of $\mathbf{L_2^{Mes}}$ (Scheme 4).[28,29] Both $B(C_6F_5)_4^-$ and BPh_4^- counterions were employed in some cases, as it was reasoned that the former would provide superior stability, while the latter would offer enhanced crystallinity to aid X-ray crystal structure determination. Reaction of these salts with dimethylzinc generated the expected cationic zinc-methyl compounds **5a**



Scheme 4. Synthesis of cationic Zn and Mg complexes of the ligand L_2^{Mes}.

and **5b**, of which the latter was characterized crystallographically (Figure 8). The structure revealed the zinc center was bound to both phosphinimines symmetrically, but did not interact with the dibenzofuran oxygen atom, resulting in trigonal planar coordination geometry. The ligand adopts a C_2-symmetric orientation in which the mesityl groups are orientated in opposite directions away from the plane of the dbf backbone. The magnesium complexes **6a** and **6b** were similarly prepared by reaction of the aminophosphonium salts with

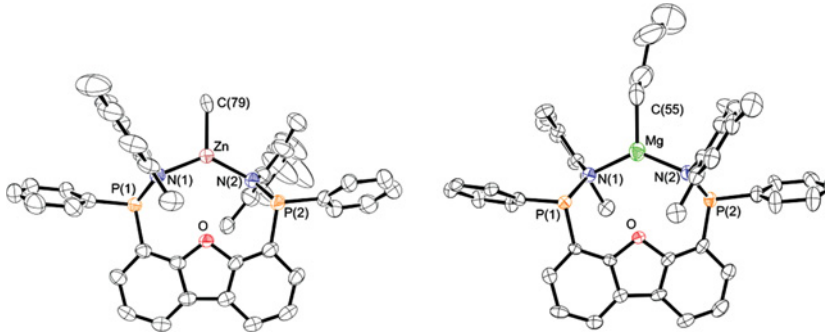


Figure 8. Displacement ellipsoid plots (30% probability) of the cations of **5b** (left) and **6b** (right), with hydrogen atoms and disordered atomic positions omitted for clarity. (Color figure available online.)

di*n*butylmagnesium.[28] The molecular structure of **6b** (Figure 8) was determined, establishing the complex to be isostructural with the zinc analogue **5b**.

In an effort to install non-alkyl initiating groups, reactions between the requisite aminophosphonium salts and zinc precursors of the general formula $[RZnOR']_x$ (e.g., R = Me, Et; R' = Me, ^{i}Pr, ^{t}Bu) were undertaken. Unfortunately, such attempts were only successful for metal complexes with electron deficient OR' groups (e.g., R' = $COCH_3$, C_6F_5). In this way, cationic zinc-acetate (**7**) and zinc-aryloxide (**8**) complexes were obtained (Scheme 4). The X-ray crystallographic studies of these compounds (Figure 9) revealed solid-state structures similar to **5b** and **6b**, in which the ligand adopts a C_2-symmetric orientation and the metal center is bound to the ancillary ligand only by the phosphinimine nitrogen atoms.

3.2. Polymerization Studies

3.2.1. Polymerization of Rac-Lactide. Regrettably, it was found that neither of the metal-alkyl cations (**5** and **6**) were active catalysts for the ring-opening polymerization of lactide. No reactivity was observed upon exposure of these complexes to lactide at ambient temperature, while more forcing conditions (70°C) promoted complex decomposition. Both the acetate and perfluorophenoxide derivatives **7** and **8** were also determined to be inactive for ROP of lactide, and thus, these initiating groups were deemed unsuitable.

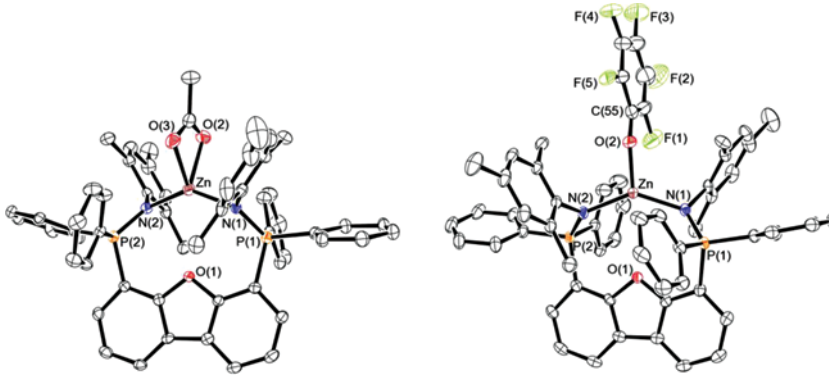


Figure 9. Displacement ellipsoid plots (30% probability) of the cations of **7** (left) and **8** (right), with hydrogen atoms and disordered atomic positions omitted for clarity. (Color figure available online.)

In an effort to ascertain whether the lack of reactivity of these complexes was solely a result of initiating group effects, attempts were made to prepare an analogous zinc complex bearing a methyl-lactate initiating group, which is an excellent structural and electronic mimic of a growing polymer chain. It was reasoned that such a species would likely exhibit a rate of initiation similar to that of propagation, as has been observed for several neutral zinc complexes.[4b] Reaction of the protonated ligand with EtZn(methyl-lactate) gave partial conversion to the desired product, yielding [L_2^{Mes} Zn(methyl-lactate)][$B(C_6F_5)_4$] (**9**) in approximately 85% purity, in addition to the zinc-ethyl complex [L_2^{Mes}ZnEt][$B(C_6F_5)_4$] as a major byproduct. Although the purity of the compound could not be improved despite repeated efforts, the alkyl byproduct was already known to be inactive, and thus the efficacy of **9** as a lactide polymerization catalyst was examined. Compound **9** displayed good activity under relatively mild conditions (60°C in C_6H_5Br) at an initial monomer concentration of 0.25 M and a catalyst loading of 2%, giving 90% conversion of LA to PLA within 3.5 hours (Table 2). End-group analysis (MALDI-ToF mass spectrometry and NMR spectroscopy) provided clear evidence of methyl-lactate end group incorporation, which is

