Amido phosphine complexes of zinc: synthesis, structure, and catalytic ring-opening polymerization of ε-caprolactone†

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Received 19th April 2010, Accepted 10th June 2010
DOI: 10.1039/c0dt00327a

A series of diarylamido phosphine ligands of the type *N*-(2-dihydrocarbylphosphinophenyl)-2,6-dialkylanilide **1a–d** have been prepared and employed to investigate the coordination chemistry of zinc. Protonolysis of $ZnMe_2$ with one equivalent of *N*-(2-diphenylphosphinophenyl)-2,6-dimethylaniline (H[**1a**]) produced a mixture of [**1a**]ZnMe (**2a**) and Zn[**1a**]$_2$ (**4a**), whereas that involving $ZnEt_2$ gave exclusively the three-coordinate [**1a**]ZnEt (**3a**). In contrast, treatment of ZnR_2 (R = Me, Et) with *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylaniline (H[**1b**]), *N*-(2-diisopropylphosphinophenyl)-2,6-dimethylaniline (H[**1c**]), or *N*-(2-diisopropylphosphinophenyl)-2,6-diisopropylaniline (H[**1d**]) under similar conditions generated quantitatively the corresponding three-coordinate zinc methyl **2b–d** and zinc ethyl **3b–d**. The bis-ligand complexes **4a,b,d** were isolated by either protonolysis of alkyls **2–3** with one equivalent of H[**1**] or metathesis of ZnX_2 (X = Cl, OAc) with the corresponding lithium derivatives **5**. Attempts to prepare [**1a–d**]ZnX (X = Cl, OAc) were not successful regardless of stoichiometry of the starting materials employed. Alcoholysis of zinc alkyls **2–3** led undesirably to protonation on the amido nitrogen donor of **1**, highlighting perhaps its higher basicity than alkyls. The reaction of $ZnCl_2$ with H[**1c**] generated the phosphorus-bound adduct $\{H[\mathbf{1c}]ZnCl(\mu\text{-}Cl)\}_2$ (**6c**). Interestingly, attempts to deprotonate **6c** with *n*-BuLi produced unexpectedly the alkylated product [**1c**]Zn(*n*-Bu) (**7c**) instead of [**1c**]ZnCl; analogous reactions employing NEt_3 led to Lewis base substitution to give H[**1c**] and $[ZnCl_2(NEt_3)]_2$. Structural characterization of all new compounds was achieved by multi-nuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{7}Li) and X-ray crystallography (**2c–d**, **3c**, **4d**, **5c–d**, and **6c**) where appropriate. On the basis of the NMR and X-ray data, in combination with the synthetic investigations, the steric nature of these amido phosphine ligands is recognized to follow the order of **1a** < **1b** < **1c** < **1d**. Interestingly, zinc alkyls **2–3** are all active initiators for catalytic ring-opening polymerization of ε-caprolactone whereas the bis-ligand complexes **4** are not.

Introduction

Organozinc complexes and their derivatives have long been recognized as useful reagents for stoichiometric and catalytic chemical transformations.[1] The non-toxic, inexpensive, and biocompatible nature of zinc[2] makes it an attractive candidate as initiators for biocompatible polymer synthesis.[3,4] With sterically demanding ligands, zinc complexes have shown remarkable activities to catalytically polymerize a number of heterocyclic substrates,[5–9] and in some cases, in a controlled manner, *e.g.*, those supported by tris(pyrazolyl)hydroborate[5] or β-diketiminate ligands.[6]

We are interested in coordination chemistry involving complexes of hybrid chelating ligands.[10,11] In particular, a number of diarylamido phosphine complexes[10,12,13] have been prepared and structurally characterized. In an effort to expand the territory of this particular ligand set, we have set out to prepare a series of bidentate chelates bearing variable substituents at both donor atoms and apply these ligands to explore the coordination chemistry with zinc, aiming at the development of active initiators for catalytic polymerization of heterocycles. In this contribution, we describe the preparation and structural characterization of these molecules and demonstrate their reactivity with respect to catalytic ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). Solution NMR spectroscopic and X-ray crystallographic data concerning the electronic and steric properties of these molecules are also discussed. A preliminary result of synthetic investigations was communicated previously.[14] Catalytic examinations of these molecules are unprecedented.

Results and discussion

Ligand synthesis

Scheme 1 illustrates the synthetic protocols to prepare the desired protio ligand precursors. Such strategies have been successfully employed for the synthesis of a number of tridentate amido diphosphine ligands.[15] Preparation of H[**1a**] and H[**1b**] *via* the fluorinated precursors has been described previously,[14,16] with the employment of nucleophilic phosphide reagents. Alternatively, these molecules may be accessible by bromide intermediates, which, upon lithiation, serve as nucleophiles to react with electrophilic chlorodiphenylphosphine or chlorodiisopropylphosphine to give H[**1a–b**] and H[**1c–d**], respectively. Compounds H[**1a**]

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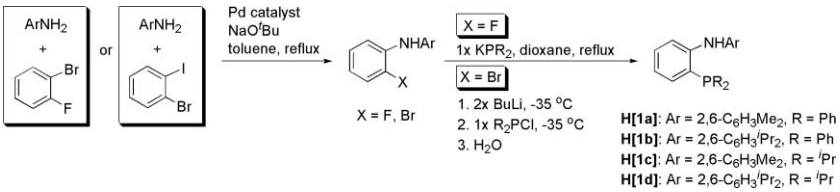
† CCDC reference numbers 773056–773062. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00327a

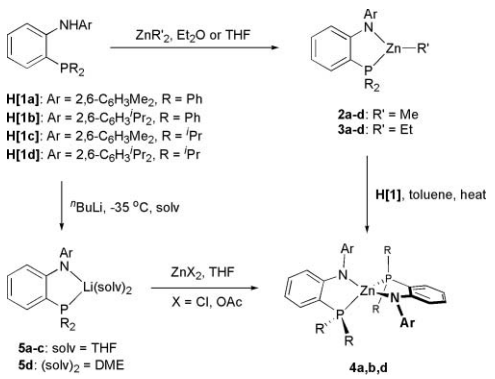


Scheme 1 Ligand synthesis.

