DOI: 10.1002/ejic.201001362

Synthesis, Structure, and Ring-Opening Polymerization Catalysis of Zinc Complexes Containing Amido Phosphinimine Ligands

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Keywords: Zinc / N,P ligands / Ring-opening polymerization

A series of amido phosphinimine ligands of the type $[(NAr^1)\text{-}o\text{-}(Ph_2P{=}NAr^2)C_6H_4]^-$ (**2a**: Ar^1 = 2,6-$C_6H_3iPr_2$, Ar^2 = 2,6-$C_6H_3iPr_2$; **2b**: Ar^1 = 2,6-$C_6H_3iPr_2$, Ar^2 = 2,4,6-$C_6H_2Me_3$; **2c**: Ar^1 = 2,6-$C_6H_3Me_2$, Ar^2 = 2,4,6-$C_6H_2Me_3$), which are electronic variations of monoanionic β-diketiminates, have been employed to examine the coordination chemistry of zinc. Alkane elimination reactions of ZnR_2 (R = Me, Et) with H[**2a**–**c**] in toluene or ethereal solutions at –35 °C afforded cleanly the corresponding organozinc complexes [**2a**–**c**]ZnMe (**3a**–**c**) and [**2a**–**c**]ZnEt (**4a**–**c**). Deprotonation of H[**2a**–**c**] with *n*BuLi at –35 °C generated [**2a**–**c**]Li (**5a**–**c**), which may be isolated as either solvent-free complexes or solvated adducts depending on the reaction solvents employed (toluene, OEt2, or THF). Metathetical reactions of **5a**·OEt_2 with $Zn(OAc)_2$ in THF at –35 °C produced [**2a**]Zn(OAc) (**6a**). These amido phosphinimine derivatives all display solution C_s symmetry on the NMR timescale. The mononuclear nature of the three-coordinate alkyls **3**–**4** and four-coordinate acetate **6a** was confirmed by single-crystal X-ray diffraction analyses. Interestingly, the alkyl complexes **3a**–**c** and **4a**–**c** are all active initiators for the catalytic ring-opening polymerization of ε-caprolactone, whereas the acetate **6a** is comparatively inactive.

Introduction

The search for controlled methods to prepare biocompatible and biodegradable polymers such as poly(ε-caprolactone) (PCL) and polylactide is of current interest in view of their potential applications in drug delivery, absorbable stitches, and environmentally friendly thermoplastics, etc.[1,2] Significant recent advances in this respect have been made with the metal-mediated ring-opening polymerization (ROP) of lactones.[3–6] The active catalysts involved are usually alkoxide complexes of main group metals (e.g. Li,[7–9] Mg,[10–13] Zn,[11–23] Al,[24,25] Sn,[26] etc.), group 3 and lanthanides (e.g. Y,[27] La,[28] etc.), and transition metals (e.g. group 4,[29] Fe,[30] etc.). Of particular note are zinc complexes of tris(pyrazolyl)hydroborates[11] and β-diketiminates,[12,13] which have shown remarkable catalytic activities in a controlled manner. We are currently exploring the reaction chemistry with metal complexes of amido phosphinimine ligands,[31] which may be regarded as an electronic modification of β-diketiminates. The amido phosphinimine ligands are oxidative derivatives of amido phosphanes,[32–41] and the catalytic activities of zinc alkyl complexes of these ligands with respect to the ROP of ε-caprolactone (ε-CL) have recently been demonstrated.[42] Herein, we describe the synthesis, structural characterization, and ROP activities of zinc amido phosphinimine complexes. Differences in the structure and reactivity of these compounds relative to those of their parent amido phosphane[42,43] and β-diketiminate derivatives[12,13] are discussed.

Results and Discussion

Ligand Synthesis

Following established protocols,[31] the protio ligand precursors H[**2**] were readily prepared by Staudinger reactions[44] of *N*-(2-diphenylphosphanylphenyl)-2,6-dialkylaniline (H[**1**])[36,43] with appropriate organoazides[45–47] in toluene or DME solutions at 80 °C (Scheme 1). Piers et al. recently described a distinct strategy to prepare H[**2a**][48] and H[**2b**].[49] Compounds H[**2a**–**c**] were all isolated as colorless crystalline materials. Solution ^1H and ^{13}C NMR spectroscopic data of these compounds are consistent with a time-averaged C_s symmetry. For instance, the two *o*-alkyl groups in each *N*-aryl moiety are all chemically equivalent, so are the two phosphorus-bound phenyl rings. Consistent with the more oxidized nature of the phosphinimine functionality, the ^{31}P chemical shifts of H[**2a**–**c**] (Table 1) are all comparatively downfield from those of H[**1**] (ca. –20 ppm).[36,43] The acidic NH proton of H[**2a**–**c**] resonates at 9–10 ppm.

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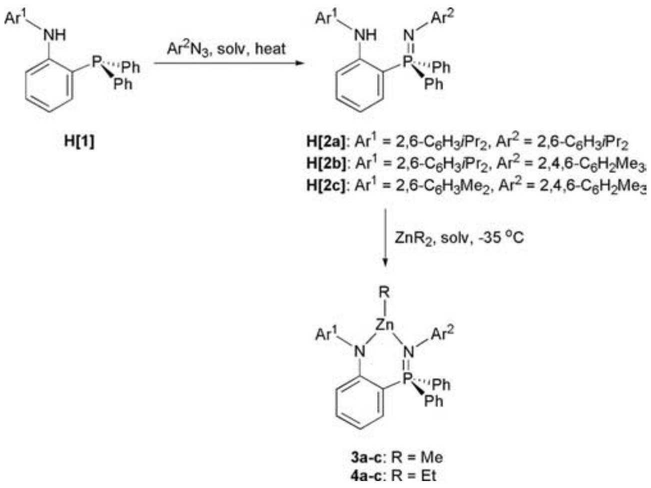
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201001362.



Scheme 1. Synthesis of ligands and zinc alkyl complexes.

Table 1. Selected NMR spectroscopic data.[a]

Compound	$\delta_{H\alpha}$	$\delta_{C\alpha}$	δ_P
H[**2a**]			0.7
H[**2b**]			0.9
H[**2c**]			1.6
3a	–0.42	–17.2	28.5
3b	–0.50	–16.0	24.4
3c	–0.46[b]	–16.5	23.9
4a	0.52	–0.8	27.4
4b	0.40	–0.8[c]	24.0
4c	0.44	–1.2[d]	23.3
5a·OEt$_2$			19.0
5a·THF			19.9
5a			19.4
5b			13.3
5c·OEt$_2$			14.7
6a			32.3[e]

[a] All spectra were recorded in C_6D_6 at room temperature unless otherwise noted, chemical shifts in ppm. [b] $^4J_{HP}$ = 1.5 Hz. [c] $^3J_{CP}$ = 1.9 Hz. [d] $^3J_{CP}$ = 1.4 Hz. [e] Recorded in $CDCl_3$.

Figure S1 depicts the molecular structure of H[**2c**]. Bond lengths and angles are unexceptional. The *N*-phenylene-P atoms are essentially co-planar; the phosphinimine nitrogen atom, however, is notably displaced from the mean *N*-phenylene-P plane by 0.641 Å. A similar phenomenon is also found for H[**2a**][48] and H[**2b**].[49] These results are in sharp contrast to the coplanarity of the N2C3 backbone in β-diketimine derivatives such as [{(2,6-$R_2C_6H_3$)NCMe}$_2$-CH]H ([BDI-R]H, R = *i*Pr),[50] which indicates an inferior π-delocalization nature for H[**2a**–**c**].

Synthesis and Characterization of the Zinc Complexes

Alkane elimination reactions of dialkylzinc with H[**2a**–**c**] in toluene or ethereal solutions at –35 °C produced the corresponding complexes [**2a**–**c**]ZnR {R = Me (**3a**–**c**), Et (**4a**–**c**)} in high isolated yields. Conversely, relatively harsh conditions (≥80 °C, overnight to 3 d) appear to be necessary for similar reactions involving β-diketimines.[51,52] No sign of the formation of the bis-**2** complex was detected (NMR spectroscopy evidence) even at elevated temperatures (e.g. 100 °C), a result that is markedly different from that found with **1**,[42,43] but ascribable to the increased steric hindrance for the amido phosphinimine ligands because of the larger chelating rings. The formation rates of **3**–**4** appear to increase in the order **a** < **b** < **c**, consistent with that expected from a steric standpoint. Prior to the formation of the zinc alkyls **3**–**4**, no intermediate was detected by $^{31}P\{^1H\}$ NMR spectroscopy, in contrast to that found for the corresponding aluminum chemistry.[31] Interestingly, these three-coordinate zinc alkyls do not bind strong coordinating solvents such as THF or diethyl ether in spite of their coordinatively unsaturated nature, which highlights the sufficient steric crowdedness imposed by these amido phosphinimine ligands. The preparation of three-coordinate zinc complexes that are free of coordinating solvents is of current interest.[14,42,43,52–57] The successful isolation of **3c** and **4c** from THF solutions is noteworthy in view of the relatively small steric size of **2c**. In general, these alkyls are thermally stable under an inert atmosphere, even at elevated temperatures (100 °C, >24 h), but extremely sensitive to moisture, producing exclusively H[**2**] as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

Solution NMR spectroscopic data of **3**–**4** are all consistent with a time-averaged C_s symmetry for these molecules. In all cases, the *o*-alkyl moieties in each *N*-aryl group are chemically equivalent. The ^{31}P chemical shifts all move significantly downfield from those of their corresponding protio ligands (Table 1). This phenomenon is notably different from the parent amido phosphane chemistry.[42,43] Where resolved, the H_α or C_α atom exhibits a doublet resonance, e.g. in **3c**, **4b**, and **4c**, consistent with the coordination of phosphinimine functionality to the zinc center.