Table 2. GPC data for polymer samples prepared from **9**, **14–16**, and **18** (Conditions: $[LA]_0 = 1.0$ M, CH_2Cl_2 solvent. Notable exceptions are listed in the table footnote)

	T_{rxn} (°C)	Time (min)	$[LA]_0/[I]$	Conv. (%)	$M_{n,calc}$ (kg mol^{-1})[b]	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	P_r
9[a]	60	210	50	90	6.6	18.5	22.6	1.22	–
14	40	480	200	90	26.0	18.0	24.7	1.37	0.61
15	25	60	200	98	28.3	28.7	33.0	1.15	0.63
16	25	75	200	97	28.1	18.9	25.8	1.36	0.70
18	25	30	200	96	27.8	18.9	23.5	1.24	atactic
15	25	60	100	99	14.4	12.9	17.3	1.34	–
15	25	90	300	92	39.9	35.0	37.8	1.08	–
15	25	150	400	90	52.0	33.4	36.5	1.09	–
15	25	150	500	98	70.7	41.9	50.7	1.21	–
15	25	300	1000	99	142.8	49.9	63.4	1.30	–
18	25	20	100	90	13.1	10.2	12.6	1.25	–
18	25	45	300	96	41.6	17.3	24.2	1.39	–
18	25	60	400	92	53.1	19.7	28.2	1.43	–
18	25	75	500	71	51.3	23.4	31.0	1.32	–

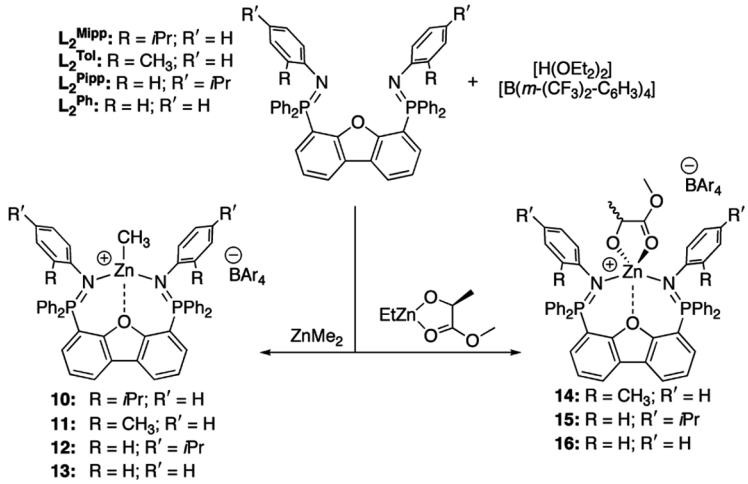
[a] $[LA]_0 = 0.25$ M, C_6H_5Br solvent.
[b] Calculated using $M_n = [([LA]_0/[I]) \times 144.13 \times \text{conversion}] + 104.1$.

consistent with a coordination-insertion polymerization mechanism. Furthermore, GPC studies of the polymer revealed reasonable molecular weight control (PDI = 1.2–1.3), although the molecular weights were large compared to the theoretical values ($M_{n,calc} = 6.6\,kg\,mol^{-1}$, $M_{n,GPC} = 18\,kg\,mol^{-1}$). Overall, it was successfully demonstrated that installation of a suitable initiating group causes these cationic zinc complexes to be active in the polymerization of lactide. It should be noted, however, that MALDI-ToF analysis gave a peak separation of 72 u, which is indicative of a significant rate of transesterification.

3.2.2. Polymerization of ε-caprolactone. The efficacy of the metal-alkyl complexes **5** and **6** for polymerization of ε-caprolactone was also probed. While the zinc compound **5** was inactive for this transformation, complex **6** proved capable of initiating the polymerization of ε-caprolactone very rapidly.[28] With a catalyst concentration of 4 mM and a monomer to initiator ratio of 130, 90% conversion of ε-caprolactone to polycaprolactone was achieved in 4 minutes at ambient temperature. The resulting polymer had a much higher than expected molecular weight ($M_n = 120\,kg\,mol^{-1}$, $M_{n,calc} = 48\,kg\,mol^{-1}$) and a broad molecular weight distribution (PDI = 1.6). Cooling to 0°C, at a reduced catalyst concentration (2.1 mM), still resulted in very rapid polymerization, giving 73% conversion to polymer in 4 minutes. Because of the extremely high activity at low temperature, which is often an indication of a cationic polymerization (i.e., activated chain end[30]), end-group analysis of the polymers was performed to gain insight into the mechanism. In-situ NMR analysis of polymerization reactions revealed an immediate and quantitative change in the chemical shifts of the signals associated with the ^{n}Bu end group. However, after workup of the polymer, no signals associated with the ^{n}Bu group could be observed in the ^{1}H NMR spectrum, suggesting that the ^{n}Bu moiety was not incorporated as the end group of the polymer chains. It was thus concluded that **6** likely initiates the polymerization of ε-caprolactone via an activated chain end mechanism.

