ORGANOMETALLICS

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pubs.acs.org/Organometallics

Synthesis and Structures of Tridentate Ketoiminate Zinc Complexes That Act As L-Lactide Ring-Opening Polymerization Catalysts

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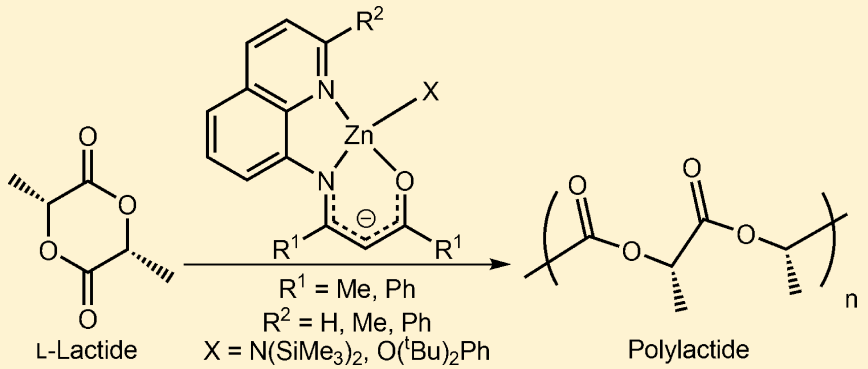
Supporting Information



ABSTRACT: A series of NNO tridentate Schiff base ligands were used to prepare zinc amide and zinc phenoxide complexes that were shown to be efficient L-lactide ring-opening polymerization (ROP) catalysts. The complexes were prepared from ketoimines bearing a pendant quinoline donor, zinc bis(trimethylsilyl)amide, and 2,6-di-*tert*-butylphenol. They were characterized with ^{1}H and ^{13}C NMR, absorbance spectroscopy, microanalysis, and X-ray crystallography. The zinc amide and zinc phenoxide structures showed mononuclear complexes with tridentate coordination by the ketoiminate ligands. ROP of L-lactide with the zinc amides and phenoxide complexes gave isotactic poly-L-lactide with generally low molecular weight distributions. As compared to their amide counterparts, the zinc phenoxide complexes showed superior lactide ROP behavior in terms of percent conversion as a function of time, measured molecular weights closer to the predicted values, and lower polydispersity index values. Increasing size of the substituent at the 2-position on quinoline (H, Me, Ph) improved the synthesis of the complexes but adversely affected the ROP.

INTRODUCTION

Significant interest and research efforts have been expended on the development of polymers from 100% renewable resources as alternatives to petrochemical-based polymers.[1] Aliphatic polyesters have drawn wide attention, and, specifically, polylactide (PLA) has seen intense interest due to its biocompatibility for use in biomedical devices (sutures, drug delivery systems, etc.).[2] The uses of PLA have expanded into consumer products as the price of manufacture has declined[1d] and the attractiveness of biodegradable polymers has increased in response to increasing emphasis on the environmental fate of such objects.

Lactide is a cyclic dimer of lactic acid that is derived from 100% renewable resources, e.g., corn or sugar beets. The presence of two chiral centers on each lactide monomer generates three isomers, L-lactide (*SS*-configurations), D-lactide (*RR*-configurations), and *meso*-lactide (*RS*-configurations). Lactide monomers are converted to PLA by ring-opening polymerization (ROP) catalysts, which utilize a coordination−insertion chain growth mechanism to produce, in the case of L- and D-lactide, highly crystalline isotactic PLA.[3] Many of these catalysts are inorganic metal complexes that include a supporting ligand and a ROP-initiating ligand.

Reviews of the field detailing the metal centers and supporting ligands utilized for lactide ROP have appeared in the literature in recent years.[3,4] Some trends among complexes employed as ROP catalysts include the use of highly Lewis acidic metal centers and the use of multidentate supporting ligands to the metal center during polymerization. In addition, several common ROP initiator ligands that have seen broad use include alkyl (Et), alkoxides (OBn, $OSiPh_3$, $O(^tBu)_2Ph$), and amides ($N(SiMe_3)_2$, NPr_2).

Recent work has focused on the use of biocompatible metal centers such as Mg,[5] Al,[6] and Zn.[6d,7] For Zn, bidentate complexes of β-diketiminate[5g,j−o,8] and salicylaldiminate ligands[9] have been widely used as lactide ROP catalysts. Tridentate Schiff bases have garnered significant interest where salicylaldiminates bearing a pendant donor group such as ethylenediamine, cyclohexylamine, pyridine, and quinoline have found purchase.[5i,6g,10] In many cases bis-trimethylsilyl amide or

Received: September 14, 2011

   dx.doi.org/10.1021/om200865w | *Organometallics* XXXX, XXX, XXX−XXX

benzyl alkoxide groups have been included as ROP-initiating substituents. Ketoiminates with pendant donor groups have been widely used in the stabilization of metal centers from across the periodic table;[11] however despite the similarities to the salicylaldiminates, these ligands have found little use in lactide ROP catalysts.[5h,6k]

Whether the supporting ligand system is a β-diketiminate, salicylaldiminate, or ketoiminate, the formation of bis-ligated zinc complexes has been regularly reported in studies concerning lactide ROP catalysts and in other settings.[5i,6d,g,8c,9,10,10j,12] In lactide settings, a few of the bis-ligated zinc complexes in either tetrahedral or octahedral coordination geometries were shown to be effective ROP catalysts.[6d,7a,12c] However, the trend is for generally inactive bis-ligated zinc complexes. The introduction of bulky groups on the ROP-initiating ligand (bis(trimethylsilyl)amide, di-*tert*-butyl phenoxide) or strategically positioned groups on the supporting ligands (^{t}Bu on salicylaldiminate) has helped to mitigate this challenge.[9a,10b−d,g,j,13] In contrast to the salicylaldiminates, ketoiminates do not offer the same opportunity to introduce such a sterically bulky group on the supporting ligand.

Here we report on the synthesis and characterization of zinc bis(trimethylsilyl)amide and zinc di-*tert*-butyl phenoxide complexes with ketoiminates bearing quinoline pendant donors and their use as L-lactide ROP catalysts. The use of a flexible architecture on the Schiff base allowed for differing substituents on the ketoimine backbone and groups of increasing steric bulk (H, Me, Ph) to be incorporated at the 2-position on the quinoline pendant to mitigate the formation of bis-ligated zinc complexes. In addition, the steric demands of bis(trimethylsilyl)amide and 2,6-di-*tert*-butylphenol were required for the synthesis of the mononuclear zinc complexes. The zinc amide and phenoxide complexes were characterized spectroscopically, and several were characterized crystallographically. All complexes were assessed for their L-lactide ROP efficiency, as well. The phenoxide complexes were both more efficient and better behaved catalysts than their amide counterparts.

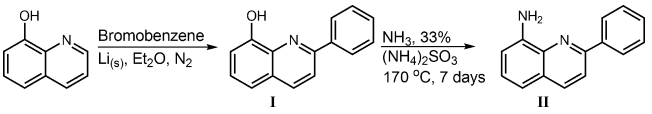
RESULTS AND DISCUSSION

Synthesis and Structural Studies. *Synthesis of Bulky Ketoimine Ligand.* The three ketoimines, **L^1-H**, **L^2-H**, and **L^3-H**, were synthesized according to the literature method and isolated in 88%, 90%, and 81% yields, respectively.[11f] When these ketoimines were previously combined with magnesium benzyl alkoxide, bis-ligated magnesium complexes formed despite the incorporation of a methyl group at the 2-position on the quinoline pendant donor.[11f] These complexes were inactive toward lactide ROP. Because many zinc bis-ligated complexes have been reported,[5i,6d,g,8c,9,10,12,14] we anticipated the need to include a larger group to prevent the formation of bis-ligated zinc complexes here. Thus, our group synthesized a new Schiff base ligand, **L^4-H**, with a more bulky phenyl group at the 2-position on the quinoline pendant donor to inhibit the formation of the bis-ligand complex.