The solid-state structures of **3a**–**c** and **4a**–**c** were all determined by X-ray crystallography (Figures 1 and 2). Selected bond lengths and angles are summarized in Tables 2 and 3, respectively. Consistent with the solution NMR studies, these complexes are monomeric, three-coordinate species that do not bind any ethereal ligands, even though these compounds were prepared in ethereal solutions. The geometry of the coordination core is best described as trigonal planar as indicated by the sum (360°) of the bond angles about the zinc atom in all cases. The N=P distances are somewhat elongated relative to those of protio H[**2a**] [1.5582(13) Å],[48] H[**2b**] [1.5634(19) Å],[49] and H[**2c**]. The Zn–N distances are slightly longer for the phosphinimine nitrogen than for the amido nitrogen, likely reflective of the anionic nature of the latter and the mismatch involving the comparatively soft phosphinimine and the hard Zn^{II} center. In comparison, the two Zn–N distances in [BDI-*i*Pr]ZnMe are virtually identical [1.9480(18) Å and 1.9429(18) Å].[52] As a result, the steric pressure imposed by the amido arm in **3a**–**c** and **4a**–**c** appears to be more significant than that of the phosphinimine side, which leads to larger C–Zn–N angles for the former. The alkyl group is thus tilted toward the phosphinimine side. In **3a**–**c** and **4a**–**c**, the N–Zn–N bite angles of ca. 101° are notably sharper than the two C–Zn–N angles, but nevertheless wider than the corresponding

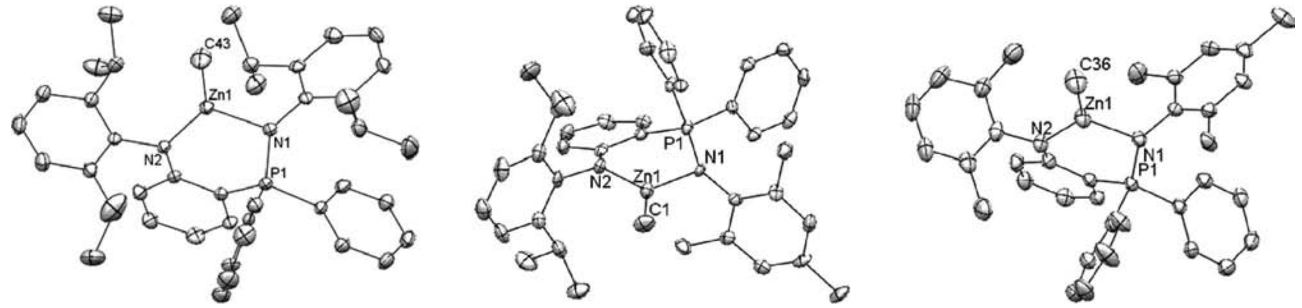


Figure 1. Molecular structures of **3a** (left), **3b** (middle), and **3c** (right) with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity.

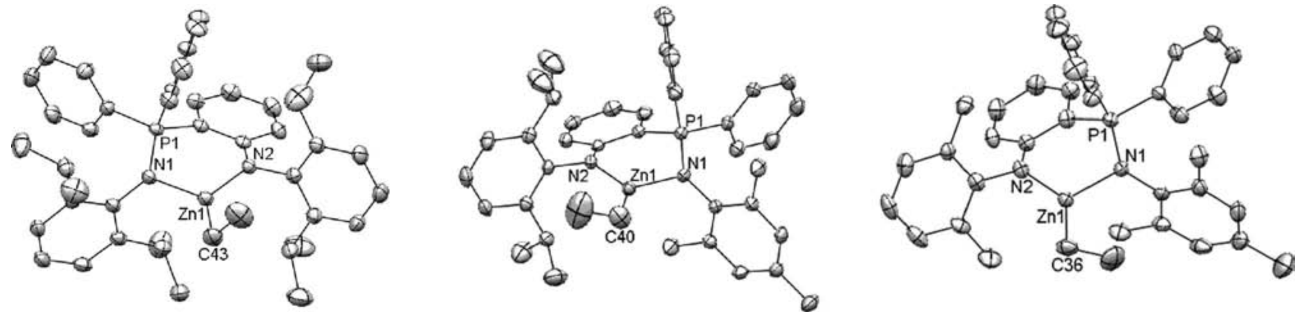


Figure 2. Molecular structures of **4a** (left), **4b** (middle), and **4c** (right) with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity.

values in derivatives of **1** (ca. 85°)[42,43] and β-diketiminate [e.g. 97.00(8)° in (BDI-*i*Pr)ZnMe[52] and 97.07(12)° in (BDI-*i*Pr)ZnEt].[51] Similarly to that of their protio ligands, the phosphinimine nitrogen atom in **3**–**4** is significantly displaced from the mean *N*-phenylene-P plane, so are the zinc center and the associated C_α atom. The π delocalization in the six-membered chelating rings of **3**–**4** is thus likely poor and insignificant.

Table 2. Selected bond lengths [Å] for **3a**–**c** and **4a**–**c**.

Compound	Zn–C	$Zn–N_{amide}$	$Zn–N_{phosphinimine}$	N=P
3a	1.949(5)	1.960(3)	2.017(3)	1.601(3)
3b[a]	1.948(9)	1.963(7)	2.006(7)	1.585(7)
3c	1.939(5)	1.959(3)	2.007(3)	1.599(3)
4a	1.962(4)	1.964(3)	2.009(3)	1.607(3)
4b	1.944(4)	1.953(3)	2.005(3)	1.604(3)
4c[a]	1.963(6)	1.942(5)	2.007(4)	1.603(4)

[a] Data represent one of two independent molecules found in the asymmetric unit.

Table 3. Selected bond angles [°] for **3a**–**c** and **4a**–**c**.

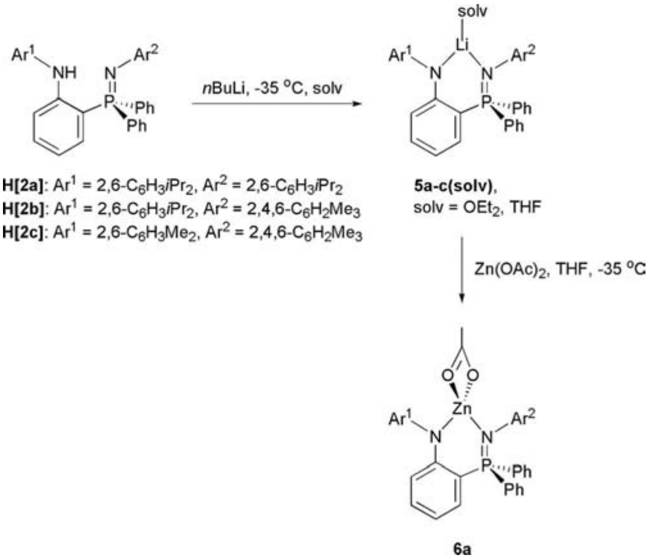
Compound	N–Zn–N	$C–Zn–N_{amide}$	$C–Zn–N_{phosphinimine}$
3a	101.84(13)	136.73(19)	121.41(19)
3b[a]	101.1(3)	130.0(4)	128.9(4)
3c	101.51(14)	132.8(2)	125.7(2)
4a	101.51(10)	130.94(14)	127.29(14)
4b	100.78(11)	132.29(17)	126.86(17)
4c[a]	100.80(19)	136.5(2)	122.7(2)

[a] Data represent one of two independent molecules found in the asymmetric unit.