4. STERIC MODIFICATIONS

The successful preparation of the moderately active zinc-lactate complex **9** prompted us to further pursue this chemistry by examining a series of



Scheme 5. Preparation of zinc-alkyl and zinc-lactate complexes of sterically modified ligands (Ar = 3,5-$(CF_3)_2C_6H_3$ (**10–16**) or BPh_4 (**10–13**)).

bis(phosphinimine) ligands with reduced steric bulk in hope of further improving the activity. Therefore, four variants of the ligand were examined, in which at least one *ortho* position of each N-aryl group was left unsubstituted. Specifically, ligands with a single *ortho* ^{i}Pr ($\mathbf{L_2^{Mipp}}$) or methyl ($\mathbf{L_2^{Tol}}$) group, a variant with a *para* ^{i}Pr substituent ($\mathbf{L_2^{Pipp}}$), and an example with unsubstituted N-phenyl groups ($\mathbf{L_2^{Ph}}$) were employed (Scheme 5).[31]

4.1. Synthesis and Characterization of ZnMe Complexes

Using the protonation–alkane elimination route, the zinc-methyl complexes **10–12** were prepared and structurally characterized to gain insight into the effect that steric changes have on the complex geometries. The structural studies were again aided by the synthesis of highly crystalline BPh_4^- salts. In this way, the molecular structures of **10-BPh$_4$**, **11-BPh$_4$**, and **12-BPh$_4$**, which are displayed in Figures 10 and 11, were obtained. The major finding of these structural studies is the continued absence of a Zn–O bonding interaction in the case of the bulkier ligands $\mathbf{L_2^{Mipp}}$ and $\mathbf{L_2^{Tol}}$. Interestingly, the ligand in the bulkier analogue **10-BPh$_4$** adopts a C_s symmetric (*anti*) orientation, while the ligand in **11-BPh$_4$** is C_2 symmetric (*syn*), analogous to the complexes of $\mathbf{L_2^{Mes}}$. Solution NMR studies

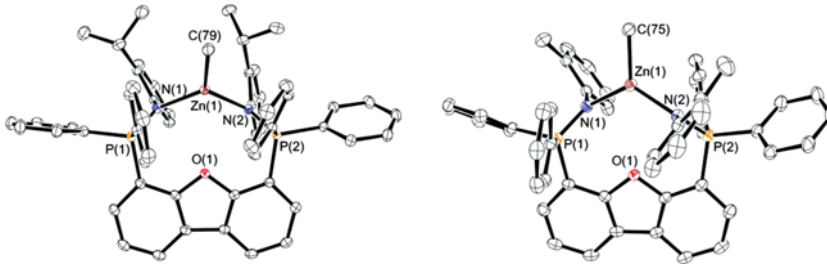


Figure 10. Displacement ellipsoid plots (30% probability) of the cations of **10-BPh$_4$** (left) and **11-BPh$_4$** (right), with hydrogen atoms and disordered atomic positions omitted for clarity. (Color figure available online.)

have shown **10** is held rigidly in the C_2 orientation, while **11** is more fluxional, equally populating both the *anti* and *syn* geometries in solution (Scheme 6).

In contrast, on determination of the solid-state structure of **12-BPh$_4$**, it was discovered that reduction in steric bulk allows the pincer ligand to coordinate in a tridentate mode, as evidenced by a significant zinc–oxygen bonding interaction (Figure 11). While the Zn–O distance of

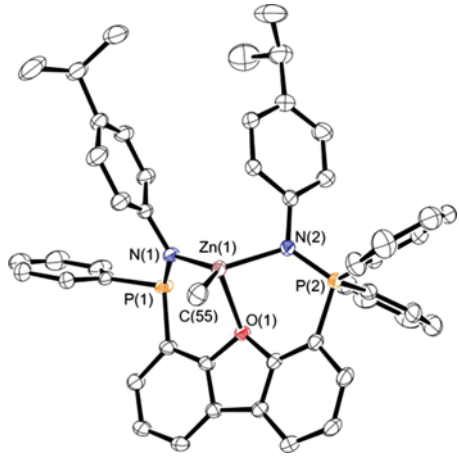
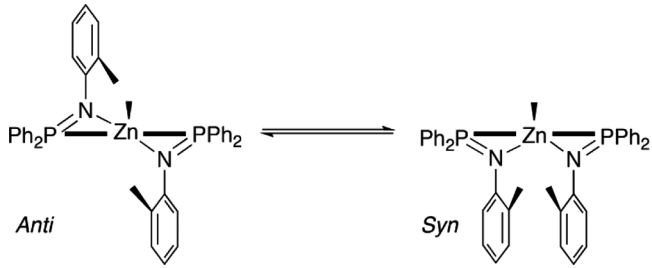


Figure 11. Displacement ellipsoid plot (30% probability) of the cation of **12-BPh$_4$**, with hydrogen atoms, a P-phenyl group, and disordered atomic positions omitted for clarity. (Color figure available online.)



Scheme 6. C_2-(*anti*) and C_s-symmetric (*syn*) isomers of the cation of **11**, with the dbf moiety of the ligand represented by a solid black line.

2.284(2) Å suggests a rather weak Lewis acid-base bond, it is well within the sum of the Van der Waals radii (2.91 Å).[32]

Unsubstituted complex **13** was also prepared, and attempts were made to grow X-ray quality crystals of **13-BPh$_4$** in an effort to structurally characterize this slightly less bulky analogue. However, the crystals obtained were composed primarily of the zinc-phenyl derivative [L_2^{Ph}ZnPh][BPh_4] as a result of phenyl transfer from the modestly nucleophilic BPh_4^- anion. No Zn–O bonding was noted in this structure, highlighting the weakness of this interaction, which was likely broken so that the complex could adopt an orientation with favorable crystal packing interactions.