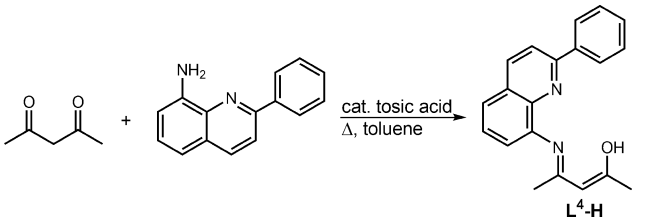
To use the synthetic methods employed for **L^1-H**−**L^3-H**, the synthesis of **L^4-H** required the preparation of 2-phenyl-8-aminoquinoline. The previously reported synthetic method for this compound required the use of arsenic pentoxide.[15] An alternate synthetic pathway was developed starting from 8-hydroxyquinoline with methods adapted from the literature (Scheme 1).[16]

Compound **I** was isolated in 75% yield by sublimation and characterized with ^{1}H and ^{13}C NMR, high-resolution mass spectrometry (HR-MS), and elemental analysis. The 2-phenyl-8-hydroxyquinoline, **I**, was converted to the amine at elevated temperature in a steel reactor over one week. Compound **II** was isolated in 31% yield with column chromatography and was characterized with ^{1}H and ^{13}C NMR, HR-MS, and elemental analysis. The 2-phenyl-8-aminoquinoline, **II**, was combined with 2,4-pentanedione under the Schiff base condensation reaction conditions to prepare **L^4-H** (Scheme 2).

Scheme 1



Scheme 2



L^4-H was isolated in 68% yield with column chromatography and was characterized by ^{1}H and ^{13}C NMR, HR-MS, and elemental analysis.

Zinc Amide Complexes. Zinc amide complexes, **1a**−**4a**, were synthesized by combining 1.1 to 1.3 equivalents of zinc bis(trimethylsilyl)amide (prepared with a method adapted from the literature[17]) and **L^1-H**−**L^4-H** under an inert atmosphere (Scheme 3).

Reaction of zinc bis(trimethylsilyl)amide with **L^1-H**−**L^4-H** gave zinc amide complexes that were isolated by precipitation from Et_2O and hexanes in 70−73% yield. A slight excess of zinc bis(trimethylsilyl)amide was required due to the formation of bis-ligated zinc complexes as an impurity when equimolar ratios were used. The ^{1}H and ^{13}C NMR spectra of **1a**−**4a** show the incorporation of a single ketoiminate ligand and a single bis(trimethylsilyl)amide in the zinc complexes. The ^{1}H NMR spectra of **1a**−**4a** show sharp signals, indicating there is no fluctuation in the zinc coordination environment. For example, the methine proton on the ketoimine backbone of **1a** is a sharp singlet at 5.08 ppm, indicating the oxygen and nitrogen are coordinated to the zinc. Additionally, the proton at the 2-position on the quinoline pendant is a sharp doublet of doublets at 8.53 ppm, indicating no fluxional coordination of the quinolyl nitrogen to zinc. Despite the incorporation of the bulky bis(trimethylsilyl)amide group, complexes **1a**−**4a** were thermally unstable when not in the presence of zinc bis(trimethylsilyl)amide and formed bis-ligated complexes in solution at room temperature over the course of hours.

Zinc Phenoxide Complexes. Complexes **1a**−**4a** were converted to the phenoxide analogues by addition of 2,6-di-*tert*-butylphenol, yielding **1b**−**4b** (Scheme 3). Compounds **1b**−**4b** were insoluble in hexanes and isolated by filtration in 59−76% yield. Attempts to prepare zinc alkoxide complexes with **L^1-H** and **L^2-H** in a 1:1 ratio of zinc amide (**1a** and **1b**) to alcohol with benzyl alcohol, 4-methylbenzyl alcohol, and 2,6-dimethylphenol were unsuccessful, yielding bis-ligated complexes as shown in the ^{1}H NMR spectra. The presence of the

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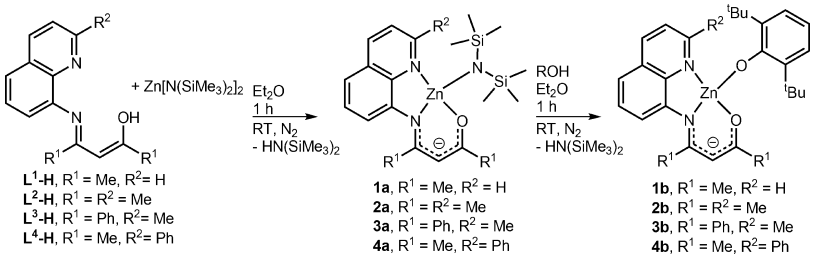
Scheme 3



tert-butyl groups on 2,6-di-*tert*-butylphenol prevented formation of the bis-ligand complex.

The ^{1}H and ^{13}C NMR spectra of **1b**−**4b** show the incorporation of one ketoiminate and a single phenoxide. The chemical shifts of the ^{1}H NMR signals for the ketoiminate in the spectra of **1b**−**4b** are similar to those observed in **1a**−**4a**, suggesting a similar coordination mode between the amide and phenoxide complexes. The methyl peaks of the amide complex are at 1.75 and 2.07 ppm for **1a**, and the methyl peaks for **1b** are at 1.65 and 2.30 ppm, indicating a similar chemical environment. The proton at the 2-position on quinoline in **L^{1}-H** appears as a sharp doublet of doublets at 8.53 and 8.20 ppm, respectively, for the amide and phenoxide complexes. Because the signals in the NMR spectra of **1b**−**4b** are sharp, there is no indication of a fluctuating zinc coordination number as was observed in other studies where dinuclear zinc complexes were reported.[5j]

Structures of Zinc Amide and Phenoxide Complexes. The crystal structures of **1a**, **2a**, **4a**, and **4b** confirm the tridentate coordination of zinc by the ketoiminate and the coordination of one bis(trimethylsilyl)amide or di-*tert*-butyl phenoxide to the zinc center, Figures 1, 2, and 3 and

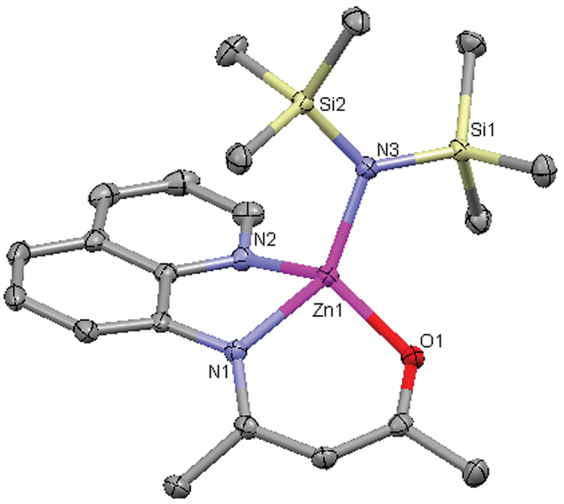


Figure 1. X-ray crystal structure of **1a** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

Supporting Information SI Figure 1. Crystals suitable for X-ray crystallography for **1a**, **2a**, and **4a** were grown by the slow evaporation of hexanes and dichloromethane under an inert atmosphere at −35 °C, while **4b** was prepared by cooling a dichloromethane solution to −35 °C. Crystallographic and refinement data can be seen in Supporting Information SI Table 1, while selected bond lengths and angles of interest are shown in Table 1. The zinc amide complexes did not contain