In addition to zinc alkyls, zinc alkoxides and carboxylates are both intriguing as they are also potential initiators for catalytic ROP of heterocycles.[13–15,51,58–63] Our initial plans to prepare zinc alkoxides of **2** involve alcoholysis of zinc alkyls **3**–**4** with a variety of alcohols. Unfortunately, these reactions undesirably led to protonation on the amido nitrogen donor in **2**, consistent with the moisture sensitivity of **3**–**4** as mentioned before. Similar phenomena, however, have also been reported for systems employing **1**[42] or bis(phosphinimine)methyl ligands.[53]

Scheme 2 illustrates a second strategy involving a lithium intermediate. The lithium complexes **5a**–**c** were readily prepared by treating H[**2a**–**c**] with *n*BuLi in toluene or ethereal solutions at –35 °C. Depending on the reaction solvents employed, **5** may be isolated as solvent-free derivatives or ethereal adducts. Piers et al. recently reported the preparation of solvent-free **5a**,**b**;[48,49] however, the NMR spectroscopic data of those solvent-free compounds appear not to differ much from those of ethereal adducts prepared in this study. For instance, the phosphorus atom in **5a**, **5a**·OEt_2, and **5a**·THF consistently resonates at ca. 19.5 ppm in the $^{31}P\{^1H\}$ NMR spectra. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are consistent with a C_s symmetry on the NMR timescale.

Treatment of $Zn(OAc)_2$ with **5a**·OEt_2 in THF at –35 °C led to slow dissolution of $Zn(OAc)_2$ and generated cleanly [**2a**]Zn(OAc) (**6a**) as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. Conversely, similar reactions involving **5b**, **5c**, or their corresponding ethereal adducts gave a mixture of products; attempts to isolate the desired acetate complexes



Scheme 2. Synthesis of lithium and zinc acetate complexes.

from these reaction mixtures were not successful. Reactions of **5a**–**c** with $ZnCl_2$ led undesirably to intractable materials. In comparison, analogous experiments employing **1** and ZnX_2 (X=OAc, Cl), regardless of stoichiometry employed, produced exclusively bis-ligated Zn[**1**]$_2$ without any detection of the desired [**1**]ZnX complexes.[42,43] The successful isolation of **6a** thus highlights the advantage of **2** relative to **1** in view of the synthesis of zinc acetate derivatives. Similarly to **3** and **4**, **6a** is thermally stable at elevated temperatures (100 °C, >24 h).

Complex **6a** was isolated as colorless crystals in high yield from a concentrated diethyl ether solution at –35 °C. All NMR spectroscopic data are consistent with a time-averaged C_s symmetry. The acetate ligand exhibits a singlet at δ = 1.79 ppm in the ^{1}H NMR spectrum and a diagnostic C=O signal at δ = 184.7 ppm in the ^{13}C NMR spectrum. Coates et al. previously reported a monomer/dimer equilibrium in solution for {[BDI-*i*Pr]Zn(μ-OAc)}$_2$ and the exclusive dimer for sterically less-demanding {[BDI-Et]Zn(μ-OAc)}$_2$ and {[BDI-Me]Zn(μ-OAc)}$_2$.[51,58] The solution structure of these species is apparently a function of the steric size of the β-diketiminate ligands. Nevertheless, they all exist as a dimer in the solid state.[51,58] In contrast, we found no evidence for such an equilibrium mixture in solution in the ^{1}H and ^{31}P{^{1}H} NMR spectra of **6a**. An X-ray diffraction analysis confirms a monomeric core for this molecule (Figure 3). The coordination geometry around the zinc atom is best described as distorted tetrahedral. The Zn–N$_{\text{amide}}$, Zn–N$_{\text{phosphinimine}}$, and N=P distances are all similar to those of **3**–**4**. The N–Zn–N bite angle of **6a**, however, is notably wider than the corresponding values of **3**–**4**. In comparison, the N–Zn–N bite angles of mononuclear (BDI)ZnR are comparable to those of dinuclear [(BDI)-Zn(μ-OAc)]$_2$.[51] The wider N–Zn–N bite angle in **6a** than in **3**–**4** is thus ascribed to the coordination mode (chelating instead of bridging) of the acetate ligand, wherein the sharp O–Zn–O angle implies a more s character is involved in the hybrid orbitals of zinc to bind the amido phosphinimine ligand. The four-membered Zn(η^2-acetate) ring is essentially coplanar. The Zn–O distance is slightly shorter for O1 than for O2 and the C1–O1 length is a bit longer than C1–O2, which indicates a somewhat stronger π character for the C1–O2 bond.

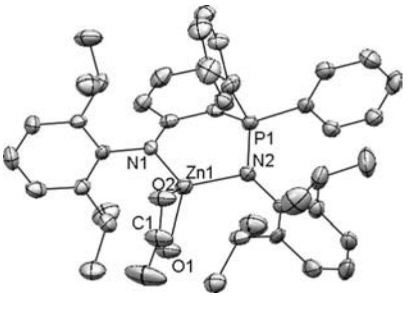


Figure 3. Molecular structure of **6a** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Zn1 1.951(8), N2–P1 1.616(8), N2–Zn1 1.977(8), O1–Zn1 2.022(7), O2–Zn1 2.100(7), C1–O2 1.230(13), C1–O1 1.284(13), N1–Zn1–N2 106.6(3), O1–Zn1–O2 63.5(3).

Catalysis

Catalytic ROP of ε-CL by the derived zinc complexes was examined. Table 4 summarizes the polymerization results and characterization data. Interestingly, the alkyl derivatives **3a**–**c** and **4a**–**c** are all quite active (93% to quantitative conversion) under the conditions investigated. In general, the (corrected)[64,65] number-averaged molecular weights (M_n) of PCL measured by gel permeation chromatography (GPC) are comparatively higher than those expected (Entries 1–11). Nevertheless, they are approximately proportional to the theoretical values or to the monomer-to-catalyst ratios (Entries 6–11, Figures S2 and S3), which indicates that the propagating chains grow in a reasonably controlled manner. Similar phenomena were also found for zinc alkyl complexes of **1**.[42] The relatively low polydispersity index (PDI) of ca. 1.6 for these PCLs indicates reasonably narrow molecular weight distributions, which suggests that the catalytically active species are conformationally similar, though not single-site.[11,13] The comparatively higher PDI found for reactions conducted with lower monomer-to-catalyst ratios (e.g. Entries 6 and 8) indicates that transesterification is more significant. In sharp contrast, polymerization initiated by acetate **6a** under similar conditions is rather unsatisfactory (48% conversion), which produces only low molecular weight oligomers (Entry 13). This result is surprising as {[BDI-*i*Pr]Zn(μ-OAc)}$_2$ is a highly active ROP catalyst for a number of cyclic molecules.[13,51,58] It has been shown that the steric hindrance imposed by the β-diketiminate ligands in {[BDI]Zn(μ-OAc)}$_2$ is essential to encourage the formation of catalytically active [BDI]Zn(μ-OAc) in solution.[51] Given that **6a** is mononuclear, even in the solid state, its low activity in ROP catalysis thus reflects intrinsic discrepancy between

Table 4. Catalytic ROP of ε-CL by **3a**–**c**, **4a**–**c**, and **6a**.[a]

Entry	[ε-CL]$_0$/[Zn]$_0$	Catalyst	Conv. [%][b]	$10^{-3}M_n$ (calcd.)[c]	$10^{-3}M_n$ (GPC)[d]	Corrected $10^{-3}M_n$ (GPC)[e]	PDI[d]
1	125	**3a**	100	14.3	60.0	33.6	1.31
2	125	**4a**	100	14.3	50.6	28.3	1.63
3	125	**3b**	100	14.3	64.3	36.0	1.68
4	125	**4b**	94	13.3	55.6	31.1	1.43
5	125	**3c**	100	14.3	67.3	37.7	1.52
6	25	**4c**	100	2.9	12.2	6.8	2.52
7	50	**4c**	93	5.3	27.9	15.6	1.80
8	75	**4c**	100	8.6	45.8	25.7	2.95
9	100	**4c**	95	10.8	57.1	32.0	1.57
10	125	**4c**	100	14.3	75.8	42.4	1.50
11	150	**4c**	100	17.1	98.3	55.0	1.47
12[f]	150	**4c**	100	17.1	23.2	13.0	1.20
13	100	**6a**	48	5.5	1.7[b]		

[a] Conditions: [Zn]$_0$ = 2.0 mM, toluene, 80 °C, 1.5 h;[66] M_n values are reported in g/mol. [b] Determined by ^{1}H NMR analysis. [c] Calculated from (F_w of ε-CL) × ([ε-CL]$_0$/[Zn]$_0$) × conversion, by assuming one propagation chain per zinc atom. [d] Measured by GPC in THF, calibrated with polystyrene standards. [e] Multiplied by a factor of 0.56.[64,65] [f] Conducted in the presence of 2-propanol (2.0 mM).

amido phosphinimines and β-diketiminates, particularly in view of the observed larger N–Zn–N bite angle for the former, which allows η^2-acetate coordination. End group analysis by ^{1}H NMR spectroscopy on PCL prepared with **3c** reveals the presence of keto methyl and hydroxy methylene signals with an integral ratio of 3:2, which suggests that the Zn–Me bond in **3c** participates in the initial ring opening of the coordinated ε-CL. The zinc alkoxide intermediate thus generated then undergoes successive ring opening for chain propagation. Upon acidic workup, the zinc alkoxide chain end is protonated to produce the hydroxy end group. A coordination–insertion mechanism is thus likely to be in operation in this system. In reactions conducted in [D$_8$]toluene with 1 equiv. of monomer, PCL is produced upon complete monomer consumption, while the majority of the zinc alkyl remains intact (>70%), as indicated by ^{1}H NMR studies. This result strongly suggests that the zinc alkyl initiation rates are significantly slower than the zinc alkoxide propagation rates. This also explains, at least in part, why the measured M_n value is larger than the expected value. Accordingly, when the catalysis was conducted in the presence of alcohol (1 equiv. with respect to zinc), the experimental and theoretical M_n values are much closer (Entry 12) with a slightly lower PDI.