4.2. Synthesis and Characterization of Zinc-Lactate Complexes

To gain insight into structure–activity relationships of the system, the analogous zinc-lactate complexes (**14–16**) were prepared according to the same protocol utilized for the synthesis of **9**, affording the desired complexes in analytical purity. Thorough characterization by means of X-ray crystallography and solution NMR studies was then undertaken. The molecular structure of complex **14** is depicted in Figure 12. The zinc center in this complex exists in a four-coordinate, trigonal pyramidal geometry, with O(2) of the lactate moiety occupying the apical site. Like the methylzinc complex of L_2^{Tol} (**11**), the ligand coordinates in a κ^2 binding mode through the two phosphinimines. Intriguingly, the ligand orientation is *syn* rather than *anti* in the solid state. However, solution NMR studies indicated that this complex undergoes a fluxional process with rapid interconversion between the *anti* and *syn* isomers. In fact, three

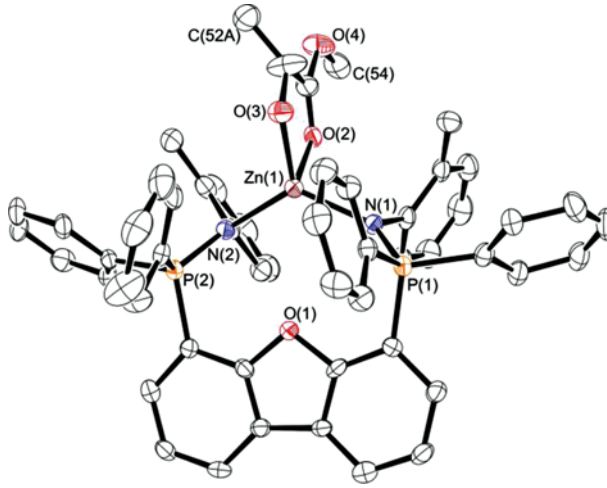
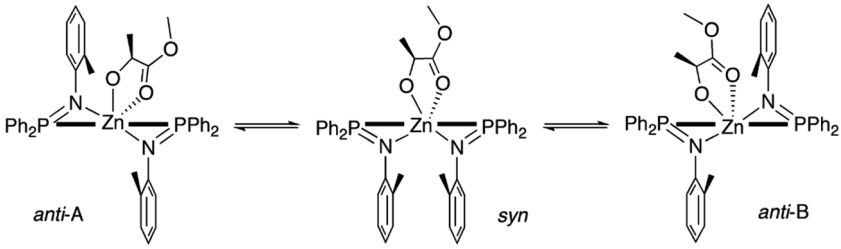


Figure 12. Displacement ellipsoid plot (30% probability) of the cation of the zinc-lactate complex **14**, with hydrogen atoms omitted for clarity. (Color figure available online.)

peaks appear in the ^{31}P NMR spectrum at ambient temperature, suggesting a more complicated fluxional process due to the presence of the chiral lactate moiety. This creates the possibility of two diastereomers associated with the *anti* orientation (Scheme 7).

The solid-state structures of complexes **15** and **16** (Figure 13) indicate a κ^3 ligand coordination similar to that observed for **12-BPh$_4$**, in which the dbf oxygen binds weakly to the 5-coordinate, trigonal bipyramidal metal centers. While both complexes give rise to only a single resonance in their respective ^{31}P NMR spectra, fluxional behavior that is rapid on the NMR timescale is likely.



Scheme 7. Proposed isomers of **14** that account for the observations in the NMR spectra.

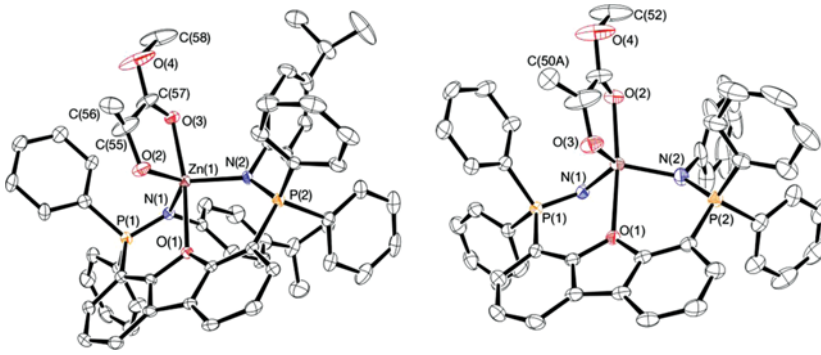


Figure 13. Displacement ellipsoid plots (30% probability) of the cations of the zinc-lactate complexes **15** (left) and **16** (right), with hydrogen atoms and one N-phenyl of **16** omitted for clarity. (Color figure available online.)

4.3. Polymerization Activity

A study of the efficacy of **14–16** as catalysts for the polymerization of *rac*-lactide was undertaken, and measured rates are given in Table 3. Compound **14** exhibits little activity for polymerization of *rac*-lactide at ambient temperature, though at 60°C substantial activity was noted. In $CDCl_3$ solvent at 60°C, polymerization occurs under first-order kinetics with an observed rate constant of $3.65(2) \times 10^{-4}\,s^{-1}$([LA]$_0$/[**14**] = 200, [LA]$_0$ = 1.0 M). This rate is only slightly greater than that observed for the L_2^{Mes} analogue **9**, despite the significant reduction in steric bulk. Unlike **14**, however, complex **15** is highly active at ambient temperature (25°C), giving 90% conversion of 200 equivalents of *rac*-lactide in 50 minutes ([LA]$_0$/[**15**] = 200, [LA]$_0$ = 1.0 M, CD_2Cl_2). Measurement of the rate under these conditions confirmed first-order consumption of lactide with an observed rate constant of $8.65(4) \times 10^{-4}\,s^{-1}$.