and H[**1b**] are colorless crystalline solids whereas H[**1c**] and H[**1d**] are yellow viscous oil. In general, these molecules exhibit solution Cs symmetry on the NMR timescale. The ^{31}P chemical shifts of the isopropyl substituted H[**1c**] and H[**1d**] (*ca.* –17 ppm) are comparatively downfield from those of their phenyl counterparts H[**1a**] and H[**1b**] (*ca.* –20 ppm). Derivatives similar to H[**1c**] and H[**1d**] appeared recently.[17]

Synthesis of zinc complexes

Scheme 2 summarizes the preparation of corresponding zinc complexes. Treatment of H[**1a**] with one equivalent of $ZnMe_2$ in diethyl ether at –35 °C led to the formation of a mixture containing [**1a**]ZnMe (**2a**) and [**1a**]$_2$Zn (**4a**) in a 7 : 3 ratio as evidenced by ^{1}H and ^{31}P{^{1}H} NMR. Analogous reactions employing $ZnEt_2$, however, produced cleanly [**1a**]ZnEt (**3a**); no **4a** was found in the reaction aliquots. These results are phenomenal as **3a** is an adjacent higher homologue of **2a**. The concomitant formation of homoleptic **4a** in attempts to prepare **2a** thus highlights the insufficient steric size of the alkyl ligand in **2a** as compared to that in **3a**. Complex **4a** may be alternatively prepared in quantitative yield from reactions of $ZnMe_2$ with two equivalents of H[**1a**] at –35 °C or **3a** with H[**1a**] upon mild heating (60 °C).



Scheme 2 Synthesis of zinc complexes.

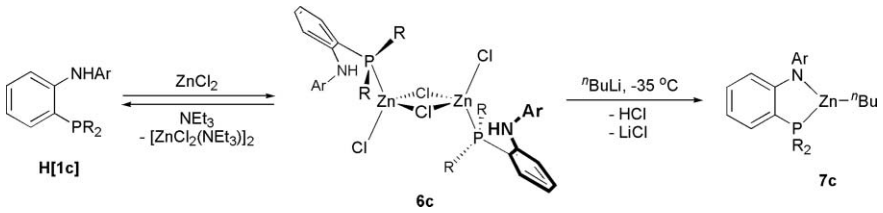
In contrast to H[**1a**], H[**1b–d**] reacts with one equivalent of $ZnMe_2$ to generate cleanly the corresponding zinc methyl complexes **2b–d**, highlighting the sufficient steric protection from the latter ligands. Analogous reactions involving $ZnEt_2$ gave **3b–d** quantitatively. Remarkably, these monomeric, three-coordinate zinc alkyls **2–3** are not associated with coordinating solvents such as THF or Et_2O (NMR evidence), in spite of their coordinatively unsaturated nature. It should be noted that three-coordinate zinc complexes that do not bind coordinating solvent molecules are extremely rare,[18] particularly for those bearing small alkyls. Compounds **2–3** are extremely sensitive to moisture, producing exclusively H[**1**] as evidenced by ^{31}P{^{1}H} NMR, but are thermally stable at elevated temperatures (> 120 °C) under an inert atmosphere. The formation of bis-ligand **4b** may be accessed by treating **2b** or **3b** with H[**1b**] upon prolonged heating (100 °C), a reaction rate that is notably slower than that of **3a** with H[**1a**]. In contrast, analogous reactions involving H[**1c–d**] in attempts to prepare **4c–d** did not proceed at all, even after a prolonged reaction time (*e.g.*, 120 °C, > 4 days), likely reflecting the steric nature of these ligands be more significant than that of phenyl substituted **1a–b**. Nevertheless, **4d** may be isolated by metathetical route (*vide infra*).

Given the fact that lithium amides are useful starting materials for metathetical reactions with metal halides, we turned our attention to prepare lithium complexes of **1**. The preparation of **5a–b** was reported previously.[14,19] Analogously, deprotonation of H[**1c–d**] with *n*-BuLi in ethereal solutions at –35 °C produced **5c–d**. Both **5c** and **5d** were isolated as pale yellow crystals; the former contains two equivalents of coordinated THF whereas the latter is a DME adduct. We note that, after multiple attempts, crystallization of lithium complex of **1d** from THF was not successful; the involvement of DME facilitates crystallization and purification.

In addition to zinc alkyls, zinc alkoxides are also intriguing as both are potential initiators for catalytic polymerization of heterocycles. Our initial plans to prepare zinc alkoxides of **1** involve alcoholysis of zinc alkyls **2–3**. Unfortunately, these reactions led undesirably to protonation on the amido nitrogen donor of **1**, highlighting perhaps its higher basicity than alkyl ligands in **2–3**. These results, however, are consistent with their moisture sensitivity as aforementioned.

With lithium complexes **5a–d** at hand, we attempted to prepare zinc chloride or zinc acetate complexes of **1**; the former may in turn lead to zinc alkoxides by metathetical reactions. Unsatisfactorily, the bis-ligand complexes **4** were the only spectroscopically decipherable or isolable products, regardless of the stoichiometry of **5** and ZnX_2 (X = Cl, OAc) employed (Scheme 2); no presumed [**1**]ZnCl or [**1**]ZnOAc (or their corresponding dimers) was found. Though less sterically congested than **4d**, complex **4c** has thus far been elusive as several approaches that we had examined gave a mixture of products (^{31}P NMR evidence), from which isolation or purification was not successful. It is interesting to note that the facile formation of **4** by metathetical reactions is in sharp contrast to what is found for slow alcoholysis rates involving H[**1**] and **2–3**, particularly H[**1b**] and H[**1d**]. Such discrepancy in reaction rates thus implies higher reactivity of [**1**]ZnX (X = Cl, OAc) than [**1**]ZnR (R = Me, Et) under the conditions investigated.

It has been shown that metal complexes of anionic ligands may be synthesized by *in situ* preparation of protio ligand adducts of metal halides followed by deprotonation with appropriate bases.[20–22] We attempted to prepare [**1**]ZnCl based on this strategy. Treatment of $ZnCl_2$ with one equivalent of H[**1c**] in THF at room temperature produced high yield of phosphorus-bound adduct



Scheme 3 Alternative strategy for the synthesis of zinc complexes.