Conclusions

We have prepared a series of amido phosphinimine complexes of zinc and established their solution and solid-state structures by means of NMR spectroscopy and X-ray crystallography. Of particular note is the successful isolation of monomeric, coordinatively unsaturated alkyls **3a**–**c** and **4a**–**c** that do not adopt strong coordinating solvents. Attempts to prepare the corresponding zinc chloride and alkoxide derivatives, however, were not successful. The successful isolation of the mononuclear acetate **6a** highlights the unique coordination property of **2a** in comparison with those of **1** and β-diketiminates. Surprisingly, though **6a** is mononuclear, it is a rather poor catalyst for the ROP of ε-CL, a result that is in contrast to those established by β-diketiminate complexes. Interestingly, **3a**–**c** and **4a**–**c** are all quite active, producing PCLs with molecular weights and molecular weight distributions in a reasonably controlled manner.

Experimental Section

General Procedures: Unless otherwise specified, all experiments were performed under nitrogen by using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. All other chemicals were obtained from commercial vendors and used as received. The NMR spectra were recorded on Varian or Bruker instruments. Chemical shifts (*δ*) are listed as parts per million downfield from tetramethylsilane, and coupling constants (*J*) and peak widths at half-height ($\Delta\nu_{1/2}$) are in Hertz. ^{1}H NMR spectra are referenced by using the residual solvent peak at *δ* = 7.16 for C_6D_6 and *δ* = 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced to the internal solvent peak at *δ* = 128.39 for C_6D_6 and *δ* = 77.23 for $CDCl_3$. The assignment of the carbon atoms for all new compounds is based on DEPT ^{13}C NMR spectroscopy. ^{31}P and ^{7}Li NMR spectra are referenced externally by using 85% H_3PO_4 at *δ* = 0 and LiCl in D_2O at *δ* = 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. After multiple attempts, we were not able to obtain satisfactory analysis for some complexes reported herein likely because of incomplete combustion of the samples examined. Gel permeation chromatography (GPC) analyses were carried out on a Waters instrument equipped with two Styragel HR columns in series and a 2414 RI detector. HPLC grade THF was supplied at a constant flow rate of 1.0 mL/min with a 1515 Isocratic HPLC Pump. Molecular weights (M_n and M_w) were determined by interpolation from calibration plots established with polystyrene standards.

Materials: Compounds *N*-(2-diphenylphosphanylphenyl)-2,6-dimethylaniline,[36] *N*-(2-diphenylphosphanylphenyl)-2,6-diisopropylaniline,[43] 2,6-diisopropylphenylazide,[45,46] 2,4,6-trimethylphenylazide,[47] H[**2a**],[31] **5a**,[48] and **5b**[49] were prepared according to literature procedures.

Synthesis of H[2b]: To a toluene solution (4 mL) of *N*-(2-diphenylphosphanylphenyl)-2,6-diisopropylaniline (107.8 mg, 0.25 mmol) was added 2,4,6-trimethylphenylazide (39.7 mg, 0.25 mmol) at room temperature. The solution was transferred to a Teflon-sealed reaction vessel and heated to 80 °C overnight. After being cooled to room temperature, the solution was filtered through a pad of Celite, and the solvents evaporated to dryness under reduced pressure. Acetonitrile (3 mL) and diethyl ether (2 mL) were added. Slow evaporation of the solution at room temperature afforded the product as pale yellow crystals. Yield: 112.5 mg (80%). Spectroscopic data are identical to those reported by Piers et al. by a different synthetic strategy.[49]

Synthesis of H[2c]: To a DME solution (4 mL) of *N*-(2-diphenylphosphanylphenyl)-2,6-dimethylaniline (200 mg, 0.52 mmol) was added 2,4,6-trimethylphenylazide (101 mg, 0.63 mmol, 1.2 equiv.) at room temperature. The solution was transferred to a Teflon-sealed reaction vessel and heated to 80 °C for 2 d. After being cooled to room temperature, the solution was filtered through a pad of Celite, and the solvents evaporated to dryness under reduced pressure. The orange solid thus obtained was washed with pentane (2 mL × 2) and triturated with acetonitrile (4 mL) to give the product as an off-white solid. Yield: 210 mg (78%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 9.60 (s, 1, NH), 7.76 (m, 4, Ar), 7.09 (dd, 1, Ar), 7.00 (m, 2, Ar), 6.95 (m, 5, Ar), 6.92 (m, 3, Ar), 6.88 (s, 2, Ar), 6.43 (t, 1, Ar), 6.36 (dd, 1, Ar), 2.34 (s, 6, o-$\mathrm{C_6H_2}Me_3$), 2.22 (s, 3, p-$\mathrm{C_6H_2}Me_3$), 1.96 (s, 6, o-$\mathrm{C_6H_3}Me_2$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 1.61 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 152.00 (d, J_{CP} = 4.14 Hz, 1 C), 145.37 (d, J_{CP} = 4.51 Hz, C), 138.62 (s, C), 136.46 (s, C), 133.37 (d, J_{CP} = 3.63 Hz,CH), 133.34 (s, C), 133.32 (d, J_{CP} = 5.14 Hz, CH), 133.19 (s, C), 133.18 (d, J_{CP} = 9.16 Hz, CH), 132.58 (s, C), 131.60 (d, J_{CP} = 2.63 Hz, CH), 129.79 (d, J_{CP} = 2.79 Hz, CH), 129.28 (s, CH), 128.79 (d, J_{CP} = 11.9 Hz, CH), 126.29. (s, CH), 116.52 (d, J_{CP} = 13.3 Hz, CH), 115.46 (d, J_{CP} = 107.42 Hz, C), 113.93 (d, J_{CP} = 8.15 Hz, CH), 21.88 (s, o-$\mathrm{C_6H_2}Me_3$), 21.23 (s, p-$\mathrm{C_6H_2}Me_3$), 18.95 (s, o-$\mathrm{C_6H_3}Me_2$) ppm. $C_{35}H_{35}N_2P$ (514.25): calcd. C 81.67, H 6.86, N 5.45; found C 82.04, H 6.86, N 5.08.

Synthesis of 3a: Solid H[**2a**] (102.9 mg, 0.17 mmol) was dissolved in toluene (2 mL) and cooled to –35 °C. To this was added $ZnMe_2$ (0.14 mL, 1.2 M in toluene, 0.17 mmol). The reaction solution was naturally warmed to room temperature and stirred for 12 h. After being filtered through a pad of Celite, the solution was concentrated to ca. 1 mL and cooled to –35 °C to afford the product as pale yellow crystals suitable for X-ray diffraction analysis. Yield: 97 mg (84%). ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.57 (dd, 4, Ar), 7.27 (m, 3, Ar), 7.00 (m, 11, Ar), 6.35 (m, 1, Ar), 6.20 (m, 1, Ar), 3.60 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 2.87 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.40 (d, 6, $\mathrm{CH}Me_2$), 1.08 (dd, 12, $\mathrm{CH}Me_2$), 0.93 (d, 6, $\mathrm{CH}Me_2$), –0.42 (s, 1, $ZnCH_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 80.95 MHz): δ = 27.76 ppm. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58 (m, 2, Ar), 7.50 (m, 4, Ar), 7.42 (m, 4, Ar), 7.11 (m, 3, Ar), 6.97 (m, 2, Ar), 6.95 (m, 2, Ar), 6.78 (dd, 1, Ar), 6.23 (m, 1, Ar), 6.00 (t, 1, Ar), 3.36 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 2.64 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.23 (d, 6, $\mathrm{CH}Me_2$), 0.88 (d, 6, $\mathrm{CH}Me_2$), 0.85 (d, 6, $\mathrm{CH}Me_2$), 0.80 (d, 6, $\mathrm{CH}Me_2$), –0.99 (d, 3, $\mathrm{ZnC}H_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ = 28.49 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.5 MHz): δ = 160.36 (d, J_{CP} = 4.64 Hz, C), 145.81 (s, C), 145.42 (s, C), 145.37 (s, C), 141.24 (d, J_{CP} = 8.28 Hz, C), 133.21 (d, J_{CP} = 9.04 Hz, CH), 133.11 (s, CH), 132.48 (d, J_{CP} = 11.92 Hz, CH), 132.34 (d, J_{CP} = 2.76 Hz, CH), 128.46 (d, J_{CP} = 11.92 Hz, CH), 127.07 (d, J_{CP} = 98.77 Hz, C), 124.25 (s, CH), 123.74 (s, CH), 123.62 (d, J_{CP} = 3.64 Hz, CH), 123.16 (d, J_{CP} = 2.76 Hz, CH), 116.92 (d, J_{CP} = 8.16 Hz, CH), 110.92 (d, J_{CP} = 13.68 Hz, CH), 108.44 (d, J_{CP} = 105.17 Hz, C), 29.16 (s, $C\mathrm{HMe_2}$), 27.31 (s, $C\mathrm{HMe_2}$), 25.11 (s, $\mathrm{CH}Me_2$), 24.92 (s, $\mathrm{CH}Me_2$), 24.76 (s, $\mathrm{CH}Me_2$), 22.71 (s, $\mathrm{CH}Me_2$), –17.15 (s, $\mathrm{Zn}C\mathrm{H_3}$) ppm. $C_{43}H_{51}N_2PZn$ (691.79): calcd. C 74.59, H 7.43, N 4.05; found C 70.69, H 7.98, N 3.78.