Complex **16** also displays high activity at ambient temperature with a first-order rate constant of $5.11(3) \times 10^{-4}\,s^{-1}$. Interestingly, this rate is

Table 3. Kinetic measurements for polymerization of *rac*-lactide with **14–16**

	Temperature (°C)	[LA]$_0$/[Zn]	Solvent	k_{obs} ($\times 10^{-4}\,s^{-1}$)
14	60	200	$CDCl_3$	3.65(2)
15	25	200	CD_2Cl_2	8.65(4)
16	25	200	CD_2Cl_2	5.11(3)

slightly lower than that determined for **15** ($8.65(4) \times 10^{-4}\,s^{-1}$) under identical conditions, despite similar steric demands near the metal center. The modest reduction in activity was thus attributed predominantly to electronic effects, whereby the lack of a *para-iso*propyl group on the N-aryl ring reduces the electron donating capacity of the ligand. These results signify a high dependence of activity on the electrophilicity of the metal center and suggest improved activity upon better moderation of that electrophilicity. Furthermore, it was proposed that the large difference in activity between the bulkier (**9** and **14**) and less sterically hindered (**15** and **16**) analogues is also largely an electronic effect arising from the difference in coordination geometry. It was thus concluded that reduced steric demands of the ligand and the associated change in coordination geometry act synergistically to promote enhanced lactide polymerization activity.

It is also noteworthy that all three of these catalysts (**14–16**) exhibited possible living polymerization characteristics, in that complete consumption of monomer did not result in deactivation of the catalyst. This behavior was quantified using **15**, and it was found that a second batch of 200 equivalents of monomer was consumed under first-order kinetics with an observed rate constant of $8.1(1) \times 10^{-4}\,s^{-1}$, representing only a slight reduction in activity.

4.4. Polymer Characterization

Polymer samples prepared from each of the zinc-lactate complexes **14–16** were examined by MALDI-ToF mass spectrometry, and all spectra are consistent with the incorporation of the methyl-lactate initiating group as the polymer end group. Also, the peaks were separated by 72 u, revealing that transesterification continues to be a problem for these highly electrophilic catalysts.

All of the catalyst derivatives exhibited little stereochemical control, producing polylactide with only a slight heterotactic bias, presumably due to a chain end control mechanism.[4b,33] The tacticity was most pronounced for complex **16**, albeit still rather modest ($P_r = 0.70$). Polymer samples prepared using each of the catalysts **14–16** were prepared and studied by GPC (Table 2). Overall, complex **15** gave the best molecular weight control, with the experimental M_n ($28.7\,kg\,mol^{-1}$) being an almost perfect match to the theoretical value ($28.3\,kg\,mol^{-1}$). The polydispersity was also lowest with this catalyst (1.15). Conversely, catalysts **14** and **16**

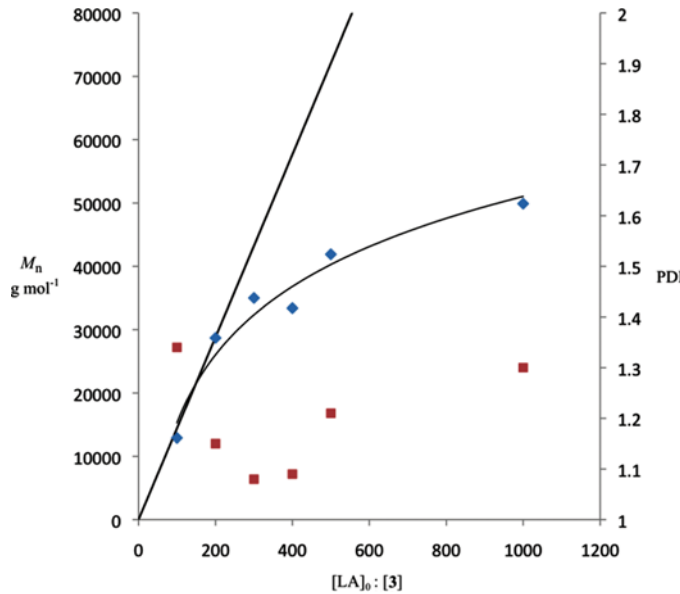


Figure 14. Plot of observed M_n (◆) and PDI (■) as a function of monomer to catalyst ratio for 15 as catalyst. The straight line represents calculated M_n values, while the curved line demonstrates the general experimental trend. (Color figure available online.)

gave lower than expected molecular weights and significantly greater PDIs. For these reasons, complex **15** was selected for a more detailed study.[34]

Polylactide samples prepared using varying ratios of [LA]:**15**, ranging from 100–1000, were analyzed by GPC (Table 2), and the results are depicted in Figure 14. In general, it was observed that at high catalyst loading, the molecular weights are a close match to the calculated values, while at reduced catalyst loading the experimental M_n values are lower than expected. This was attributed to solvent and/or monomer impurities acting as chain-transfer agents. Additionally, the PDI values were found to be very low at moderate catalyst loadings (<1.1) but somewhat higher at both higher and lower loadings.