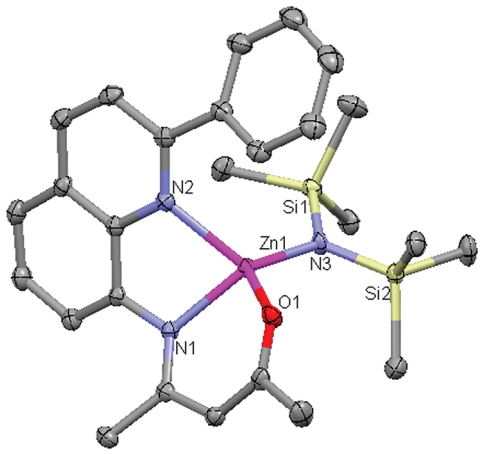


Figure 2. X-ray crystal structure of **4a** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

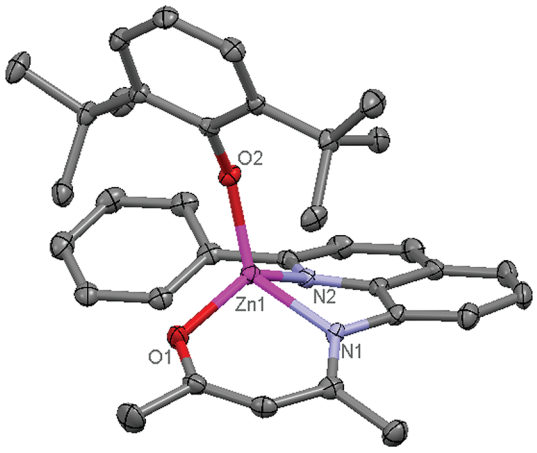


Figure 3. X-ray crystal structure of **4b** with thermal ellipsoids drawn at the 50% probability level. One molecule of **4b** in the asymmetric unit, the hydrogen atoms, and the cocrystallized molecule of dichloromethane are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−N1 2.013 (2), Zn1−N2 2.099 (2), Zn1−O1 1.937 (2), Zn1−O2 1.887 (1), N1−Zn1−N2 80.21 (6), N1−Zn1−O2 129.84 (6), N2−Zn1−O2 105.84 (6), O1−Zn1−N1 95.77 (6), O1−Zn1−N2 131.58 (6), O1−Zn1−O2 112.77 (6).

cocrystallized solvent molecules, while the structure of **4b** contained dichloromethane.

These four-coordinate zinc complexes adopt distorted tetrahedral geometries, with only a few angles being close to ideal (e.g., in **1a** O1−Zn1−N3 112.2°, in **2a** N2−Zn1−N3 110.0° and O1−Zn1−N3 111.7°, and in **4b** O1−Zn1−O2 112.77°). The rigidity of the ketoiminate backbone and the pendant quinolyl donor restrict the bite angles to zinc to be

dx.doi.org/10.1021/om200865w | *Organometallics* XXXX, XXX, XXX−XXX

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Zn Complexes 1a, 2a, and 4a

	1a	2a	4a
Bond Lengths			
Zn1−N1	2.0138(11)	2.034(2)	2.0329(9)
Zn1−N2	2.2260(12)	2.108(2)	2.1144(9)
Zn1−O1	1.9618(10)	1.970(2)	1.9752(8)
Zn1−N3	1.9059(11)	1.925(2)	1.9201(9)
Bond Angles			
N1−Zn1−N2	77.57(5)	79.88(9)	79.78(3)
N1−Zn1−N3	142.26(5)	135.65(10)	129.05(4)
N2−Zn1−N3	102.23(5)	109.95(8)	118.25(4)
O1−Zn1−N1	94.36(4)	93.36(8)	92.07(3)
O1−Zn1−N2	130.20(4)	125.57(8)	116.65(3)
O1−Zn1−N3	112.16(5)	111.72(8)	115.02(4)

much smaller than the ideal bond angles for tetrahedral coordination (e.g., N1−Zn1−N2 77.6° in **1a**, 79.9° in **2a**, 79.8° in **4a**, and 80.2° in **4b**). The angles between the ketoiminate and the amide or phenoxide ligand are much larger than the ideal 109.5° (e.g., the angle N1−Zn1−N3 in **1a** 142.3°, in **2a** 135.7°, in **4a** 129.1° or the angle N1−Zn1−O2 in **4b** 129.8°). As a result, an open site for coordination of a lactide monomer for the initiation of ROP is present. Despite the incorporation of different groups on the quinolyl substituent, the bond lengths between the four complexes are quite similar, with the exception of Zn1−N2, being slightly longer for **1a** (2.23 Å) as compared to **2a**, **4a**, and **4b** (2.10−2.11 Å), which have substituents on the quinoline ring. The Zn−N3 bond is slightly longer (1.92 Å) in the amide complexes than the Zn−O2 bond in **4b** (1.89 Å).

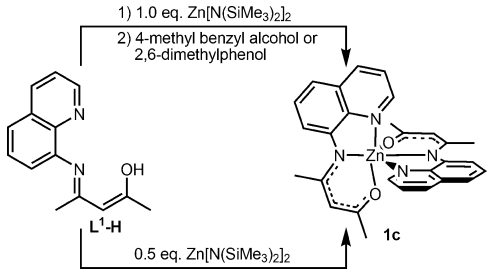
Only one other set of zinc amide complexes analogous to **1a**, **2a**, and **4a** has been reported where a tridentate NNO salicylaldiminate ligand was employed in addition to the bis(trimethylsilyl)amide.[10d] There are many similarities between the literature structures and **1a**, **2a**, and **4a** including distorted tetrahedral coordination geometry around zinc and bond lengths and angles that are in close agreement. For example, the average Zn−N(amide) bond distance for **1a**, **2a**, and **4a** is 1.92 Å, and that for the salicylaldiminate complexes reported is 1.91 Å. The average N1−Zn−N2 angle for the salicylaldiminates and for the ketoiminates in **1a**, **2a**, and **4a** differs by only 0.2°. Other bis(trimethylsilyl)amide zinc complexes have been prepared with bidentate NN β-diketiminate (BDI) or bidentate NO salicylaldiminate ligands.[5j,k,9a] For BDI complexes, the Zn−N(amide) bond distances were slightly shorter, at 1.88 and 1.89 Å, than the bond distances reported here.[5j,k] For salicylaldiminate NO zinc amide complexes, the Zn−N(amide) bond distances was 1.87 Å.[9a]

The structure of **4b** joins a small group of mononuclear zinc alkoxide complexes where, as in this structure, sterically encumbered groups were required.[5m,9a,17] More often the reported structures of zinc alkoxide complexes show dinuclear complexes with bridging alkoxides with BDI,[8b,c] salicylaldiminate,[5f,10a,d,g] or ketoiminate ligands.[12c] For the tridentate NNO dinuclear zinc complexes longer Zn−N1, Zn−N2, Zn−O1, and Zn−O2 bond lengths were reported than those in **4b**, reflecting the influence of the bridging alkoxide on those zinc coordination geometries.[5f,10a,d,g] In the case of a zinc complex with a bidentate ketoiminate and a di-*tert*-butyl phenoxide moiety the Zn−O bond distance was 1.82 Å, which is slightly shorter than the 1.89 Å Zn−O bond distance reported here.[9a] Zinc−oxygen bonds of similar length were reported in zinc phenoxide complexes in the absence of multidentate supporting ligands.[17]

Comparison to structures in which ketoiminates bear pendant donors is possible for metals other than zinc. Structures of bis-ligated magnesium complexes with L^2-H and L^3-H were reported to form octahedral magnesium complexes with meridional coordination by the two ligands.[11f] Zinc and magnesium have very similar ionic radii and often yield similar metal−oxygen bond distances.[18] Here where L^2-H was employed in **2a** the Zn−O bond distance was 1.97 Å, while an average Mg−O distance of 2.01 Å was previously reported. The slighter longer bond distances for the magnesium complex can be attributed to the crowding from the two ligands around magnesium. The bond distances between the metal center and the quinoline nitrogen are also longer in the magnesium complexes, where an average Mg−N distance 2.26 Å was observed compared to 2.10−2.11 Å for Zn−N(2) in **2a**, **4a**, and **4b**. Without the presence of a second NNO ligand in **2a**, the zinc center is positioned closer to the quinolyl moiety, yielding a wider N−Zn−N bite angle of 79.9° than in N−Mg−N, where the angle was 73.6°.