Synthesis of 3b: Solid H[**2b**] (109.4 mg, 0.19 mmol) was dissolved in diethyl ether (4 mL) and cooled to –35 °C. To this was added $ZnMe_2$ (0.16 mL, 1.2 M in toluene, 0.19 mmol). The reaction solution was naturally warmed to room temperature and stirred for 7 h. All volatiles were removed. The solid residue was triturated with pentane (4 mL) and dissolved in diethyl ether (2 mL). Cooling of the ether solution to –35 °C afforded the product as pale yellow crystals. Yield: 96 mg (77%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.63 (m, 4, Ar), 7.25 (m, 3, Ar), 6.98 (m, 4, Ar), 6.90 (m, 4, Ar), 6.67 (s, 2, Ar), 6.38 (t, 1, Ar), 6.21 (td, 1, Ar), 2.96 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 2.40 (s, 6, o-$\mathrm{C_6H_2}Me_3$), 2.07 (s, 3, p-$\mathrm{C_6H_2}Me_3$), 1.11 (d, 6, $\mathrm{CH}Me_2$), 1.09 (d, 6, $\mathrm{CH}Me_2$), –0.50 (s, 3 $\mathrm{ZnC}H_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 24.39 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 161.08 (d, J_{CP} = 4.39 Hz, C), 146.41 (s, C), 145.67 (s, C), 142.41 (d, J_{CP} = 7.61 Hz, 1 C), 135.30 (d, J_{CP} = 5.90 Hz, 1 C), 134.36 (s, CH), 133.77 (d, J_{CP} = 9.29 Hz, CH), 133.08 (d, J_{CP} = 11.80 Hz, CH), 132.79 (d, J_{CP} = 2.38 Hz, CH), 132.61 (d, J_{CP} = 3.39 Hz, C), 130.06 (d, J_{CP} = 3.01 Hz, CH), 129.02 (d, J_{CP} = 11.78 Hz, CH), 128.83 (d, J_{CP} = 36.40 Hz, C), 125.54 (s, CH), 124.64 (s, CH), 117.18 (d, J_{CP} = 8.28 Hz, CH), 111.80 (d, J_{CP} = 13.80 Hz, CH), 109.22 (d, J_{CP} = 103.63 Hz, C), 28.20 (s, $C\mathrm{HMe_2}$), 25.33 (s, $\mathrm{CH}Me_2$), 25.30 (s, $\mathrm{CH}Me_2$), 21.10 (s, p-$\mathrm{C_6H_2}Me_3$), 21.04 (s, o-$\mathrm{C_6H_2}Me_3$), –15.99 (s, $ZnCH_3$) ppm. $C_{40}H_{45}N_2PZn$ (649.74): calcd. C 73.88, H 6.98, N 4.31; found C 74.05, H 7.16, N 4.04.

Synthesis of 3c: Solid H[**2c**] (100 mg, 0.19 mmol) was dissolved in THF (3 mL) and cooled to –35 °C. To this was added $ZnMe_2$ (0.16 mL, 1.2 M in toluene, 0.19 mmol). The reaction solution was naturally warmed to room temperature and stirred for 1 h. After being filtered through a pad of Celite, the solution was evaporated to dryness under reduced pressure. The solid was then triturated with pentane (4 mL) and dissolved in diethyl ether (2 mL). Cooling of the ether solution to –35 °C afforded the product as colorless crystals. Yield: 84 mg (74%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.63 (dd, 4, Ar), 7.13 (m, 2, Ar), 6.97 (m, 5, Ar), 6.88 (m, 4, Ar), 6.66 (s, 2, Ar), 6.41 (t, 1, Ar), 6.27 (td, 1, Ar), 2.33 (s, 6, o-$\mathrm{Ar}Me$), 2.06 (s, 3, p-$\mathrm{C_6H_2}Me_3$), 1.90 (s, 6, o-$\mathrm{Ar}Me$), –0.46 (d, 3, $^4J_{PH}$ = 1.5 Hz, $\mathrm{ZnC}H_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 23.87 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 159.64 (d, J_{CP} = 4.64 Hz, C), 150.60 (s, C), 142.50 (d, J_{CP} = 7.28 Hz, C), 135.33 (s, C), 135.27 (s, C), 134.96 (d, J_{CP} = 1.88 Hz, CH), 133.86 (d, J_{CP} = 9.16 Hz, CH), 133.04 (d, J_{CP} = 11.42 Hz, CH), 132.76 (d, J_{CP} = 2.76 Hz, CH), 132.60 (d, J_{CP} = 3.64 Hz, C), 130.01 (d, J_{CP} = 2.76 Hz, CH), 129.47 (s, CH), 128.95 (d, J_{CP} = 11.92 Hz, CH), 127.75 (s, C), 124.36 (s, CH), 115.61 (d, J_{CP} = 8.28 Hz, CH), 112.03 (d, J_{CP} = 13.68 Hz, CH), 109.94 (d, J_{CP} = 104.29 Hz, C), 21.18 (d, J_{CP} = 1.38 Hz, o-$\mathrm{C_6H_2}Me_3$), 21.11 (d, J_{CP} = 1.38 Hz, p-$\mathrm{C_6H_2}Me_3$), 18.91 (s, o-$\mathrm{C_6H_3}Me_2$), –16.49 (s, $\mathrm{Zn}C\mathrm{H_3}$) ppm. $C_{36}H_{37}N_2PZn$ (593.68): calcd. C 72.77, H 6.28, N 4.72; found C 72.17, H 6.84, N 4.33.

Synthesis of 4a: Solid H[**2a**] (110.5 mg, 0.18 mmol) was dissolved in diethyl ether (2 mL) and cooled to –35 °C. To this was added $ZnEt_2$ (0.18 mL, 1 M in hexene, 0.18 mmol). The reaction solution was naturally warmed to room temperature and stirred for 2 d. All volatiles were removed. The solid residue was triturated with pentane (4 mL) and dissolved in diethyl ether (2 mL). Cooling of the ether solution to –35 °C afforded the product as colorless crystals. Yield: 104 mg (82%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.56 (dd, 4, Ar), 7.25 (m, 3, Ar), 6.99 (m, 4, Ar), 6.93 (m, 6, Ar), 6.87 (m, 1, Ar), 6.28 (dd, 1, Ar), 6.18 (dt, 1, Ar), 3.60 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 2.87 (septet, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.40 (d, 6, $\mathrm{CH}Me_2$), 1.20 (t, 3, $\mathrm{ZnCH_2C}H_3$), 1.08 (m, 12, $\mathrm{CH}Me_2$), 0.87 (d, 6, $\mathrm{CH}Me_2$), 0.52 (q, 2, $\mathrm{ZnC}H_2\mathrm{CH_3}$)

ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 27.38 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 161.29 (d, J_{CP} = 4.52 Hz, C), 146.75 (s, C), 145.94 (s, C), 145.91 (s, C), 142.15 (d, J_{CP} = 8.28 Hz, C), 134.11 (s, CH), 133.83 (d, J_{CP} = 8.28 Hz, CH), 133.06 (d, J_{CP} = 11.92 Hz, CH), 132.80 (d, J_{CP} = 1.88 Hz, CH), 129.00 (d, J_{CP} = 11.80 Hz, CH), 127.62 (s, C), 125.64 (s, CH), 124.82 (s, CH), 124.74 (d, J_{CP} = 3.64 Hz, CH), 124.17 (d, J_{CP} = 3.77 Hz, CH), 117.86 (d, J_{CP} = 8.16 Hz, CH), 111.95 (d, J_{CP} = 13.68 Hz, CH), 109.23 (d, J_{CP} = 105.17 Hz, C), 29.98 (s, *C*HMe$_2$), 28.18 (s, *C*HMe$_2$), 26.20 (s, CH*Me*$_2$), 25.96 (s, CH*Me*$_2$), 25.48 (s, CH*Me*$_2$), 23.58 (s, CH*Me*$_2$), 13.19 (s, ZnCH$_2$*C*H$_3$), –0.81 (s, Zn*C*H$_2$CH$_3$) ppm. $C_{44}H_{53}N_2PZn$ (705.80): calcd. C 74.81, H 7.57, N 3.97; found C 75.09, H 8.04, N 3.63.