{H[**1c**]ZnCl(μ-Cl)}$_2$ (**6c**, Scheme 3). This compound is thermally stable; attempts to eliminate hydrochloride by thermolysis were not successful (80 °C, 3 days). Surprisingly, addition of two equivalents of *n*-BuLi to a THF solution of the dimeric **6c** at −35 °C did not lead to deprotonation to eliminate butane. Instead, alkylation occurred to afford [**1c**]Zn(*n*-Bu) (**7c**) in high yield and presumably produce LiCl and HCl concurrently. Employment of non-alkylating bases such as NEt_3 gave H[**1c**] and $[ZnCl_2(NEt_3)]_2$ *via* Lewis base substitution (NMR evidence). The presumed [**1c**]ZnCl remains elusive from these reactions.

NMR studies

All NMR spectroscopic data of alkyls **2–3** and **7c** are consistent with solution Cs symmetry. Though **2a** was not isolable due to concomitant formation of **4a**, its identity was deduced by ^{1}H and ^{31}P{^{1}H} NMR spectra of product mixtures in comparison with those of **2b–d** and **4a**, respectively. Interestingly, the ^{31}P chemical shifts of *ca.* −28 ppm for **2a–b** and **3a–b** are relatively upfield from those of H[**1a–b**] whereas the signals for **2c–d**, **3c–d**, and **7c** (*ca.* −14 ppm) are downfield shifted in comparison with H[**1c–d**]. This discrepancy likely reflects electronic identities of the substituents at the phosphorus donors in **1**. A similar upfield change in the ^{31}P chemical shift was also observed for $(2,6\text{-}^tBu_2C_6H_3O)_2Zn(PCy_3)$ (−2.1 ppm)[23] and $[(\mu\text{-Cl})(ZnLCl)_2][ClO_4]$ (−3.2 ppm, L = N-(diphenylphosphinopropyl)-1,4,7-triazacyclononane)[24] as compared to their corresponding free phosphines. Consistent with the coordination of the phosphorus donors, the H_α and C_α atoms in these alkyl complexes exhibit a diagnostic coupling where resolved, *e.g.*, $^3J_{PH\alpha} = 4.2$ Hz for **2c** and $^2J_{PC\alpha} = 37$ Hz for **3d**, in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The isopropylmethyl groups in **2–3** and **7c**, where appropriate, are all diastereotopic as evidenced by the ^{1}H and ^{13}C{^{1}H} NMR spectra, implying steric congestion of these molecules.

The homoleptic **4a**, **4b**, and **4d** display solution C_2 symmetry on the NMR timescale; no internal symmetry is found within each amido phosphine ligand. Similar to what has been described for alkyls **2–3**, the phosphorus donors in **4a–b** resonate relatively upfield from their protio ligands whereas those in **4d** resonate downfield from H[**1d**]. Coincidentally, the ^{31}P chemical shifts of **4a** and **4d** are comparable to those of their corresponding alkyl counterparts **2–3**. In the ^{1}H NMR spectrum of **4d**, one of the isopropylmethyl groups associated with the phosphorus donors resonates unusually upfield (0.34 ppm, doublet of doublets) as compared to other derivatives of **1d**. We ascribe this phenomenon to ring current effect arising from adjacent N-aryl substituents (X-ray evidence, *vide infra*).

The most diagnostic NMR data for lithium complexes **5** concern perhaps the P–Li bonding; ^{31}P{^{1}H} NMR exhibits a 1 : 1 : 1 : 1 quartet resonance whereas ^{7}Li{^{1}H} NMR shows a doublet signal (Fig. S1, see ESI†), consistent with the coordination of the phosphorus donor in **1** to a quadrupolar ^{7}Li atom ($I = 3/2$, natural abundance 92.6%). The $^1J_{PLi}$ values range from 34 (**5a**) to 49 Hz (**5d**). In the cases of **5a** and **5c**, lowering temperature to ≤ −20 °C is necessary for P–Li coupling observation whereas the multiplicity for **5b** and **5d** is detected at room temperature. In contrast to those observed for zinc complexes **2–4** and **7c**, the ^{31}P chemical shifts of **5** are all relatively downfield from their corresponding protio ligands regardless of the substituents at the phosphorus donors. The identity of coordinating solvents in **5** appears to affect the ^{31}P chemical shifts more significantly (**5a–c**: *ca.* −11 ppm; **5d**: −7 ppm) than that of the phosphorus substituents. The ^{1}H and ^{13}C{^{1}H} NMR data are consistent with solution Cs symmetry for these molecules.

The ^{31}P{^{1}H} NMR spectrum of complex **6c** exhibits a diagnostic downfield shift from that of its protio ligand **1c**. This signal, detected at −8 ppm, is relatively broad ($\Delta\nu_{1/2} = 65$ Hz) as compared to the others reported in this study. Such broadening is ascribable to a dynamic equilibrium involving association/dissociation of the bridging chloride atoms. The absolute structure was elucidated by a single-crystal diffraction study.

Table 1 Selected bond distances (Å) for **2c–d**, **3b–c**, **4b**, and **4d–e**

Compound	Zn–N	Zn–P	Zn–C	Reference
2c	1.951(3)	2.4036(11)	1.963(4)	This work
2d	1.954(4)	2.3897(14)	1.941(5)	This work
3b	1.911(4)	2.4450(14)	1.956(5)	14
3c	1.953(2)	2.3956(7)	1.962(3)	This work
4b	1.971(5), 1.974(5)	2.4545(19), 2.4387(19)		14
4d	2.015(4), 2.014(3)	2.4333(11), 2.4319(12)		This work
4e[a]	1.9685(15), 1.9685(15)	2.3720(13), 2.3720(13)		27

[a] Bis(*N*-(2-diisopropylphosphinophenyl)anilide)zinc.