4.5. Mechanistic Studies

The polymerization process using **15** as the catalyst was examined in greater detail. To determine the order of the reaction with respect to [**15**], the

Table 4. Activation parameters for polymerization of lactide with **15** and selected literature examples

Catalyst	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
15	47(1)	147(4)
[{(NNO)InCl}$_2$(μ-OEt)(μ-Cl)][35a]	49(2)	140(12)
ph$_2$Sn(O^{i}Pr)$_2$[35b]	46(4)	188(12)

reaction rate was measured at various concentrations of catalyst. The resulting plot of k_{obs} versus **[15]** was linear, thereby establishing an overall second-order rate law (rate $= k$[**25**][LA]) with $k = 0.17(1)\,s^{-1}\,M^{-1}$ at ambient temperature. The activation parameters were also determined through measurement of the rate over a temperature range from 37°C to −7°C. The resulting Eyring plot was linear and the activation parameters were calculated to be $\Delta H^{\ddagger} = 47(1)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -147(4)$ J K^{-1} mol^{-1}. The large negative entropy of activation suggests a highly ordered transition state consistent with a coordination–insertion mechanism. Furthermore, the activation parameters closely match literature values for catalyst systems known to undergo coordination–insertion polymerization processes (Table 4),[35] and thus **15** was established to polymerize lactide via a coordination–insertion mechanism.

In summary, comparison of ligands differing in steric bulk has shown these variations have a significant impact on the polymerization activity of the resultant complexes. The major factors determining the level of activity include steric bulk and ligand coordination mode, which appear to behave synergistically. Better moderation of the electrophilicity of the metal center in the less bulky, κ^3 complexes is proposed to be the predominant factor that promotes the high rate of polymerization. This work ultimately resulted in the first cationic metal catalyst capable of ring-opening polymerization of lactide at ambient temperature.[34]

5. ALKYL-SUBSTITUTED LIGAND

More recently, a preliminary investigation was initiated to explore the effect of placing alkyl substituents on both the phosphorus and nitrogen atoms of the phosphinimine moieties, with the aim of generating a more electron rich ancillary ligand.[36] To this end, the neutral pincer ligand L_3, which features ethyl groups at phosphorus and benzyl groups at

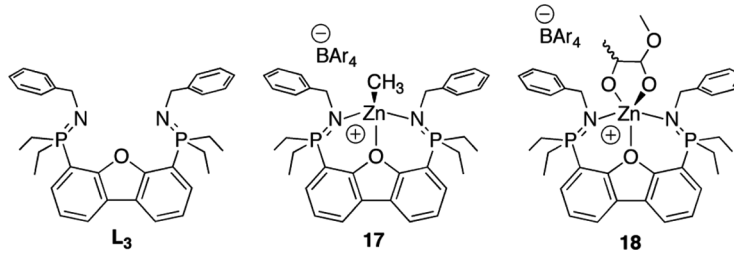


Figure 15. Cationic zinc complexes of the alkylated ligand L_3.

nitrogen, was prepared. The cationic zinc complexes **17** and **18** were subsequently generated as previously described (Figure 15).[36]

The solid-state structure of complex **18** was determined and is depicted in Figure 16. The X-ray crystal structure revealed that the ligand chelates zinc in a κ^3 mode similar to the related zinc-lactate complexes **15** and **16**, including a substantial Zn–O interaction (Zn(1)–O(1) = 2.525(1) Å). This observation is in agreement with the already apparent trend that κ^3 binding prevails with sterically less-hindered ligands.

Complex **18** was determined to be an extremely active lactide polymerization catalyst, giving 90% conversion of 200 equivalents of

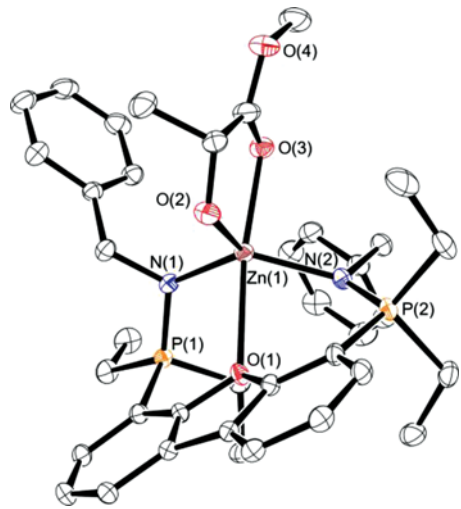


Figure 16. Displacement ellipsoid plot (30% probability) of the cation of **18**, with hydrogen atoms and disordered atomic positions omitted for clarity. (Color figure available online.)

monomer to atactic ($P_r = 0.50$) polylactide in under 20 minutes at 25°C (CH_2Cl_2 solvent, $[LA]_0 = 1.0$ M). Examination of the kinetics revealed first-order consumption of lactide and an observed rate constant of $1.88(1) \times 10^{-3}\ s^{-1}$. This rate is greater than that of compound **15**, measured under identical conditions, by a factor of 2.2.

Although activity increased, GPC analyses of polymer samples prepared at various catalyst loadings suggest that molecular weight control is reduced for **18** compared with the slightly less active complex **15**. Even at a high catalyst loading ($[LA]_0/[\mathbf{18}] = 100$, 200), the polydispersity remained somewhat elevated (PDI = 1.24–1.25), although molecular weights were close to theoretical values. Upon decreasing the catalyst loading ($[LA]_0/[\mathbf{18}] = 300$, 400, 500), an increase in molecular weight distribution (PDI = 1.39–1.43) was coupled with much lower than calculated M_n values (Table 2).

Analysis of polylactide samples isolated at varying degrees of conversion (200 equivalents of LA) provided some insight into the lack of molecular weight control. It was found that PDIs were narrow during early stages of polymerization (PDI = 1.11–1.13), but as the reaction progressed further, the molecular weight of the polymer samples increased very little, and toward the final stages of reaction the M_n values actually decreased (Table 5). This behavior was attributed to a significant degree of intramolecular transesterification, which resulted in the generation of a substantial quantity of low molecular weight cyclic oligomer.