Synthesis of 4b: Solid H[**2b**] (100.3 mg, 0.18 mmol) was dissolved in THF (4 mL) and cooled to –35 °C. To this was added $ZnEt_2$ (0.18 mL, 1 M in hexene, 0.18 mmol). The reaction solution was naturally warmed to room temperature and stirred for 7 h. All volatiles were removed. The solid residue was triturated with pentane (4 mL) and dissolved in diethyl ether (2 mL). Cooling of the ether solution to –35 °C afforded the product as pale yellow crystals. Yield: 87 mg (74%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.64 (m, 4, Ar), 7.24 (m, 3, Ar), 6.99 (m, 2, Ar), 6.92 (m, 6, Ar), 6.68 (s, 2, Ar), 6.37 (dd, 1, Ar), 6.21 (td, 1, Ar), 2.95 (septet, 2, C*H*Me$_2$), 2.41 (s, 6, *o*-C$_6$H$_2$*Me*$_3$), 2.06 (d, 3, *p*-C$_6$H$_2$*Me*$_3$), 1.19 (t, 3, ZnCH$_2$C*H*$_3$), 1.12 (d, 6, CH*Me*$_2$), 1.08 (d, 6, CH*Me*$_2$), 0.40 (q, 2, ZnC*H*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 23.99 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 160.94 (d, J_{CP} = 4.64 Hz, C), 146.56 (s, C), 145.64 (s, C), 142.56 (d, J_{CP} = 7.28, C), 135.23 (d, J_{CP} = 5.52, C), 134.33 (d, J_{CP} = 1.88, CH), 133.76 (d, J_{CP} = 9.16, CH), 133.08 (d, J_{CP} = 11.92, CH), 132.79 (d, J_{CP} = 2.64, CH), 132.56 (d, J_{CP} = 3.64, C), 130.02 (d, J_{CP} = 2.76, CH), 129.02 (d, J_{CP} = 11.92, CH), 128.82 (d, J_{CP} = 33.76, C), 125.54 (s, CH), 124.63 (s, CH), 117.02 (d, J_{CP} = 8.28, CH), 111.81 (d, J_{CP} = 13.81, CH), 109.40 (d, J_{CP} = 104.29, C), 28.20 (s, *C*HMe$_2$), 25.38 (s, CH*Me*$_2$), 25.24 (s, CH*Me*$_2$), 21.11(s, *p*-C$_6$H$_2$*Me*$_3$), 21.02 (s, *o*-C$_6$H$_2$*Me*$_3$), 13.00 (s, ZnCH$_2$*C*H$_3$), –0.77 (d, J_{CP} = 1.88, Zn*C*H$_2$CH$_3$). $C_{41}H_{47}N_2PZn$ (663.76): calcd. C 74.12, H 7.14, N 4.22; found C 74.59, H 7.56, N 4.31.

Synthesis of 4c: Solid H[**2c**] (104 mg, 0.20 mmol) was dissolved in THF (3 mL) and cooled to –35 °C. To this was added $ZnEt_2$ (0.20 mL, 1 M in toluene, 0.20 mmol). The reaction solution was naturally warmed to room temperature and stirred for 1 h. After being filtered through a pad of Celite, the solution was evaporated to dryness under reduced pressure. The solid was then triturated with pentane (4 mL) and dissolved in diethyl ether (2 mL). Cooling of the ether solution to –35 °C afforded the product as colorless crystals. Yield: 93 mg (76%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.64 (dd, 4, Ar), 7.12 (m, 2, Ar), 6.99 (m, 5, Ar), 6.89 (m, 4, Ar), 6.67 (s, 2, Ar), 6.40 (dd, 1, Ar), 6.27 (td, 1, Ar), 2.36 (s, 6, *o*-Ar*Me*), 2.06 (d, 3, *p*-C$_6$H$_2$*Me*$_3$), 1.91 (s, 6, *o*-Ar*Me*), 1.20 (t, 3, ZnCH$_2$C*H*$_3$), 0.44 (q, 2, ZnC*H*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 23.29 ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 159.50 (d, J_{CP} = 4.64 Hz, C), 150.18 (s, C), 142.61 (d, J_{CP} = 7.28 Hz, C), 135.28 (s, C), 135.22 (s, C), 134.95 (d, J_{CP} = 1.75 Hz, CH), 133.83 (d, J_{CP} = 9.66 Hz, CH), 133.06 (d, J_{CP} = 11.42 Hz, CH), 132.76 (d, J_{CP} = 2.76 Hz, CH), 132.56 (d, J_{CP} = 3.64 Hz, C), 129.97 (d, J_{CP} = 3.26 Hz, CH), 129.43 (s, CH), 128.96 (d, J_{CP} = 11.92 Hz, CH), 127.76 (s, C), 124.38 (s, CH), 115.44 (d, J_{CP} = 8.79 Hz, CH), 112.01 (d, J_{CP} = 13.67 Hz, CH), 110.04 (d, J_{CP} = 104.29 Hz, C), 21.15 (d, J_{CP} = 1.38 Hz, *o*-C$_6$H$_2$*Me*$_3$), 21.14 (s, *p*-C$_6$H$_2$*Me*$_3$), 18.83 (s, *o*-C$_6$H$_3$*Me*$_2$), 13.00 (s, ZnCH$_2$*C*H$_3$), –1.15 (d, J_{CP} = 1.38 Hz, Zn*C*H$_2$CH$_3$) ppm. $C_{37}H_{39}N_2PZn$ (607.69): calcd. C 73.06, H 6.47, N 4.61; found C 72.75, H 7.08, N 4.31.

Synthesis of 5a·OEt$_2$: To a diethyl ether solution (5 mL) of H[**2a**] (214.4 mg, 0.35 mmol) at –35 °C was added *n*BuLi (0.14 mL, 2.5 M in hexane, 0.35 mmol). The solution was stirred at room temperature for 3 h and concentrated under reduced pressure until a volume of ca. 2 mL. The precipitate thus formed was collected and dried in vacuo to give the product as a yellow solid. Yield: 216 mg (89%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.65 (br. s, 4, Ar), 7.22 (m, 2, Ar), 7.15 (m, 2, Ar), 7.08 (t, 2, Ar), 7.05 (m, 2, Ar), 7.02 (m, 4, Ar), 6.93 (t, 1, Ar), 6.89 (td, 1, Ar), 6.17 (dd, 1, Ar), 6.07 (td,1, Ar), 3.65 (septet, 2, C*H*Me$_2$), 2.92 (q, 4, OC*H*$_2$CH$_3$), 2.85 (br. s, 2, C*H*Me$_2$), 1.32 (d, 6 CH*Me*$_2$), 1.19 (d, 6, CH*Me*$_2$), 0.98 (d, 6 CH*Me*$_2$), 0.91 (br. d, 6, CH*Me*$_2$), 0.58 (t, 6, OCH$_2$C*H*$_3$) ppm. ^{7}Li{^{1}H} NMR (C_6D_6, 194 MHz): δ = 1.75 ($\Delta\nu_{1/2}$ = 12.19) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ = 19.04 ($\Delta\nu_{1/2}$ = 5.72) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ = 163.21 (d, J_{CP} = 5.89 Hz, C), 150.93 (s, CH), 146.32 (d, J_{CP} = 8.78 Hz, C), 145.17 (s, C), 145.14 (s, CH), 134.42 (d, J_{CP} = 12.82 Hz, CH), 133.68 (d, J_{CP} = 8.65 Hz, CH), 133.36 (d, J_{CP} = 1.75 Hz, CH), 131.70 (d, J_{CP} = 2.76 Hz, CH), 131.54 (d, J_{CP} = 95.63 Hz, C), 128.52 (d, J_{CP} = 15.5 Hz, CH), 124.36. (s, CH), 123.98 (d, J_{CP} = 3.2 Hz, CH), 123.12. (s, CH), 122.55 (d, J_{CP} = 4.1 Hz, CH), 117.12. (d, J_{CP} = 8.65 Hz, CH), 110.47 (d, J_{CP} = 108.93 Hz, C), 107.83 (d, J_{CP} = 14.1 Hz, CH), 65.51 (s, O*C*H$_2$CH$_3$), 29.32 (s, *CH*Me$_2$), 27.84 (s, *C*HMe$_2$), 26.58 (s, CH*Me*$_2$), 25.71 (s, CH*Me*$_2$), 24.91 (s, CH*Me*$_2$), 24.15 (s, CH*Me*$_2$), 14.36 (s, OCH$_2$*CH*$_3$) ppm. $C_{46}H_{58}LiN_2OP$ (692.44): calcd. C 79.72, H 8.44, N 4.04; found C 77.43, H 7.78, N 4.04.