X-Ray crystallographic studies†

Three-coordinate zinc complexes of phosphine are extremely rare.[23,25,26] Yellow crystals of alkyls **2c** and **3c** suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at −35 °C whereas those of **2d** from *n*-hexane. The homoleptic **4d** crystallizes from *n*-pentane solutions. Molecular structures are depicted in Fig. 1; selected bond distances and angles are summarized in Tables 1 and 2, respectively, in comparison with corresponding values of previously established **3b**,[14] **4b**,[14] and a closely related bis(*N*-(2-diisopropylphosphinophenyl)anilide)zinc (**4e**).[27]

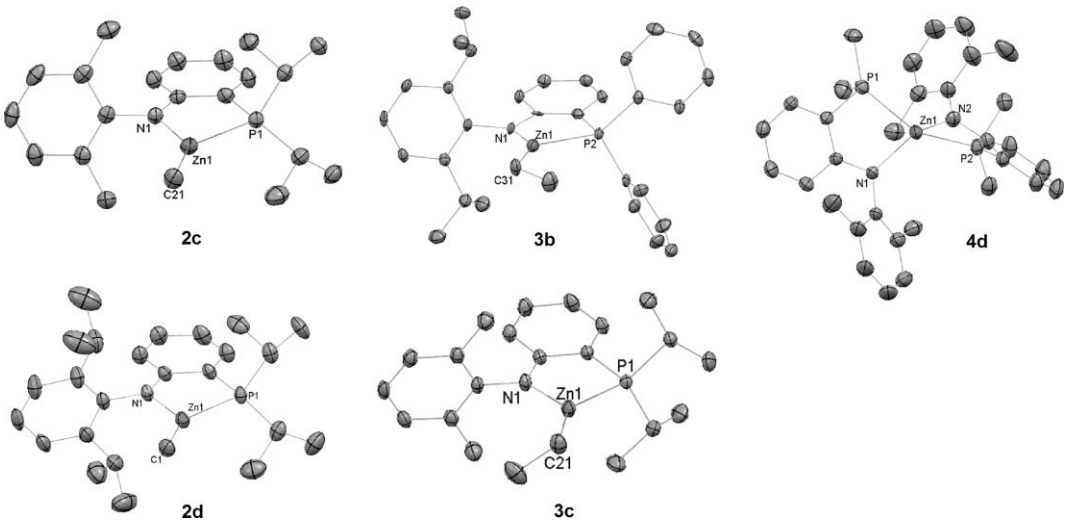


Fig. 1 Molecular structures of **2c–d**, **3b–c**, and **4d** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms in **2c–d**, **3b–c**, **4d** and methyl groups in **4d** are omitted for clarity.

Table 2 Selected bond angles (°) for **2c–d**, **3b–c**, **4b**, and **4d–e**

Compound	N–Zn–P[a]	N–Zn–C	P–Zn–C	Reference
2c	85.46(9)	135.70(17)	138.69(14)	This work
2d	85.73(12)	130.1(2)	143.9(2)	This work
3b	85.04(12)	140.55(19)	134.22(16)	14
3c	84.96(6)	131.03(10)	143.81(9)	This work
4b	84.24(15), 83.15(15)			14
4d	82.78(10), 82.85(10)			This work
4e[b]	85.72(4), 85.72(4)			27

[a] Bite angles. [b] Bis(*N*-(2-diisopropylphosphinophenyl)anilide)zinc.

The Zn–N, Zn–P, and Zn–C distances are all unexceptional. The Zn–N distances in three-coordinate **2c–d** and **3b–c** do not change much with different aryl substituents, nor do Zn–P lengths, though that associated with phenyl substituted phosphine (**3b**) is slightly longer than those of isopropyl counterparts (**2c–d** and **3c**), likely reflecting their distinct electronic nature. A similar phenomenon is also found for four-coordinate bis-ligand derivatives (**4b** *versus* **4d** and **4e**).

The zinc atom in **2c–d** and **3b–c** lies virtually on the mean N–phenylene–P plane with a slight deviation whereas that in **4b** and **4d** is displaced significantly by 0.69 and 0.88 Å (average), respectively. With relatively smaller sterics, the corresponding deviation of 0.32 Å (average) for **4e** is much less.[27]

In three-coordinate **2c–d** and **3b–c**, the N–Zn–P bite angles are all similar; the sum of the angles about Zn is close to 360°, indicating a trigonal planar geometry at zinc for these molecules. Interestingly, the P–Zn–C angles associated with isopropyl substituted phosphines (*i.e.*, **2c–d** and **3c**) are all wider than N–Zn–C whereas that with phenyl substituents (*i.e.*, **3b**) is sharper. These results likely reflect the steric demand of substituents at these heteroatoms following the order of P^iPr_2 > $N(C_6H_3{}^iPr_2$-2,6) > PPh_2. Consistently, the C_β atom in both **3b** and **3c**, though tilted in different directions, is disposed towards the less sterically congested side with the Zn–C_α–C_β angle of **3b** (115.4(4)°) and **3c** (113.8(2)°) being both larger than what is anticipated for an sp^3 carbon atom. To accommodate the steric repulsion with the tilted N–aryl ring (dihedral angle of 79.24° with mean coordination plane), the C_β atom in **3c** is displaced from the mean coordination plane by 0.794 Å.

The core geometry for bis-ligated **4b** and **4d** is best described as distorted tetrahedral. Consistent with the increased steric repulsion between the substituents at all donor atoms, the N–Zn–P bite angles in these homoleptic complexes are generally sharper than those of three-coordinate alkyls, particularly **4d** (average 82.8°), which is apparently the most sterically congested molecule in this study. In agreement with this steric argument, these bite angles are even smaller than those of bis-ligated Zn[2-(Ph_2P)-6-(Me_3Si)C_6H_3S]$_2$ (average 87.6°)[28] though the Zn–S distances (average 2.279 Å) are significantly longer. In **4d**, two methyl groups (C2 and C26 in Fig. S2, see ESI†) in P^iPr_2 lie right above the *N*-$C_6H_3{}^iPr_2$-2,6 rings, leading to the usually upfield resonance observed in the ^{1}H NMR spectrum.