To summarize, the new alkyl-substituted bis(phosphinimine) pincer ligand proved valuable at stabilizing cationic zinc-lactate complex **18**,

Table 5. GPC data for PLA samples quenched at varying degrees of conversion using **18** as catalyst

t (min)	Isolated yield (%)	Calculated conversion (%)[a]	Calc. M_n[b] ($\times 10^3$)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI
4.5	39	40	11.2	11.3	12.6	1.11
8	53	60	15.3	12.4	13.9	1.13
11	74	70	21.3	12.8	16.1	1.26
14	78	80	22.5	13.1	16.5	1.27
20	84	90	24.2	12.6	17.0	1.35
42	89	99	25.6	10.7	14.4	1.35

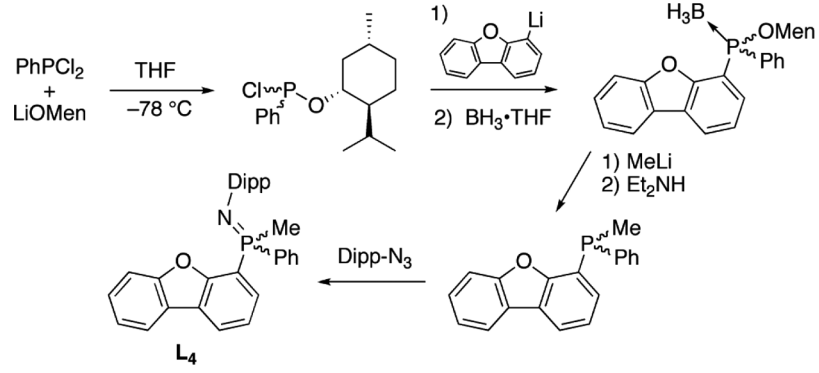
[a]Calculated based on the observed rate constant ($k_{obs} = 0.00188\ s^{-1}$) measured under identical conditions, using the equation $\ln[LA] = -k_{obs} \times t$.

[b]Calculated using $M_n = [([LA]_0/[I]) \times 144.13 \times$ isolated yield].

which exhibited higher activity for lactide polymerization catalysis than the analogous complexes of the aryl-substituted ligands. This increase in activity, however, was realized at the cost of a modest reduction in molecular weight control.

6. P-STEREOGENIC LIGANDS

Given the successful development of cationic zinc complexes that polymerize lactide via a coordination–insertion mechanism, a chiral analogue was targeted as such a complex might impart better control over the stereoselectivity of the polymerization via enantiomorphic-site-control, chain end control, or a cooperative combination of the two processes.[37] Specifically, the P-stereogenic monophosphinimine ligand L_4 was employed.[38] The synthetic protocol followed a modification of Imamoto's route (Scheme 8),[39] and made use of a phosphine–borane intermediate, with (−)-menthol as the chiral resolving agent. First, lithium *l*-menthoxide was reacted with dichlorophenylphosphine to afford pure (OMen)PhPCl. This phosphine was then allowed to react with 4-lithiodibenzofuran at −78°C, followed by $BH_3 \cdot THF$, to give the phosphine-borane adduct as a mixture of diastereomers. Attempts to separate the diastereomers by column chromatography proved unsuccessful. Therefore, conversion of OMen to Me by reaction with MeLi, followed by removal of the borane with diethylamine, gave the chiral phosphine as a racemic mixture, which was converted to racemic L_4 upon addition of Dipp-azide.



Scheme 8. Synthesis of the P-stereogenic monophosphinimine ligand L_4.

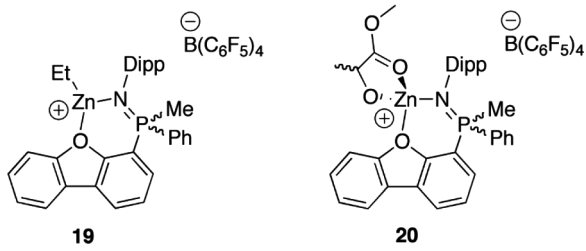


Figure 17. Synthesis of cationic zinc-ethyl **(19)** and zinc-lactate **(20)** complexes of the chiral phosphinimine ligand $\mathbf{L_4}$.

Zinc complexes of the ligand were synthesized by the established protonation–alkane elimination pathway, affording the zinc-ethyl complex **19** and the zinc-lactate complex **20** (Figure 17). The efficacy of both species to mediate lactide polymerization was examined, though complex **19** was established to be virtually inactive under even harsh conditions (100°C, 3 hours). Complex **20** was marginally active, giving 90% conversion to PLA after 9 hours at 100°C ($[LA]_0/[20] = 100$, $[LA]_0 = 0.50$ M). Similar results were also achieved at lower catalyst loading (Table 6). Unfortunately, multinuclear NMR studies provided no evidence for a coordination−insertion polymerization mechanism,

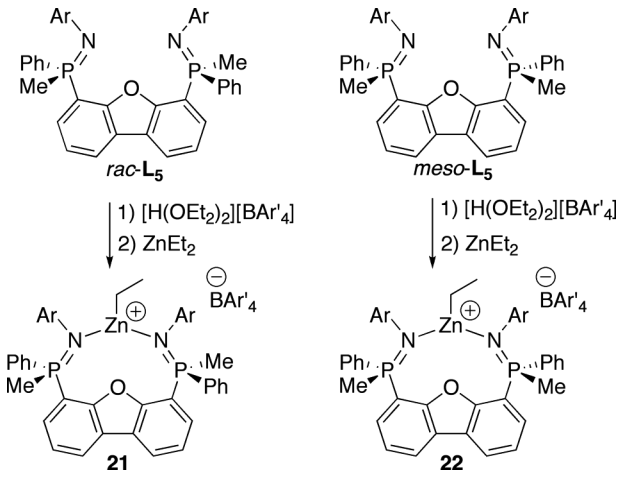
Table 6. GPC data for polylactide samples prepared using complexes **20–22**