Bis-ketoiminate Zinc Complex. A side product was observed during the synthesis of **1a** and **1b** when less than a slight excess of zinc bis(trimethylsilyl)amide was used in the preparation of **1a** or when benzyl alcohol, 4-methylbenzyl alcohol, or 2,6-dimethylphenol was used in attempts to prepare **1b** (Scheme 4). The side product was identified as a bis-

Scheme 4



ketoiminate zinc complex through its intentional synthesis. Compound **1c** was synthesized by adding 2 equivalents of L^1-H to zinc bis(trimethylsilyl)amide at ambient temperatures in Et_2O under an inert atmosphere. An immediate color change from faint yellow to bright yellow was observed when the first aliquot of ligand solution was added to the zinc amide solution. The bis-ketoiminate complex precipitated from solution and was isolated by filtration in 72% yield.

Compound **1c** was characterized by ^{1}H and ^{13}C NMR, HR-MS, absorbance spectroscopy, and elemental analysis. The ^{1}H NMR spectrum of **1c** revealed the absence of the hydroxyl proton signal (δ ~13.5 ppm) in L^1-H and the bis-(trimethylsilyl)amide peak (δ ~0.3 ppm) as compared to **1a**. The proton at the 2-position on the quinolyl moiety was observed to shift upfield by ~0.7 ppm, while the methine proton shifted upfield by ~0.2 ppm. Both changes suggest coordination of the ketoimine to the zinc center. The coupling constants for **1c** were consistent with those for L^1-H. In addition, the spectrum showed an average symmetric metal coordination by two ketoiminate ligands with no apparent fluctuations in coordination. Mass spectra of **1c** were collected

dx.doi.org/10.1021/om200865w | *Organometallics* XXXX, XXX, XXX−XXX

from a 100% acetonitrile solution with ESI-MS, where $[(C_{14}H_{13}N_2O)_2Zn + H]^+$ was observed at m/z 515.14 with an isotope pattern consistent with C, H, N, O, and Zn incorporation. The composition was confirmed with high-resolution ESI-MS by comparison to leucine enkephalin, where the observed mass and the calculated mass differed by 1.9 ppm. While crystals suitable for X-ray diffraction analysis could not be prepared, an octahedral coordination geometry around zinc in **1c** can be inferred based on the octahedral structures reported for bis-salicylaldiminate zinc complexes bearing pyridyl or quinolyl pendant donors and from the previous use of **L^1-H** in octahedral bis-ligated magnesium complexes.[11f,14] Unfortunately, bis-ligated zinc complexes were formed with **L^4-H** when zinc bis(trimethylsilyl)amide was not in slight excess but to a lesser extent than with **L^1-H**–**L^3-H**. The ^{1}H NMR spectrum of the bis-ligated complex from **L^4-H** showed an average symmetric metal coordination by ketoiminate ligands but with broad signals suggesting a fluxional and different coordination around zinc. It is likely that the phenyl group on quinoline was too large to allow metal coordination by the quinoline nitrogen, possibly leading to a tetrahedral coordination geometry in a similar manner to literature reports.[5i,6g]

L-Lactide ROP Studies. Polymerization studies were conducted to compare percent conversions, molecular weights, and polydispersity index (PDI) values between and among the amide and phenoxide complexes. All ROP reactions were carried out at ambient temperatures in CH_2Cl_2 for 24 h for complexes **1a**–**4a** and for 1 h for **1b**–**4b**. The total reaction volume was kept at 3 mL except for **2b** due to lower solubility in CH_2Cl_2. Preliminary studies conducted using THF as the polymerization solvent yielded lower percent conversion with longer reaction times. This is consistent with the literature, where the phenomenon was attributed to competition between THF and lactide monomers for coordination.[5b]

The activities of the amide and phenoxide complexes with the same Schiff bases were compared to each other, as shown in Table 2. In all cases, the phenoxide complexes showed higher catalytic activity than their amide counterparts. Polymerizations with **1a**–**4a** were shown to require longer reaction times. Even after 24 h, ROP experiments with **3a** and **4a** had only modest conversions of monomer to PLA, entries 3 and 4. On the other hand, **1b**–**4b** showed much higher catalytic activity toward the ROP of lactide. This follows the trend that alkoxide initiators generally have higher activities than the corresponding amide complexes.[5m]

Table 2. Polylactides Produced from the ROP of L-Lactide in CH_2Cl_2 at Ambient Temperatures

entry	complex	lactide/Zn[a]	conv[b] (%)	$M_{n,calc}$[c] (10^3, g/mol)	$M_{n,obs}$[d] (10^3, g/mol)	PDI (M_w/M_n)
1	**1a**	250	100	36.0	156.0	1.07
2	**2a**	250	100	36.0	33.6	1.23
3	**3a**	250	67	24.1	118.6	1.10
4	**4a**	250	35	12.6	77.6	1.18
5	**1b**	50	100	7.2	15.1	1.15
6	**1b**	100	100	14.4	24.0	1.10
7	**1b**	250	100	36.0	50.7	1.11
8	**1b**	500	100	72.0	74.7	1.18
9	**2b**	250	97	34.9	38.9	1.11
10	**3b**	250	44	15.8	93.7	1.14
11	**4b**	250	35	12.6	61.7	1.20

[a]All reactions were carried out at in CH_2Cl_2 at ambient temperature. [b]Lactide conversion as determined by ^{1}H NMR. [c]$M_{n,calc}$ = (M/I) × (% conv) × (mol wt of lactide). [d]$M_{n,obs}$ values were determined by GPC in THF vs polystyrene standards and were corrected with a Mark–Houwink factor of 0.58.[23]

Studies were also conducted to compare the polymerization rates of different ketoiminate complexes with the same phenoxide initiator. Entries 7 and 9–11 in Table 2 show that catalytic activity decreases from **1b** to **4b**. For example, entries 9 and 11 show that catalytic activity is drastically decreased from 97% to 35% conversion in 1 h when the methyl group at the 2-position on quinoline is replaced by a phenyl group. The presence of the phenyl group likely interferes with lactide monomer coordination to the zinc center during ROP. Additionally, entries 9 and 10 show that catalytic activity is again significantly reduced from 97% to 44% conversion in 1 h upon the addition of the phenyl groups added to the ketoimine backbone. Electron-donating groups have been found to increase polymerization rates, and the electron-withdrawing phenyl substituents in **3b** and **4b** showed diminished ROP activity resulting from both steric and electronic effects.[10a,e]

NMR spectroscopy was used to study the ROP of L-lactide with the zinc amide and phenoxide complexes. ^{1}H NMR spectra demonstrated the conversion of L-lactide to PLA (Supporting Information Figures 14 and 16 for **1a** and **1b**, respectively). Homonuclear decoupled ^{1}H NMR spectra (Supporting Information Figures 15 and 17 for **1a** and **1b**, respectively) show that the isolated polymeric materials are isotactic PLA where the stereochemistry of L-lactide was retained, yielding poly-L-lactide (PLLA) with both the amide and phenoxide initiating ligands.[19] An NMR study of percentage conversion and molecular weight for [L-lactide]/[**1b**] = 100 was conducted in $CDCl_3$ (Supporting Information SI Figures 18 and 19).