Yellow crystals of **5c** and **5d** were grown from a concentrated pentane and diethyl ether solution, respectively, at –35 °C. Molecular structures are depicted in Fig. 2; selected bond distances and angles are summarized in Table 3, in comparison with those of **5a**.[19] The geometry at lithium is distorted tetrahedral; the N–Li–P/O–Li–O dihedral angle decreases following the order of **5a** < **5c** < **5d**. The Li–N, Li–P, and Li–O distances are all unexceptional. Reminiscent of what is found for zinc derivatives (*vide supra*), the Li–E (E = N, P, O) distances do not change

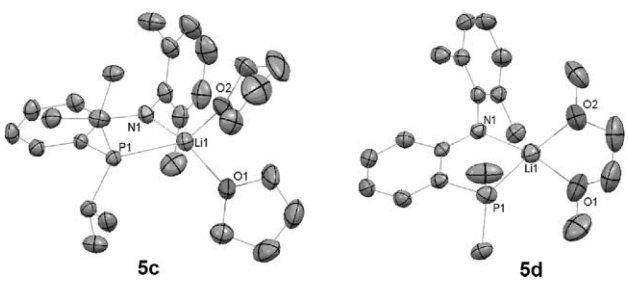


Fig. 2 Molecular structures of **5c–d** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms in **5c–d** and isopropylmethyl groups in **5d** are omitted for clarity.

Table 3 Selected bond distances (Å), bond angles (°), and dihedral angles (°) for **5a**, **5c**, and **5d**

Compound	**5a**[a]	**5c**	**5d**
Li–N	1.990(5)	1.957(9)	1.958(10)
Li–P	2.620(5)	2.573(8)	2.547(9)
Li–O	1.921(5), 1.942(5)	2.003(9), 1.959(8)	2.026(10), 1.957(10)
N–Li–P	76.63(17)	81.6(3)	82.6(3)
O–Li–O	99.8(2)	97.6(4)	82.1(4)
N–Li–P/O–Li–O	86.89	85.93	75.10

[a] Reference 19.

much with different substituents, though Li–P^{i}Pr$_2$ lengths (**5c–d**) are slightly shorter than Li–PPh$_2$ (**5a**), a result ascribable to different electronic properties of these phosphorus substituents. A similar phenomenon is also found for tridentate PNP analogues that carry distinct aliphatic and aromatic groups at phosphorus donors.[15,29,30] Consistent with the trend in Li–P distances, the N–Li–P bite angles of **5c–d** are wider than that of **5a**. The O–Li–O angle of **5d** is notably sharper than those of **5a** and **5c** due to chelation of the bidentate DME.

Pale yellow prisms of **6c** were grown from a concentrated diethyl ether solution at −35 °C. This chloride bridged dimer is Ci symmetric (Fig. 3); its core is isostructural to {[Et$_3$P]ZnI(μ-I)}$_2$[31] and {[(Me$_3$Si)$_3$P]ZnI(μ-I)}$_2$.[32] The Zn–Cl and Zn–P distances are unexceptional.

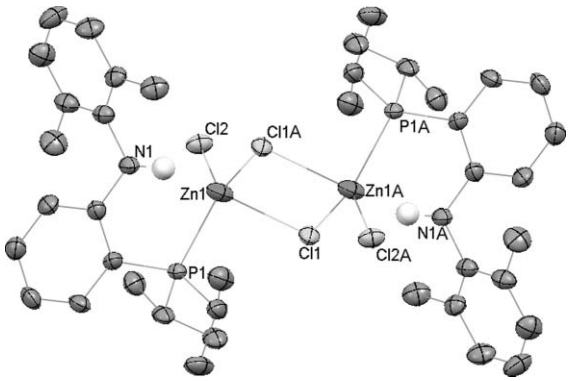


Fig. 3 Molecular structure of **6c** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zn(1)–Cl(2) 2.190(2), Zn(1)–Cl(1) 2.304(2), Zn(1)–P(1) 2.356(2), Zn(1)–Cl(1A) 2.573(2), Cl(2)–Zn(1)–Cl(1) 114.32(9), Cl(2)–Zn(1)–P(1) 125.27(9), Cl(1)–Zn(1)–P(1) 116.16(9), Cl(2)–Zn(1)–Cl(1A) 105.28(9), Cl(1)–Zn(1)–Cl(1A) 88.51(7), P(1)–Zn(1)–Cl(1A) 95.83(8), Zn(1)–Cl(1)–Zn(1A) 91.49(7).

Catalysis

ROP of ε-CL by the derived zinc complexes was examined. The homoleptic complexes **4** are virtually inactive; only a negligible amount of products was obtained. In contrast, alkyls **2–3** are all active. The high propensity of amide protonation for **2–3** (*vide supra*) precludes catalysis investigation of these molecules in the presence of alcohols. Table 4 summarizes polymerization results and characterization data of the derived poly(ε-caprolactone) (PCL). In general, these zinc catalysts are quite active (*ca.* 90% to quantitative conversion) under the conditions employed, except **3a** due likely to relatively insufficient steric protection imposed by **1a**. Fig. S3 (see ESI†) depicts a representative ^{1}H NMR spectrum of PCL prepared by ROP with catalytic **2c**. End group analysis shows that the integral ratio of keto methyl group (H_a at 1.86 ppm) to hydroxyl methylene group (H_f, 3.75 ppm) equals 1.5, consistent with the initiation step occurring with insertion of the coordinated monomer into the Zn–Me bond. Subsequent cleavage of the acyl–oxygen bond then ring-opens the monomer and generates a reactive zinc alkoxide intermediate for chain propagation. A coordination–insertion mechanism is thus likely operating in this system. Upon acidic work-up, the zinc alkoxide chain end is protonated to give the hydroxyl group. Gel permeation chromatography (GPC) analyses show that the (corrected)[33,34] number averaged molecular weights (M_n) of PCLs are consistently higher than the corresponding theoretical values, implying possibly only a portion of zinc complexes participates in catalysis. The relatively low polydispersity index (PDI) of *ca.* 1.5 indicates reasonably narrow molecular weight distributions, suggesting the identity of catalytically active species be nearly uniform, though not single-site.[5,6] The PDIs of *ca.* 2 found for **3a–b** (entries 1 and 3), however, reflect that transesterification processes are likely taking place. Interestingly, the found M_n of PCLs is approximately proportional to the monomer-to-catalyst ratio or the anticipated M_n (entries 5–8, Fig. S4 and S5, see ESI†), indicating propagating chains grow in a reasonably controlled manner.