Synthesis of 5a·THF: To a THF solution (3 mL) of H[**2a**] (91.9 mg, 0.15 mmol) at –35 °C was added *n*BuLi (0.06 mL, 2.5 M in hexane, 0.15 mmol). The solution was stirred at room temperature for 1.5 h, filtered through a pad of Celite, and concentrated under reduced pressure until a volume of ca. 1 mL. Layering of pentane (2 mL) on top of the concentrated solution followed by cooling of the solution to –35 °C afforded the product as a yellow crystalline solid. Yield 75 mg (72%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.66 (dd, 4, Ar), 7.20 (m, 1, Ar), 7.17 (m, 1, Ar), 7.10 (m, 1, Ar), 7.05 (m, 9, Ar), 6.97 (m, 1, Ar), 6.92 (m, 1, Ar), 6.21 (dd, 1, Ar), 6.08 (dt, 1, Ar), 3.68 (septet, 2, C*H*Me$_2$), 3.03 (t, 4, OC*H*$_2$CH$_2$), 2.93 (septet, 2, C*H*Me$_2$), 1.34 (d, 6, CH*Me*$_2$), 1.20 (d, 6, CH*Me*$_2$), 1.02 (q, 4, OCH$_2$C*H*$_2$), 1.00 (d, 6, CH*Me*$_2$), 0.97 (d, 6, CH*Me*$_2$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ = 19.88 ($\Delta\nu_{1/2}$ = 5.0) ppm. ^{7}Li{^{1}H} NMR (C_6D_6, 194 MHz): δ = 2.63 ($\Delta\nu_{1/2}$ = 11.4) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ = 163.06 (d, J_{CP} = 5.53 Hz, C), 150.46 (s, C), 146.21 (d, J_{CP} = 7.79 Hz, C), 145.18 (s, C), 145.10 (d, J_{CP} = 6.91 Hz, C), 134.63 (d, J_{CP} = 12.82 Hz, CH), 133.68 (d, J_{CP} = 8.80 Hz, CH), 133.52 (d, J_{CP} = 1.76 Hz, CH), 131.79 (d, J_{CP} = 96.66 Hz, C), 131.61 (d, J_{CP} = 2.77 Hz, CH), 128.57 (d, J_{CP} = 11.44 Hz, CH), 124.26 (s, CH), 123.95 (d, J_{CP} = 3.65 Hz, CH), 123.05 (s, CH), 122.46 (d, J_{CP} = 3.77 Hz, CH), 116.39 (d, J_{CP} = 8.30 Hz, CH), 110.98 (d, J_{CP} = 109.11 Hz, C), 107.71 (d, J_{CP} = 14.71 Hz, CH), 68.59 (s, O*C*H$_2$CH$_2$), 29.40 (s, *C*HMe$_2$), 27.81 (s, *C*HMe$_2$), 26.26 (s, CH*Me*$_2$), 26.12 (s, CH*Me*$_2$), 25.57 (s, CH*Me*$_2$), 25.43 (s, OCH$_2$*C*H$_2$), 23.96 (s, CH*Me*$_2$) ppm. $C_{46}H_{56}LiN_2OP$ (690.43): calcd. C 79.95, H 8.18, N 4.06; found C 80.07, H 8.21, N 3.76.

Synthesis of 5c·OEt$_2$: To a diethyl ether solution (3 mL) of H[**2c**] (102.9 mg, 0.20 mmol) at –35 °C was added *n*BuLi (0.08 mL, 2.5 M in hexane, 0.20 mmol). The solution was stirred at room temperature for 3 h, filtered through a pad of Celite, and concentrated under reduced pressure until a volume of ca. 2 mL. Cooling of the solution to –35 °C afforded the product as a yellow solid. Yield: 102 mg (85%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.73 (dd, 4, Ar), 7.13 (d, 2, Ar), 7.05 (m, 4, Ar), 6.98 (m, 3, Ar), 6.94 (t, 2, Ar), 6.80

(s, 2, Ar), 6.32 (dd, 1, Ar), 6.18 (tdd, 1, Ar), 2.84 (q, 4, OCH_2CH_3), 2.39 (d, 6, o-$C_6H_2Me_3$), 2.19 (d, 3, p-$C_6H_2Me_3$), 1.92 (s, 6, o-$C_6H_3Me_2$), 0.60 (t, 6, OCH_2CH_3) ppm. $^7Li\{^1H\}$ NMR (C_6D_6, 194 MHz): $\delta = 1.85$ ($\Delta v_{1/2} = 15.21$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 202.5 MHz): $\delta = 14.70$ ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ = 160.92 (d, J_{CP} = 4.64 Hz, C), 153.61 (s, C), 146.20 (d, J_{CP} = 6.77 Hz, C), 134.75 (d, J_{CP} = 6.40 Hz, C), 134.61 (d, J_{CP} = 12.42 Hz, CH), 134.74 (s, C), 134.29 (d, J_{CP} = 1.88 Hz, CH), 133.50 (d, J_{CP} = 8.65 Hz, CH), 132.74 (s, C), 131.95 (s, C), 131.54 (d, J_{CP} = 2.76 Hz, CH), 129.63 (d, J_{CP} = 3.26 Hz, CH), 128.91 (s, CH), 128.63 (d, J_{CP} = 11.9 Hz, CH), 121.75 (s, CH), 114.24 (d, J_{CP} = 8.20 Hz, CH), 110.96 (d, J_{CP} = 105.16 Hz, C), 107.96 (d, J_{CP} = 14.18 Hz, CH), 65.51 (s, OCH_2CH_3), 21.30 (s, o-$C_6H_2Me_3$), 21.23 (s, p-$C_6H_2Me_3$), 19.27 (s, o-$C_6H_3Me_2$), 14.65 (s, OCH_2CH_3) ppm. $C_{39}H_{44}LiN_2OP$ (594.33): calcd. C 78.74, H 7.46, N 4.71; found C 79.16, H 7.23, N 4.38.

Synthesis of 6a: Solid $Zn(OAc)_2$ (35.5 mg, 0.19 mmol) was suspended in THF (2 mL) and cooled to –35 °C. To this was added a prechilled THF solution (3 mL) of 5a·OEt_2 (122 mg, 0.18 mmol) at –35 °C. The reaction mixture was naturally warmed to room temperature and stirred for 3 h. All volatiles were removed. The solid residue was triturated with pentane (4 mL). Diethyl ether (6 mL) was added. The ether solution was filtered through a pad of Celite and concentrated to ca. 4 mL. Cooling of the ether solution to –35 °C afforded the product as colorless crystals. Yield: 99 mg (76%). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.68 (dd, 1, Ar), 7.58 (m, 1, Ar), 7.50 (m, 5, Ar), 7.44 (m, 3, Ar), 7.09 (m, 4, Ar), 6.99 (m, 2, Ar), 6.94 (m, 1, Ar), 6.82 (qd, 1, Ar), 6.25 (td, 1, Ar), 6.04 (t, 1, Ar), 3.38 (br. m, 2, $CHMe_2$), 2.67 (br. m, 2, $CHMe_2$), 1.79 (s, 3, OAc), 1.23 (d, 6,$CHMe_2$), 0.87 (m, 12, $CHMe_2$), 0.81 (d, 6, $CHMe_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.5 MHz): δ = 32.25 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ = 184.67 (s, CH_3CO_2), 161.01 (d, J_{CP} = 5.27 Hz, C), 145.89 (s, C), 145.72 (d, J_{CP} = 5.27 Hz, C), 144.16 (s, C), 140.21 (d, J_{CP} = 8.28 Hz, C), 133.51 (d, J_{CP} = 9.28 Hz, CH), 133.26 (s, CH), 132.82 (d, J_{CP} = 11.92 Hz, CH), 132.60 (d, J_{CP} = 2.63 Hz, CH), 128.56 (d, J_{CP} = 12.05 Hz, CH), 124.60 (s, CH), 124.27 (d, J_{CP} = 3.63 Hz, CH), 123.86. (s, CH), 123.33 (d, J_{CP} = 3.13 Hz, CH), 117.22 (d, J_{CP} = 8.40 Hz, CH), 111.30 (d, J_{CP} = 14.06 Hz, CH), 108.03 (d, J_{CP} = 101.53 Hz, C), 29.17 (s, $CHMe_2$), 27.27 (s, $CHMe_2$), 25.07 (s, $CHMe_2$), 24.48 (s, $CHMe_2$), 23.78 (s, $CHMe_2$), 22.86 (s, $CHMe_2$), 20.03 (s, CH_3CO_2) ppm. $C_{44}H_{51}N_2O_2PZn$ (735.78): calcd. C 71.76, H 6.99, N 3.81; found C 71.70, H 7.17, N 3.52.