The disparity between the observed and calculated molecular weights for the isolated PLLA varied, Table 2. In general, polymerization with the zinc amide complexes had the largest differences. This likely resulted from a number of processes. The primary process in the case of the amide complexes would seem to be catalyst decomposition to bis-ligated complexes. The long polymerization times where the amides were in solution at ambient temperature resulted from the low nucleophilicity and slow ROP initiation of the amide ligand. As a result, the number of active catalyst sites was reduced. Transesterification has explained the molecular weight disparity in catalytic systems incorporating zinc alkoxide[20] or aluminum alkoxide complexes;[21] however, such processes are often accompanied by a broadening of the molecular weight distribution, which does not appear to be significant in this system.[22]

For **1b** and **2b**, molecular weights and PDI values are close to the predicted values. With the same catalyst:lactide ratio, the PDI values of the phenoxides shown in entries 7 and 9–11 are low, which is in agreement with the living polymerization mechanism. Additionally, Figure 4 shows that as the monomer percentage conversion increases, the polymer molecular weight increases in a linear fashion, further suggesting the living character of ROP with these complexes.

A catalytic amount of **1c** and 2,6-disubstituted phenol were added to L-lactide, and the mixture was stirred for 24 h. No PLA was observed by ^{1}H NMR or GPC. It has been previously reported that in some instances bis-ligated complexes are active

dx.doi.org/10.1021/om200865w | Organometallics XXXX, XXX, XXX–XXX

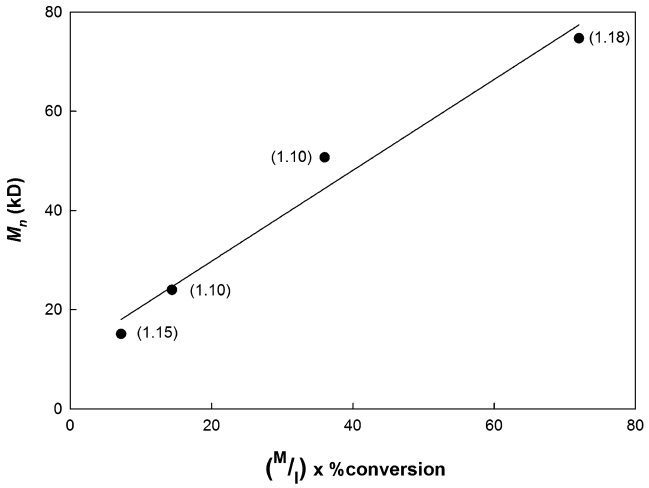


Figure 4. Linear relationship observed between M_n and monomer/initiator ratio of PLA produced from the ROP of L-lactide by **1b** in CH_2Cl_2. PDI values are provided in parentheses.

ROP catalysts in the presence of a phenol, but that was not observed here.[6d,12c]

■ CONCLUSIONS

A series of zinc amide and zinc phenoxide complexes were prepared with tridentate ketoiminate ligands. The zinc amide structures are among the few reported with monoanionic NNO Schiff bases, and the steric bulk of di-*tert*-butyl phenoxide yielded an uncommon mononuclear zinc phenoxide. While the incorporation of increasingly bulky groups minimized the formation of bis-ligated zinc complexes, the byproduct was not completely eliminated. Preliminary studies of L-lactide ROP with the zinc phenoxide complexes showed them to be more efficient and, as expected, yielded more complete ROP than the corresponding amide complexes. The addition of larger groups at the quinoline 2-position led to lower percentage conversion of L-lactide to isotactic PLLA during ROP.

■ EXPERIMENTAL SECTION

Materials. L^1-**H**, L^2-**H**, and L^3-**H** were prepared with literature methods.[11f] Zinc bis(trimethylsilyl)amide was prepared with a modified procedure from the literature.[17] The following chemicals were purchased from Acros and used without further purification unless otherwise stated: 8-aminoquinoline, 2,6-di-*tert*-butylphenol, 2,6-dimethylphenol, *p*-toluenesulfonic acid, lithium granules, anhydrous zinc chloride, sodium bis(trimethylsilyl)amide, triethylamine, dichloromethane, and chloroform. The following chemicals were purchased from Aldrich and used without further purification unless otherwise stated: 2,4-pentandione, dibenzoylmethane, L-lactide, 4-methylbenzyl alcohol, calcium hydride, benzophenone, ammonia (33%), sodium metal, ethyl acetate, toluene, tetrahydrofuran, hexanes, benzene-d_6, dichloromethane-d_2, and chloroform-d_1. 8-Hydroxyquinoline was purchased from Fisher. Bromobenzene was purchased from J.T. Baker. Ammonium sulfite monohydrate was purchased from Alfa Aesar. 8-Amino-2-methylquinoline was purchased from TCI America. Solvents used in the preparation and characterization of the zinc complexes were dried with calcium hydride and sodium benzophenone ketyl and stored under an inert atmosphere (inert atmosphere glovebox). Chloroform-d_1 and dichloromethane-d_2 were degassed and dried over 4 Å molecular sieves. L-Lactide was purified by recrystallization from toluene and held *in vacuo* at 40 °C overnight prior to use.

General Methods and Instrumentation. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were collected with a Bruker Avance III 400 spectrometer. ^{1}H (500 MHz) NMR spectra were collected with a Varian VNMR S500 spectrometer. Electronic spectra were collected with a Hewlett-Packard 8453e photodiode array spectrometer (200−1100 nm) with a 4 mL sealed quartz cuvette. Mass spectrometry data were collected with a Waters LCT Premier XE time-of-flight instrument controlled by MassLynx 4.1 software. Samples were infused using direct loop injection from a Waters Acquity UPLC into the multi-mode ionization source. The lock mass standard for accurate mass determination was leucine enkephalin (Sigma L9133). Gel permeation chromatography to determine polymer molecular weights (M_n and M_w) used a Thermo Separation Products SpectraSystem P4000 HPLC pump equipped with Phenomenex Phenogel columns (30.0 × 7.8 cm, 5 μm) with molecular weight ranges of 1−75 kDa (#00H-04440K0) or 5−500 kDa (#00H-0445-K0). Detection was performed with a Polymer Laboratories PL-ELS1000 evaporative light scattering detector. Continuously vacuum degassed THF (HPLC grade, uninhibited) was used as mobile phase at ambient temperature with a flow rate of 1.0 mL min^{-1}. Linear polystyrene standards were used as calibration standards, and a Mark−Houwink factor of 0.58 was applied.

X-ray Crystallography. Crystal data for compounds **1a**, **2a**, **4a**, and **4b** were collected at 100(2) K using a Bruker Smart 1000 APEX2 CCD diffractometer. Data collection was carried out with Mo Kα radiation (λ = 0.71073 Å) with a frame time of 30 s for **1a**, **2a**, **4a**, and **4b**. Frames were collected with 0.30° steps in ω at four different φ settings and a detector position of −28° in 2 h. The intensity data were corrected for absorption and decay with SADABS (Bruker).[24] The data were integrated with SAINT (Bruker).[25] The structure was solved and refined using SHELXTL.[26] Crystallographic data for compounds **1a**, **2a**, **4a**, and **4b** are given in SI Table 1 in the Supporting Information.