Table 4 Polymerization of ε-CL by catalysts **2** and **3**[a]

Entry	$[\varepsilon\text{-CL}]_0/[\text{Zn}]_0$	Zn	Conv (%)[b]	M_n (calc, kg mol^{-1})[c]	M_n (exp, kg mol^{-1})[d]	Corrected M_n (exp, kg mol^{-1})[e]	PDI[d]
1	152	**3a**	69	12.0	47.2	26.4	1.79
2	150	**2b**	92	15.8	44.1	24.7	1.21
3	152	**3b**	100	17.3	57.2	32.0	1.95
4	150	**2c**	97	16.6	70.1	39.3	1.52
5	25	**3c**	95	2.7	34.4	19.3	1.45
6	75	**3c**	97	8.3	58.7	32.9	1.55
7	100	**3c**	95	10.8	78.5	44.0	1.65
8	150	**3c**	87	14.9	88.5	49.6	1.53
9	150	**2d**	95	16.3	77.5	43.4	1.41
10	150	**3d**	98	16.8	53.1	29.7	1.53

[a] Conditions: $[\text{Zn}]_0$ = 2.0 mM, toluene, 80 °C, 2 h; these parameters were not optimized. [b] Determined by ^{1}H NMR analysis. [c] Calculated from fw of ε-CL × ($[\varepsilon\text{-CL}]_0/[\text{Zn}]_0$) × conversion, 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.[33,34]

Conclusions

We have prepared a series of zinc and lithium complexes supported by bidentate diarylamido phosphine ligands and characterized their solution and solid-state structures by means of NMR spectroscopy and X-ray crystallography. Of interest is the successful isolation of monomeric, coordinatively unsaturated alkyls **2–3** and **7c** that do not adopt strong coordinating solvents. Attempts to prepare the corresponding zinc alkoxide derivatives with numerous approaches, however, were not successful. Zinc chlorides and alkoxides supported by these amido phosphine ligands remain elusive in this study. In contrast, the homoleptic complexes **4** appears to be more thermally stable, even with substantial steric pressure intramolecularly (particularly **4d**) as evidenced by X-ray crystallographic data. On the basis of the NMR and X-ray studies, in combination with the synthetic results, the steric size of these amido phosphine ligands thus follows the order of **1a** < **1b** < **1c** < **1d**. Interestingly, zinc alkyls **2–3** are all active initiators for catalytic ROP of ε-CL, producing PCLs with molecular weights and molecular weight distributions in a reasonably controlled manner.

Experimental

General procedures

Unless otherwise specified, all experiments were performed under nitrogen 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) are in hertz. ^{1}H NMR spectra are referenced 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 using the internal solvent peak at δ 128.4 for C_6D_6 and δ 77.2 for $CDCl_3$. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P and ^{7}Li NMR spectra are referenced externally 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. With multiple attempts, we were unable to obtain satisfactory analysis for some metal complexes due to their extreme moisture-sensitivity.

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^{-1} with a 1515 Isocratic HPLC Pump. Molecular weights (M_n and M_w) were determined by interpolation from calibration plots established with polystyrene standards.

X-Ray crystallography.[35]

Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using maXus or WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The structure of **4d** contains disordered pentane molecules. Attempts to obtain a suitable disorder model failed. The SQUEEZE procedure of Platon program[36] was used to obtain a new set of F^2 (hkl) values without the contribution of solvent molecules, leading to the presence of significant voids in this structure. The refinement reduced R_1 value to 0.0599.

Materials

Compounds *N*-(2-fluorophenyl)-2,6-dimethylaniline,[16] *N*-(2-fluorophenyl)-2,6-diisopropylaniline,[14] **2b**,[14] **3b**,[14] **4b**,[14] **5a**,[19] and **5b**[14] were prepared according to literature procedures.

Synthesis of *N*-(2-bromophenyl)-2,6-dimethylaniline

A Schlenk flask was charged with 1-bromo-2-iodobenzene (10.08 g, 35.64 mmol), 2,6-dimethylaniline (4.32 g, 35.64 mmol), $Pd(OAc)_2$ (40 mg, 0.18 mmol, 0.5% equiv.), bis[2-(diphenylphosphino)phenyl]ether (DPEphos, 144 mg, 0.27 mmol, 0.75% equiv.), sodium *tert*-butoxide (4.80 g, 49.9 mmol, 1.4 equiv.), and toluene (70 mL) under nitrogen. The flask was sealed with a rubber septum and heated to 95 °C with stirring for 3 d. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The solid residue was dissolved in deionized water (70 mL) and CH_2Cl_2 (100 mL). The organic portion was separated from the aqueous layer, which was further extracted with dichloromethane (40 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to yield brown viscous oil, which was subjected to flash column chromatography on Al_2O_3 using Et_2O as the eluant. The first band (pale yellow) was collected and solvent was removed *in vacuo*, affording the product as pale yellow oil, which solidified upon standing at room temperature; yield 9.72 g (99%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (dd, 1H, Ar), 7.18 (m, 3H, Ar), 7.06 (t, 1H, Ar), 6.64 (td, 1H, Ar), 6.21 (dd, 1H, Ar), 5.75 (br s, 1H, NH), 2.25 (d, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.5 MHz) δ 143.3 (s, C), 137.5 (s, C), 136.5 (s, C), 132.4 (s, CH), 128.5 (s, CH), 128.3 (s, CH), 126.5 (s, CH), 118.6 (s, CH), 112.5 (s, CH), 109.5 (s, C), 18.1 (s, CH_3). Anal. Calcd for $C_{14}H_{14}BrN$: C, 60.89; H, 5.11; N, 5.07. Found: C, 61.19; H, 5.47; N, 5.15.