Catalyst	Temp. (°C)	$[LA]_0$/[Zn]	Time (h)	Isolated yield (%)	Calc. M_n (kg mol^{-1})[a]	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI
20	100	200	9.0	74	21.3	29.8	59.0	1.98
20	100	300	9.0	69	29.8	36.9	69.9	1.89
20	100	400	9.0	69	39.7	46.7	84.6	1.81
21	40	200	2.0	97	28.0	93.4	165.2	1.77
21	40	400	2.7	99	56.8	102.5	172.9	1.69
21	40	600	3.3	97	84.1	38.3	70.7	1.85
21	40	800	3.7	93	107.1	65.5	111.8	1.71
21	40	1000	4.0	90	129.1	56.3	96.5	1.71
22	40	200	2.0	99	28.6	87.0	187.1	2.15
22	40	400	2.5	98	56.6	71.7	188.1	2.62
22	40	600	3.2	99	86.4	60.5	120.0	1.98
22	40	800	3.5	98	112.7	89.2	211.9	2.38
22	40	1000	3.8	95	137.4	208.3	390.7	1.87

[a]Calculated using $M_n = [([LA]_0/[I]) \times 144.13 \times \text{conversion}]$.

and MALDI-ToF analysis of a polymer sample revealed predominantly cyclic oligomers, suggesting a high rate of intramolecular transesterification. Notably, GPC analysis revealed molecular weights only slightly lower than the calculated values, although the molecular weight distributions were broad (PDI = 1.8–2.0). Despite the chirality of the ligand, complex **20** generated only atactic polylactide from *rac*-lactide.

The low activity, lack of stereocontrol and unknown polymerization mechanism for complexes of $\mathbf{L_4}$ prompted us to synthesize chiral derivatives of the bis(phosphinimine) ligand framework, as complexes of the achiral analogue were established to polymerize lactide via a well-controlled, coordination–insertion mechanism. Thus, the chiral bis(phosphinimine) analogue ($\mathbf{L_5}$) was prepared (Scheme 9) via a similar methodology to that used for $\mathbf{L_4}$.[40] The synthesis was ultimately lacking in diastereoselectivity, and as a result, *rac* and *meso* forms of the ligand were generated together and separated chromatographically. The corresponding alkylzinc complexes **21** (*rac*) and **22** (*meso*) were generated (Scheme 9), but attempts to synthesize the related zinc-lactate complexes proved ineffective. As a result, complexes **21** and **22** were studied as catalysts for the ROP of lactide. Although initiation was found to be slow relative to propagation, as evidenced by a long induction period, these zinc-alkyl compounds were found to be competent catalysts for ROP



Scheme 9. Synthesis of cationic zinc-ethyl complexes (**21** and **22**) of *rac* and *meso* forms of a chiral bis(phosphinimine) ligand (Ar = 4-*iso*propylphenyl, Ar′ = 3,5-$(CF_3)_2$-C_6H_3).

of lactide under relatively mild conditions (40°C, CH_2Cl_2). As a result of the slow initiation, polymers prepared using both **21** and **22** had broad molecular weight distributions (PDI = 1.7–2.6), and experimental M_n values did not match those predicted (Table 6). Furthermore, MALDI-ToF mass spectra of polymer samples revealed that the ethyl group of the complex was not incorporated as the end group, suggesting that the complex undergoes conversion to a new species prior to catalyzing the polymerization, which is consistent with the observed induction period. Neither the nature of the active catalyst, nor the exact mechanism of polymerization, has yet been determined. Disappointingly, neither catalyst gave significant stereocontrol in the polymerization of *rac*-lactide. Clearly, additional work needs to be done to broaden our understanding of this catalyst system. Efforts are currently underway to prepare new types of chiral ligand architectures.

7. SUMMARY AND CONCLUSIONS

The work summarized in this manuscript represents some of the first examples of cationic metal complexes with demonstrated efficacy for the polymerization of lactide. Notably, complex **15** was the first reported cationic metal catalyst with ambient temperature activity for ROP of lactide. The studies performed thus far have revealed important structure–activity relationships. Alkoxide-type initiating groups have been confirmed as a necessary feature for a suitable rate of initiation, as has already been established for related neutral catalysts. Furthermore, an electron-rich ligand is also a key element, as ligands that only possess a single phosphinimine donor (L_1, L_4) were found to be ineffective catalysts at low temperature and poorly controlled under harsh conditions. For the more strongly donating bis(phosphinimine) ligands, it has been shown that too much steric bulk close to the metal center (*ortho* N-aryl sites) prevents the κ^3 binding mode, which appears necessary to achieve high polymerization activity. However, increased steric demands distal to the metal center (*para* N-aryl sites) do not greatly impact catalytic activity. They do, however, appear to lead to improved control by reducing the rates of undesirable competing reaction pathways.

This review also discussed recent efforts to introduce chirality in the ligand framework as a means of improving tacticity control. While P-chiral monophosphinimine and bis(phosphinimine) ligands were

successfully prepared, we have thus far achieved limited success in regard to eliciting stereoselective lactide polymerization. However, we are continuing to work toward this goal.

Overall, the work described in this review demonstrates the suitability of cationic zinc complexes as lactide polymerization catalysts when an appropriately designed ancillary ligand is employed. This new catalyst class has significant potential for further development, which will be aided by the structure–activity relationships that have already been established.

ACKNOWLEDGMENTS

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