Synthesis of 2-Phenyl-8-hydroxyquinoline, I. The synthesis of compound **I** was completed using methods adapted from the literature.[16a] Under an inert atmosphere, bromobenzene (9.1 g, 28 mmol) was added dropwise to lithium granules (850 mg, 122 mmol) suspended in 40 mL of Et_2O and stirred for 1 h. A solution of 8-hydroxyquinoline (4.0 g, 58.0 mmol) in Et_2O (70 mL) was added dropwise to the reaction and stirred at 35 °C for 1 h. The flask was cooled to room temperature, and air was bubbled through the reaction for 2 h. Diethyl ether (80 mL) and water (40 mL) were added, and the solution was neutralized with 6 M HCl and 1 M Na_2CO_3. The aqueous layer was extracted with Et_2O (2 × 75 mL), and the organic layer was filtered and dried *in vacuo*. The white solid was isolated by sublimation (4.60 g, 20.7 mmol, 75.4%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.22 (d, J = 7.0 Hz, 1H, Ar*H*), 7.36 (d, J = 8.0 Hz, 1H, Ar*H*), 7.46 (t, J = 8.0 Hz, 1H, Ar*H*), 7.50 (t, J = 7.0 Hz, 1H, Ar*H*), 7.56 (t, J = 7.5 Hz, 2H, Ar*H*), 7.93 (d, J = 9.0 Hz, 1H, Ar*H*), 8.17 (d, J = 8.0 Hz, 2H, Ar*H*), 8.24 (d, J = 9.0 Hz, 1H, Ar*H*), 8.45 (s, br, 1H, −O*H*). ^{13}C NMR (100 MHz; $CDCl_3$): δ 110.63, 117.79, 119.74, 127.49, 127.53, 127.74, 129.03, 129.82, 137.36, 137.92, 138.69 (Ar), 152.36 (−*C*-OH), 155.09. ESI-HRMS observed m/z = 222.0926 ([M + H]$^+$), calculated exact mass $C_{15}H_{12}NO$ = 222.0919, error: 3.2 ppm. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.71; H, 4.93; N, 6.26.

Synthesis of 2-Phenyl-8-aminoquinoline, II. The conversion of **I** to 2-phenyl-8-aminoquinoline was performed with a method adapted from the literature.[16b] Compound **I** (1.1 g, 5.0 mmol) was added to ammonium sulfite monohydrate, $(NH_4)_2SO_3{\cdot}H_2O$ (6.7 g, 50 mmol), and 20 mL of NH_3 (33%). The reactants were sealed in a steel reactor and heated to 175 °C for 7 days. The reactor was cooled and washed with CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the solvent was removed *in vacuo*. The bright yellow solid was isolated with column chromatography (silica, hexanes/EtOAc, 12:1, 3% Et_3N) (0.340 g, 1.45 mmol, 31%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.11 (s, br, 2H, −N*H*$_2$), 6.95 (dd, J = 1.2, 7.5 Hz, 1H, Ar*H*), 7.16 (dd, J = 1.2, 8.0 Hz, 1H, Ar*H*), 7.33 (t, J = 7.8 Hz, 1H, Ar*H*), 7.48 (t, J = 7.5 Hz, 1H, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.86 (d, J = 8.6 Hz, 2H, Ar*H*), 8.13 (d, J = 8.6 Hz, 1H, Ar*H*), 8.21 (d, J = 7.0 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz; $CDCl_3$): δ 110.36, 115.85, 118.99, 127.32, 127.42, 127.80, 128.83, 129.18, 136.90, 138.19, 139.75, 144.29

(Ar), 154.23 (*C*-OH). ESI-HRMS observed m/z = 221.1076 ([M + H]$^+$), calculated exact mass $C_{15}H_{13}N_2$ = 221.1079, error: 1.4 ppm. Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.92; H, 5.77; N, 12.63.

Synthesis of ***L^4-H.*** The synthesis of **L^4-H** was conducted with a similar method to previously reported.[11f] A toluene solution (20 mL) containing 2,4-pentanedione (1.500 g, 15.0 mmol) and *p*-toluenesulfonic acid (catalytic amount) was sparged with N_2 for 20 min. Compound **2** (0.680 g, 3.09 mmol) was added to the flask, which was heated to reflux for azeotropic distillation for 20 h. Water produced by the reaction was removed at regular intervals. The pale yellow solid was isolated with column chromatography (silica, hexanes/EtOAc, 7:1, 3% Et_3N) (0.633 g, 2.10 mmol, 68%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.21 (s, 3H, −CH_3), 2.31 (s, 3H, −CH_3), 5.34 (s, 1H, −C*H*), 7.40 (m, 3H, Ar*H*), 7.48 (t, J = 7.2 Hz, 1H, Ar*H*), 7.58 (t, J = 8.0 Hz, 2H, Ar*H*), 7.98 (d, J = 8.8 Hz, 1H, Ar*H*), 8.16 (d, J = 8.8 Hz, 1H, Ar*H*), 8.52 (d, J = 7.2 Hz, 2H, Ar*H*), 13.68 (s, 1H, −O*H*). ^{13}C NMR (100 MHz; $CDCl_3$): δ 21.57 (−CH_3), 29.77 (−CH_3), 100.80 (−CH), 118.70, 119.05, 122.13, 126.01, 127.83, 127.90, 129.06, 129.71, 136.95, 137.20, 138.92, 140.76, 155.89 (Ar), 157.09 (−*C*═N−), 196.24 (−*C*−OH). ESI-HRMS observed m/z = 303.1508 ([M + H]$^+$), calculated exact mass $C_{20}H_{19}N_2O$ = 303.1497, error: 3.6 ppm. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.91; H, 6.01; N, 9.20. UV (Et_2O) λ_{max}: 288, 384 nm.

Preparation of Zinc Bis(trimethylsilyl)amide Complexes with Ketoimines, Procedure A. Under an inert atmosphere, Et_2O (10 mL) was added to a Schlenk flask containing zinc bis(trimethylsilyl)amide (1.1−1.2 equivalents). The ketoimines (1.0 equivalent) were dissolved or slurried in Et_2O (5 mL) and added dropwise to the flask. An immediate color change from pale yellow to orange was observed. The reaction was stirred for 1 h. The reaction volume was reduced *in vacuo* to approximately 1 mL, and 1 mL of cold hexanes was added. The flask was placed in the freezer at −35 °C for 1 h to reduce solubility. Compounds **1a**−**4a** were isolated by filtration, washed with cold hexanes, and dried *in vacuo*. Compounds **1a**−**4a** were insufficiently stable to obtain suitable microanalysis results. NMR spectra of **1a**−**4a** are provided in the Supporting Information.

Synthesis of ***1a.*** Following procedure A, **L^1-H** (0.212 g, 0.94 mmol) was dissolved in Et_2O and added dropwise to zinc bis(trimethylsilyl)amide (0.430 g, 1.11 mmol) dissolved in Et_2O. The yellow solid was isolated by filtration (0.296 g, 0.65 mmol, 70.0%). ^{1}H NMR (500 MHz; C_6D_6): δ 0.29 (s, 18H, −Si(CH_3)$_3$), 1.75 (s, 3H, −CH_3), 2.07 (s, 3H, −CH_3), 5.08 (s, 1H, −C*H*), 6.58 (dd, J = 4.0, 8.0 Hz, 1H, Ar*H*), 6.94 (dd, J = 2.0, 7.0 Hz, 1H, Ar*H*), 7.04 (m, 2H, Ar*H*), 8.53 (dd, J = 1.5, 2.5 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 5.04 (−Si(CH_3)$_3$), 24.36 (−CH_3), 28.17 (−CH_3), 101.78 (−C*H*), 122.37, 122.57, 122.68, 127.88, 129.62, 139.59, 141.52, 149.14 (Ar), 169.78 (−N═*C*−), 187.29 (−O═*C*−). UV (Et_2O) λ_{max}: 241, 269, 340, 408 nm.