Synthesis of *N*-(2-bromophenyl)-2,6-diisopropylaniline

A Schlenk flask was charged with 1-bromo-2-iodobenzene (1.00 g, 3.54 mmol), 2,6-diisopropylaniline (627 mg, 3.54 mmol), $Pd(OAc)_2$ (4 mg, 0.018 mmol, 0.5% equiv.), bis[2-(diphenylphosphino)phenyl]ether (DPEphos, 14 mg, 0.027 mmol, 0.75% equiv.), sodium *tert*-butoxide (475 mg, 4.95 mmol, 1.4 equiv.), and toluene (25 mL) under nitrogen. The flask was sealed with a rubber septum and heated to 95 °C with stirring for 7 d. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The solid residue was dissolved in deionized water (25 mL) and CH_2Cl_2 (25 mL). The organic portion was separated from the aqueous layer, which was further extracted with dichloromethane (10 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to yield brown viscous oil, which was subjected to flash column chromatography on Al_2O_3

using Et_2O as the eluent. The first band (pale yellow) was collected and solvent was removed *in vacuo*, affording the product as pale yellow oil; yield 1.10 g (94%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (dd, 1H, Ar), 7.24 (m, 1H, Ar), 7.16 (m, 2H, Ar), 6.91 (td, 1H, Ar), 6.48 (td, 1H, Ar), 6.07 (dd, 1H, Ar), 5.61 (s, 1H, NH), 3.02 (septet, 2H, C*H*Me$_2$), 1.10 (d, 6H, CH*Me*$_2$), 1.03 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.5 MHz) δ 147.7 (s, C), 144.9 (s, C), 134.6 (s, C), 132.3 (s, CH), 128.2 (s, CH), 127.8 (s, CH), 123.9 (s, CH), 118.3 (s, CH), 112.6 (s, CH), 108.8 (s, C), 28.3 (s, *C*HMe$_2$), 24.6 (s, CH*Me*$_2$), 23.0 (s, CH*Me*$_2$).

Synthesis of H[1a]

To a solution of *N*-(2-bromophenyl)-2,6-dimethylaniline (100 mg, 0.36 mmol) in diethyl ether (6 mL) at −35 °C was added dropwise *n*-BuLi (0.29 mL, 2.5 M in hexane, 0.72 mmol, 2 equiv.). The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again and chlorodiphenylphosphine (80 mg, 0.36 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Degassed deionized water (6 mL) and diethyl ether (6 mL) were added sequentially. The diethyl ether portion was separated from the aqueous solution, which was further extracted with diethyl ether (3 mL × 2). The diethyl ether solutions were combined, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The yellow oil thus obtained was dissolved in degassed methanol (4 mL) and cooled to −40 °C to give the product as an off-white crystalline solid; yield 103 mg (74%). The NMR spectroscopic data are all identical to those reported previously.[16]

Synthesis of H[1b]

To a solution of *N*-(2-bromophenyl)-2,6-diisopropylaniline (100 mg, 0.30 mmol) in diethyl ether (6 mL) at −35 °C was added dropwise *n*-BuLi (0.24 mL, 2.5 M in hexane, 0.60 mmol, 2 equiv.). The reaction solution was naturally warmed to room temperature and stirred for 1 h, providing a pale yellow solution along with a significant amount of off-white precipitate. The reaction mixture was cooled to −35 °C again and chlorodiphenylphosphine (66 mg, 0.30 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Degassed deionized water (6 mL) and diethyl ether (6 mL) were added sequentially. The diethyl ether portion was separated from the aqueous solution, which was further extracted with diethyl ether (3 mL × 2). The diethyl ether solutions were combined, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The yellow oil thus obtained was dissolved in degassed ethanol (6 mL) and cooled to −40 °C to give the product as an off-white crystalline solid; yield 115 mg (87%). The NMR spectroscopic data are all identical to those reported previously.[14]

Synthesis of H[1c]

To a solution of *N*-(2-bromophenyl)-2,6-dimethylaniline (2.00 g, 7.24 mmol) in diethyl ether (40 mL) at −35 °C was added *n*-BuLi (9.05 mL, 1.6 M in hexane, 14.48 mmol, 2 equiv.). The reaction solution was naturally warmed to room temperature with stirring. After being stirred at room temperature for 1 h, the reaction mixture was cooled to −35 °C and chlorodiisopropylphosphine (1.11 g, 7.24 mmol) was added. The reaction solution was stirred at room temperature overnight and quenched with degassed deionized water (10 mL). The product was extracted with deoxygenated dichloromethane (50 mL). The organic solution was separated from the aqueous portion, from which the product was further extracted with dichloromethane (15 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed *in vacuo*, affording the product as yellow viscous oil; yield 2.17 g (96%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.22 (ddd, 1H, Ar), 7.07 (d, 1H, J_{HP} = 12, NH), 7.01 (s, 3H, Ar), 6.96 (td, 1H, Ar), 6.70 (td, 1H, Ar), 6.26 (dd, 1H, Ar), 2.17 (s, 6H, CH_3), 2.01 (septet of doublets, 2H, PC*H*Me$_2$), 1.14 (dd, 6H, PCH*Me*$_2$), 0.98 (dd, 6H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −17.41. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 152.9 (d, J_{CP} = 19.2, C), 139.8 (d, J_{CP} = 2.4, C), 137.2 (s, C), 133.8 (d, J_{CP} = 2.8, CH), 131.0 (s, CH), 129.2 (s, CH), 126.6 (s, CH), 117.9 (s, CH), 117.3 (d, J_{CP} = 13.7, C), 111.6 (d, J_{CP} = 2.8, CH), 24.1 (d, $^1J_{CP}$ = 9.7, *C*HMe$_2$), 20.8 (d, $^2J_{CP}$ = 18.7, CH*Me*$_2$), 19.5 (d, $^2J_{CP}$ = 8.7, CH*Me*$_2$), 18.9 (s, Ar*Me*). Anal. Calcd for $C_{20}H_{28}NP$: C, 76.63; H, 9.01; N, 4.47. Found: C, 76.66; H, 9.28; N, 4.18.