Catalytic Ring-Opening Polymerization of ε-CL: A toluene solution of **3** or **4** (2.0 mM) was added to a toluene solution of ε-CL (with a prescribed concentration based on the $[\varepsilon\text{-CL}]_0/[Zn]_0$ ratios shown in Table 4). Toluene was added, if necessary, to a total volume of 4 mL for the reaction solution. The solution was transferred to a Teflon-sealed reaction vessel and heated to 80 °C for 2 h. After the solution was cooled to room temperature, the reaction was quenched with a methanol solution of HCl. The solid thus precipitated was washed with hexane, isolated, and dried under reduced pressure until a constant weight was achieved.

X-ray Crystallography: Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 by using the maXus or WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of **6a** were of poor quality but sufficient to establish the identity of this molecule. The structures of **3c** and **6a** contain disordered diethyl ether molecules. Attempts to obtain a suitable disorder model failed. The SQUEEZE procedure of the program Platon[67] was used to obtain a new set of F^2 (hkl) values without the contribution of solvent molecules, which leads to the presence of significant voids in these structures. The refinement reduced the R_1 value to 0.0659 and 0.1131 for **3c** and **6a**, respectively. In **4a**, the methyl group in the ethyl ligand is disordered over two conformations in a ratio of 50:50. In **4c**, the ethyl ligand in one of the two independent molecules present in the asymmetric unit cell is disordered over two conformations in a ratio of 50:50.

Crystal Data for H[2c]: $C_{35}H_{35}N_2P$, M = 514.62, monoclinic, space group $P2_1/c$, a = 13.4638(2) Å, b = 16.6891(3) Å, c = 14.0599(3) Å, β = 115.1710(10)°, V = 2859.25(9) Å^3, T = 200(2) K, Z = 4, μ(Mo-K_α) = 0.122 mm^{-1}, 16780 reflections measured, 5021 unique (R_{int} = 0.0510), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0539, wR_2 [$I > 2\sigma(I)$] = 0.1514, R_1 (all data) = 0.0706, wR_2 (all data) = 0.1673, GOF (on F^2) = 1.054, CCDC-787868.

Crystal Data for 3a: $C_{57}H_{67}N_2PZn$, M = 876.47, triclinic, space group $P\bar{1}$, a = 9.855(2) Å, b = 13.685(3) Å, c = 19.478(4) Å, α = 87.787(4)°, β = 75.946(4)°, γ = 73.728(4)°, V = 2444.9 Å^3, T = 200(2) K, Z = 2, μ(Mo-K_α) = 0.573 mm^{-1}, 21413 reflections measured, 8554 unique ($\mathrm{R_{int}}$ = 0.0427), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0595, wR_2 [$I > 2\sigma(I)$] = 0.1767, R_1 (all data) = 0.0828, wR_2 (all data) = 0.1949, GOF (on F^2) = 1.092, CCDC-787869.

Crystal Data for 3b: $C_{40}H_{45}N_2PZn$, M = 650.12, triclinic, space group $P\bar{1}$, a = 9.668(2) Å, b = 14.919(4) Å, c = 24.480(5) Å, α = 88.825(4)°, β = 80.313(6)°, γ = 83.774(3)°, V = 3460.2(14) Å^3, T = 200(2) K, Z = 4, μ(Mo-K_α) = 0.786 mm^{-1}, 21269 reflections measured, 10506 unique ($\mathrm{R_{int}}$ = 0.1495), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0770, wR_2 [$I > 2\sigma(I)$] = 0.1618, R_1 (all data) = 0.2160, wR_2 (all data) = 0.2211, GOF (on F^2) = 0.924, CCDC-787870.

Crystal Data for 3c: $C_{36}H_{37}N_2PZn$, M = 594.02, monoclinic, space group $P2_1/n$, a = 16.2190(4) Å, b = 13.1028(3) Å, c = 17.1130(5) Å, β = 95.1530(10)°, V = 3622.06(16) Å^3, T = 200(2) K, Z = 4, μ(Mo-K_α) = 0.745 mm^{-1}, 21372 reflections measured, 6380 unique ($\mathrm{R_{int}}$ = 0.0761), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0659, wR_2 [$I > 2\sigma(I)$] = 0.1994, R_1 (all data) = 0.0989, wR_2 (all data) = 0.2264, GOF (on F^2) = 0.807, CCDC-787871.

Crystal Data for 4a: $C_{95}H_{114}N_4P_2Zn_2$, M = 1504.58, triclinic, space group $P\bar{1}$, a = 9.7042(2) Å, b = 13.2444(3) Å, c = 18.4008(5) Å, α = 103.0690(10)°, β = 105.4110(10)°, γ = 103.8160(10)°, V = 2105.40(9) Å^3, T = 200(2) K, Z = 1, μ(Mo-K_α) = 0.655 mm^{-1}, 24306 reflections measured, 7425 unique ($\mathrm{R_{int}}$ = 0.0559), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0504, wR_2 [$I > 2\sigma(I)$] = 0.1460, R_1 (all data) = 0.0677, wR_2 (all data) = 0.1684, GOF (on F^2) = 1.136, CCDC-787872.

Crystal Data for 4b: $C_{41}H_{47}N_2PZn$, M = 664.15, orthorhombic, space group $Pcab$, a = 15.73250(10) Å, b = 21.1429(2) Å, c = 21.7675(2) Å, V = 7240.54(11) Å^3, T = 200(2) K, Z = 8, μ(Mo-$K\alpha$) = 0.752 mm^{-1}, 50691 reflections measured, 6388 unique ($\mathrm{R_{int}}$ = 0.0695), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0512, wR_2 [$I > 2\sigma(I)$] = 0.1407, R_1 (all data) = 0.0756, wR_2 (all data) = 0.1644, GOF (on F^2) = 1.181, CCDC-787873.

Crystal Data for 4c: $C_{37}H_{39}N_2PZn$, M = 608.04, orthorhombic, space group $Pca2_1$, a = 15.3108(2) Å, b = 16.6247(3) Å, c = 25.3025(5) Å, V = 6440.43(19) Å^3, T = 200(2) K, Z = 8, μ(Mo-Kα) = 0.840 mm^{-1}, 26869 reflections measured, 10249 unique ($\mathrm{R_{int}}$ = 0.0660), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] =

0.0501, wR_2 [$I > 2\sigma(I)$] = 0.1296, R_1 (all data) = 0.0776, wR_2 (all data) = 0.1548, GOF (on F^2) = 1.064, CCDC-787874.

Crystal Data for 6a: $C_{44}H_{51}N_2O_2PZn$, M = 736.21, triclinic, space group $P\bar{1}$, a = 9.8702(6) Å, b = 13.3515(9) Å, c = 18.3945(14) Å, α = 70.536(3)°, β = 89.745(3)°, γ = 75.842(2)°, V = 2208.2(3) Å^3, T = 200(2) K, Z = 2, μ(Mo-Kα) = 0.626 mm^{-1}, 20930 reflections measured, 7544 unique (R_{int} = 0.1141), which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.1131, wR_2 [$I > 2\sigma(I)$] = 0.3024, R_1 (all data) = 0.2231, wR_2 (all data) = 0.3683, GOF (on F^2) = 1.075, CCDC-787875.

Crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Molecular structure of H[**2c**] and plots of found M_n (corrected) vs. calculated M_n and monomer-to-catalyst ratios are presented.

Acknowledgments

We thank the National Science Council of Taiwan for financial support (NSC 99–2113-M-110–003-MY3 and 99–2119-M-110–002), Mr. Ting-Shen Kuo (NTNU) for assistance with X-ray crystallography, Ms. Ching-Wei Lu (NTU), Ms. I-Chuan Chen (NCHU), and Ms. Chia-Chen Tsai (NCKU) for the elemental analysis, Ms. Chao-Lien Ho (NSYSU), Ms. Mei-Yueh Chien (NCHU), and Ms. Ru-Rong Wu (NCKU) for assistance with NMR spectrosocpy, and the National Center for High-performance Computing (NCHC) for access to chemical databases. We are also grateful to the reviewers for insightful comments.

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Received: December 29, 2010