Synthesis of ***2a.*** Following procedure A, **L^2-H** (0.228 g, 0.95 mmol) was dissolved in Et_2O and added dropwise to zinc bis(trimethylsilyl)amide (0.443 g, 1.15 mmol) dissolved in Et_2O. The yellow solid was isolated by filtration (0.324 g, 0.70 mmol, 73.3%). ^{1}H NMR (500 MHz; C_6D_6): δ 0.24 (s, 18H, Si(CH_3)$_3$), 1.76 (s, 3H, −CH_3), 2.13 (s, 3H, −CH_3), 2.67 (s, 3H, Ar-CH_3), 5.10 (s, 1H, −C*H*), 6.51 (d, J = 8.0, 1H, Ar*H*), 6.99 (d, J = 8.0, 1H, Ar*H*), 7.06 (m, 2H, Ar*H*), 7.33 (d, J = 8.0 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 5.33 (−Si(CH_3)$_3$), 24.80 (−CH_3), 26.22 (−CH_3), 28.59 (Ar-CH_3), 102.11 (−CH), 122.52, 123.66, 126.87, 127.74, 139.85, 141.37, 142.79, 159.22 (Ar), 169.79 (−N═*C*−), 187.59 (−O═*C*−). UV (Et_2O) λ_{max}: 238, 269, 334, 398 nm.

Synthesis of ***3a.*** Following procedure A, **L^3-H** (0.136 g, 0.37 mmol) was dissolved in Et_2O and added dropwise to zinc bis(trimethylsilyl)amide (0.159 g, 0.41 mmol) dissolved in Et_2O. The yellowish-orange solid was isolated by filtration (0.160 g, 0.27 mmol, 73.4%). ^{1}H NMR (500 MHz; C_6D_6): δ 0.33 (s, 18H, −Si(CH_3)$_3$), 2.79 (s, 3H, Ar-CH_3), 6.23 (s, 1H, −C*H*), 6.53 (d, J = 8.5 Hz, 1H, Ar*H*), 6.66 (d, J = 8.0 Hz, 1H, Ar*H*), 6.72 (t, J = 8.0 Hz, 1H, Ar*H*), 6.81 (d, J = 8.0 Hz, 1H, Ar*H*), 7.2 (m, 9H, Ar*H*), 8.17 (d, J = 7.0 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 5.35 (−Si(CH_3)$_3$), 26.28 (Ar-CH_3), 101.52 (−CH), 120.44, 121.29, 123.64, 126.89, 127.11, 127.61, 127.84, 127.91, 128.10, 128.53, 129.34, 129.55, 131.12, 140.09, 140.69, 140.79, 141.16, 142.12, 159.24 (Ar), 171.82 (−N═*C*−), 182.78 (−O═*C*−). UV (Et_2O) λ_{max}: 263, 355, 434 nm.

Synthesis of ***4a.*** Following procedure A, **L^4-H** (0.170 g, 0.56 mmol) was dissolved in Et_2O and added dropwise to zinc bis(trimethylsilyl)amide (0.257 g, 0.66 mmol) dissolved in Et_2O. The pale orange solid was isolated by filtration (0.190 g, 0.36 mmol, 64.6%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ −0.54 (s, 18H, −Si(CH_3)$_3$), 2.11 (s, 3H, −CH_3), 2.24 (s, 3H, −CH_3), 5.27 (s, 1H, −C*H*)), 7.6 (m, 6H, Ar*H*), 7.87 (d, J = 8.5 Hz, 1H, Ar*H*), 7.99 (dd, J = 1.7, 8.2 Hz, 2H, Ar*H*), 8.40 (d, J = 8.5 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 5.08 (−Si(CH_3)$_3$), 23.95 (−CH_3), 28.63 (−CH_3), 101.54 (−CH), 122.45, 122.72, 123.32, 126.08, 127.32, 128.53, 128.65, 129.52, 130.12, 130.65, 139.49, 140.07, 142.46, 143.56, 159.17 (Ar), 169.35 (−N═*C*−), 186.47 (−O═*C*−). UV (Et_2O) λ_{max}: 263, 312 nm.

Preparation of Zinc Phenoxide Complexes with Ketominiate Ligands, Procedure B. Under an inert atmosphere, the zinc amide complex, **1a**−**4a** (1.0 equivalent), was dissolved in Et_2O (5 mL), and a Et_2O solution (5 mL) of 2,6-di-*tert*-butylphenol (1.3−1.5 equivalents) was added to the stirring solution of zinc amide complex. The reaction was stirred for 2 h. After 30 min a precipitate was observed. The reaction solution volume was reduced to 2 mL. Et_2O and 2 mL of hexanes were added. The flask was placed into the −35 °C freezer for 1 h, and the solid was isolated by filtration and washed with 3 mL of cold hexanes. The solid was dried *in vacuo*. Compounds **1b**−**4b** were insufficiently stable to obtain suitable microanalysis results. NMR spectra of **1b**−**4b** are provided in the Supporting Information.

Synthesis of ***1b.*** Following procedure B, 2,6-di-*tert*-butylphenol (0.190 g, 0.92 mmol) was dissolved in Et_2O and added to a solution of **1a** (0.296 g, 0.66 mmol) in Et_2O. The bright yellow solid was isolated by filtration (0.191 g, 0.39 mmol, 58.5%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 1.44 (s, 18H, −C(CH_3)$_3$), 1.65 (s, 3H, −CH_3), 2.30 (s, 3H, −CH_3), 5.07 (s, 1H, −C*H*), 6.79 (t, J = 7.8 Hz, 1H, Ar*H*), 7.15 (d, J = 7.8 Hz, 2H, Ar*H*), 7.20 (dd, J = 4.4, 8.2 Hz, 1H, Ar*H*), 7.32 (dd, J = 1.2, 7.6 Hz, 1H, Ar*H*), 7.37 (dd, J = 1.2, 8.2 Hz, 1H, Ar*H*), 7.50 (t, J = 8.0 Hz, 1H, Ar*H*), 8.08 (dd, J = 1.6, 8.2 Hz, 1H, Ar*H*), 8.20 (dd, J = 1.7, 4.4 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 22.94 (−CH_3), 28.50 (−CH_3), 30.48 (−C(CH_3)$_3$), 34.61 (−*C*(CH$_3$)$_3$), 100.45 (−CH), 120.05, 120.18, 121.22, 121.37, 125.28, 127.38, 129.18, 136.43, 137.61, 141.44, 145.15, 146.76, 154.30 (Ar), 168.50 (−N═*C*−), 188.30 (−O═*C*−). Anal. Calcd for $C_{28}H_{34}N_2O_2Zn$: C, 67.80; H, 6.91; N, 5.65. Found: C, 66.32; H, 6.53; N, 5.53. UV (Et_2O) λ_{max}: 267, 345, 397 nm.

Synthesis of ***2b.*** Following procedure B, 2,6-di-*tert*-butylphenol (0.260 g, 1.26 mmol) was dissolved in Et_2O and added to a solution of **2a** (0.436 g, 0.94 mmol) in Et_2O. The bright yellow solid was isolated by filtration (0.260 g, 0.72 mmol, 75.7%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 1.15 (s, 18H, −C(CH_3)$_3$), 2.09 (s, 3H, −CH_3), 2.26 (s, 3H, −CH_3), 3.00 (s, 3H, Ar-CH_3), 5.26 (s, 1H, −C*H*), 6.33 (t, J = 7.6 Hz, 1H, Ar*H*), 6.95 (d, J = 7.6 Hz, 2H, Ar*H*), 7.51 (d, J = 8.4 Hz, 1H, Ar*H*), 7.62 (m, 3H, Ar*H*) 8.32 (d, J = 8.4 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 23.82 (−CH_3), 27.16 (Ar-CH_3), 28.57 (−CH_3), 30.62 (−C(CH_3)$_3$), 35.14 (−*C*(CH$_3$)$_3$), 101.75, (−CH) 113.47, 122.79, 123.19, 124.78, 127.09, 127.72, 138.97, 140.35, 141.07, 141.81, 159.70, 164.91 (Ar), 170.24 (−N═*C*−), 186.86 (−O═*C*−). Anal. Calcd for $C_{29}H_{36}N_2O_2Zn$: C, 68.29; H, 7.11; N, 5.49. Found: C, 67.42; H, 6.52; N, 5.15. UV (Et_2O) λ_{max}: 270, 333, 402 nm.

Synthesis of ***3b.*** Following procedure B, 2,6-di-*tert*-butylphenol (0.113 g, 0.55 mmol) was dissolved in Et_2O and added to a solution of **3a** (0.240 g, 0.41 mmol) in Et_2O. The bright yellow solid was isolated by filtration (0.174 g, 0.27 mmol, 66.7%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 1.29 (s, 18H, −C(CH_3)$_3$), 2.99 (s, 3H, Ar-CH_3), 6.08 (s, 1H, −C*H*), 6.38 (t, J = 7.6 Hz, 1H, Ar*H*), 6.61 (d, J = 8.0 Hz, 1H, Ar*H*), 7.00 (d, J = 7.7 Hz, 2H, Ar*H*), 7.16 (t, J = 8.0 Hz, 1H, Ar*H*), 7.43 (m, 10H, Ar*H*), 8.00 (d, J = 7.4 Hz, 2H, Ar*H*), 8.28 (d, J = 8.4 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 27.07 (Ar-CH_3), 30.93 (−C(CH_3)$_3$), 35.34 (−*C*(CH$_3$)$_3$), 100.66 (−CH), 121.42, 122.40, 123.64, 124.84, 127.00, 127.44, 127.78, 128.03, 128.51, 129.32, 129.40, 131.17, 139.17, 140.45, 140.50, 140.58, 140.64, 141.08, 159.79, 165.40

dx.doi.org/10.1021/om200865w | *Organometallics* XXXX, XXX, XXX−XXX

(Ar), 171.86 (−N=*C*−), 182.31 (−O=*C*−). Anal. Calcd for $C_{39}H_{40}N_2O_2Zn$: C, 73.86; H, 6.36; N, 4.42. Found: C, 73.86; H, 6.34; N, 4.27. UV (Et_2O) λ_{max}: 263, 353, 433 nm.

Synthesis of ***4b***. Following procedure B, 2,6-di-*tert*-butylphenol (0.094 g, 0.46 mmol) was dissolved in Et_2O and added to a solution of **4a** (0.190 g, 0.36 mmol) in Et_2O. The bright yellow solid was isolated by filtration (0.135 g, 0.24 mmol, 65.6%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 0.85 (s, 18H, −C(*CH*$_3$)$_3$), 2.15 (s, 3H, −*CH*$_3$), 2.30 (s, 3H, −*CH*$_3$), 5.32 (s, 1H, −*CH*), 6.23 (t, J = 7.7 Hz, 1H, Ar*H*), 6.82 (d, J = 7.6 Hz, 2H, Ar*H*), 7.66 (m, 6H, Ar*H*), 8.00 (d, J = 8.6 Hz, 1H, Ar*H*), 8.08 (d, J = 7.0 Hz, 2H, Ar*H*), 8.51 (d, J = 8.6 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 23.51 (−*CH*$_3$), 28.78 (−*CH*$_3$), 30.16 (−C(*CH*$_3$)$_3$), 34.70 (−*C*(CH$_3$)$_3$), 101.65 (−*CH*), 122.23, 123.05, 123.22, 124.47, 127.63, 128.53, 129.21, 130.39, 131.36, 138.84, 139.13, 140.96, 141.98, 142.57, 158.88, 164.46 (Ar), 169.94 (−N=*C*−), 187.04 (−O=*C*−). Anal. Calcd for $C_{34}H_{38}N_2O_2Zn$: C, 71.38; H, 6.70; N, 4.90. Found: C, 69.89; H, 6.67; N, 4.73. UV (Et_2O) λ_{max}: 264, 313 nm.

Synthesis of Bis-ligated Zinc Complex ***1c***. Under an inert atmosphere, Et_2O (10 mL) was added to a Schlenk flask, and zinc bis(trimethylsilyl)amide (0.130 g, 0.34 mmol) was added. A solution of $\mathbf{L^1}$**-H** (0.134 g, 0.59 mmol) in Et_2O (5 mL) was added dropwise. An immediate color change from colorless to yellow was observed, and a precipitate formed after 20 min. The reaction was stirred for 24 h. The reaction solution volume was reduced to approximately 2 mL. Compound **1c** was isolated by filtration, washed with cold hexanes, and dried *in vacuo* (0.109 g, 0.21 mmol, 71.7%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 1.64 (s, 6H, −*CH*$_3$), 2.30 (s, 6H, −*CH*$_3$), 5.07 (s, 2H, −*CH*), 7.21 (dd, J = 4.4, 8.2 Hz, 2H, Ar*H*), 7.33 (d, J = 7.6 Hz, 2H, Ar*H*), 7.38 (d, J = 8.1 Hz, 2H, Ar*H*), 7.28 (t, J = 7.7 Hz, 2H, Ar*H*), 8.09 (d, J = 8.3 Hz, 2H, Ar*H*), 8.21 (d, J = 4.4 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz; CD_2Cl_2): δ 22.91 (−*CH*$_3$), 28.46 (−*CH*$_3$), 100.42 (−*CH*$_3$), 120.15, 121.20, 121.34, 127.36, 129.16, 137.58, 141.42, 145.13, 146.75 (Ar), 168.49 (−N=*C*−), 188.28 (−O=*C*−). ESI-HRMS observed m/z = 515.1410 ([M + H]$^+$), calculated exact mass $C_{28}H_{27}N_4O_2Zn$ = 515.1420, error: 1.94 ppm. Anal. Calcd for $C_{28}H_{26}N_4O_2Zn$: C, 65.18; H, 5.08; N, 10.86. Found: C, 64.91; H, 5.08; N, 10.15. UV (Et_2O) λ_{max}: 244, 271, 342, 421 nm. Compound **1c** was insufficiently stable to obtain suitable microanalysis results. NMR spectra of **1c** are provided in the Supporting Information.

Ring-Opening Polymerization of L-Lactide. Under an inert atmosphere, a CH_2Cl_2 solution of catalyst was dispensed into a 25 mL round-bottom flask. L-Lactide in CH_2Cl_2 solution was added while stirring. Additional solvent was added to make the total volume of the solution 3 mL. The solutions were stirred for 1 h for the zinc phenoxide complexes and 24 h for the zinc amide complexes, and the viscosity of the solution increased. An aliquot of the reaction mixture was quenched with 1 mL of a 5% acetic acid in methanol solution to determine percent conversion of lactide to PLA by ^{1}H NMR. The remaining reaction solution was quenched with 10−20 mL of the acetic acid/methanol solution in preparation for GPC analysis. The solvent was reduced *in vacuo* and PLA precipitated. The white crystalline solid was isolated by filtration, washed with cold acetic acid/methanol solution, and dried *in vacuo*.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of the reported compounds and X-ray crystallographic data for the crystal structure determination of **1a**, **2a**, **4a**, and **4b** are available in CIF and table format and are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by a Research Corporation for Science Advancement Cottrell College Science Award (#10728), Tooma Undergraduate Research Fellowships, and the generous support of Pepperdine University undergraduate research programs. We would like to thank Daphne Green and Allison Zorn for their laboratory support. Instrumentation was made available through the support of Phil Hampton (California State University, Channel Islands, 500 MHz ^{1}H NMR), Saeed Khan (University of California, Los Angeles, X-ray crystallography of **1a**, **2a**, **4a**, and **4b**), and Greg Khitrov (University of California, Los Angeles Molecular Instrumentation Center−Mass Spectrometry Facility in the Department of Chemistry). The mass spectrometry data were collected through a project described and supported by Grant Numbers S10-RR024605 and S10-RR025631 from the National Center for Research Resources. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Center for Research Resources or the National Institutes of Health.

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