Synthesis of H[1d]

To a solution of *N*-(2-bromophenyl)-2,6-diisopropylaniline (208 mg, 0.63 mmol) in diethyl ether (6 mL) at −35 °C was added *n*-BuLi (0.8 mL, 1.6 M in hexane, 1.28 mmol, 2 equiv.). The reaction solution was naturally warmed to room temperature with stirring. After being stirred at room temperature for 1 h, the reaction mixture was cooled to −35 °C and chlorodiisopropylphosphine (0.1 mL, 0.63 mmol) was added. The reaction solution was stirred at room temperature overnight and quenched with degassed deionized water (10 mL). The product was extracted with deoxygenated dichloromethane (10 mL). The organic solution was separated from the aqueous portion, from which the product was further extracted with dichloromethane (5 mL × 2). The combined organic solution was dried over $MgSO_4$ and filtered. All volatiles were removed *in vacuo*, affording the product as yellow viscous oil; yield 210 mg (91%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.24 (d, 1H, J_{HP} = 8.5, NH), 7.20 (m, 3H, Ar), 7.15 (t, 1H, Ar), 6.96 (td, 1H, Ar), 6.67 (td, 1H, Ar), 6.30 (ddd, 1H, Ar), 3.36 (septet, 2H, ArC*H*Me$_2$), 2.02 (septet of doublets, 2H, PC*H*Me$_2$), 1.19 (d, 6H, ArCH*Me*$_2$), 1.16 (dd, 6H, PCH*Me*$_2$), 1.13 (d, 6H, ArCH*Me*$_2$), 1.10 (dd, 6H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ −17.15. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 154.7 (d, J_{CP} = 19.2, C), 148.2 (s, C), 137.3 (d, J_{CP} = 2.8, C), 133.7 (d, J_{CP} = 3.3, CH), 131.0 (s, CH), 128.0 (s, CH), 124.6 (s, CH), 117.8 (s, CH), 116.7 (d, J_{CP} = 12.8, C), 111.9 (d, J_{CP} = 2.8, CH), 29.3 (s, Ar*C*HMe$_2$), 25.3 (s, ArCH*Me*$_2$), 24.1 (d, $^1J_{CP}$ = 9.2, P*C*HMe$_2$), 23.4 (s, ArCH*Me*$_2$), 20.7 (d, $^2J_{CP}$ = 18.7, PCH*Me*$_2$), 19.4 (d, $^2J_{CP}$ = 8.7, PCH*Me*$_2$).

Synthesis of 2a

To a diethyl ether solution (3 mL) of $ZnCl_2$ (68 mg, 0.5 mmol) at −35 °C was added MeMgCl (0.33 mL, 3.0 M in THF, 0.99 mmol). The reaction mixture was naturally warmed and stirred at room temperature overnight. The solution was chilled to −35 °C again and a pre-chilled solution of H[**1a**] (191 mg, 0.5 mmol) in diethyl ether (5 mL) at −35 °C was added. After being stirred

at room temperature overnight, the reaction mixture was stripped to dryness *in vacuo*. Benzene (16 mL) was added. The benzene solution was filtered through a pad of Celite which was further washed with benzene (2 mL × 2) until the washings became colorless. The filtrates were combined and evaporated to dryness under reduced pressure to afford a yellow solid that contained **2a** and **4a** in a ratio of 7 : 3; yield 131 mg (57%). ^{1}H NMR (C_6D_6, 200 NMR) δ 7.42 (m, 5H, Ar), 7.20 (m, 3H, Ar), 7.05 (m, 7H, Ar), 6.41 (t, 1H, Ar), 6.25 (t, 1H, Ar), 2.27 (s, 6H, ArCH_3), –0.27 (br s, 3H, ZnCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz) δ –29.50.

Synthesis of 2c

To a solution of H[**1c**] (100 mg, 0.32 mmol) in diethyl ether (6 mL) at –35 °C was added $ZnMe_2$ (0.16 mL, 2 M in toluene, 0.32 mmol). The reaction mixture was naturally warmed to room temperature and stirred overnight. The diethyl ether solution was filtered through a pad of Celite, which was further washed with diethyl ether (2 mL × 2). The diethyl ether filtrate and washings were combined and evaporated to dryness under reduced pressure. The yellow solid thus obtained was washed with pentane (1 mL x 2) and dried *in vacuo*; yield 119 mg (95%). Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at –35 °C; yield 74.6 mg (60%). ^{1}H NMR (C_6D_6, 200 MHz) δ 7.22 (d, 1H, Ar), 7.05 (m, 2H, Ar), 6.91 (m, 2H, Ar), 6.42 (t, 1H, Ar), 6.23 (t, 1H, Ar), 2.31 (s, 6H, Ar*Me*), 1.80 (m, 2H, C*H*Me$_2$), 0.89 (dd, 6H, CH*Me*$_2$), 0.80 (dd, 6H, CH*Me*$_2$), –0.15 (d, 3H, $^{3}J_{HP}$ = 4.2, ZnCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz) δ –14.04. ^{31}P{^{1}H} NMR (diethyl ether, 80.95 MHz) δ –13.53. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.2 (d, J_{CP} = 15.6, C), 149.7 (d, J_{CP} = 6.9, C), 135.0 (s, C), 134.0 (s, CH), 133.7 (s, CH), 129.5 (s, CH), 124.1 (s, CH), 113.4 (d, J_{CP} = 5.5, CH), 112.4 (d, J_{CP} = 4.5, CH), 106.7 (d, J_{CP} = 37.5, C), 22.9 (d, J_{CP} = 16.9, *C*HMe$_2$), 19.8 (d, J_{CP} = 9.5, PCH*Me*$_2$), 19.4 (s, Ar*C*H$_3$), 18.4 (d, J_{CP} = 2.3, PCH*Me*$_2$), –12.6 (br s, Zn*C*H$_3$). Anal. Calcd for $C_{21}H_{30}$NPZn: C, 64.18; H, 7.70; N, 3.57. Found: C, 64.48; H, 7.63; N, 3.20.

Synthesis of 2d

To a solution of H[**1d**] (141 mg, 0.38 mmol) in diethyl ether (2 mL) at –35 °C was added $ZnMe_2$ (0.32 mL, 1.2 M in toluene, 0.38 mmol). The reaction mixture was naturally warmed to room temperature and stirred for 2 h. Removal of all volatiles under reduced pressure afforded the product as yellow oil in quantitative yield. Crystallization of the product in hexane at –35 °C gave yellow crystals; yield 64 mg (45%). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.33 (m, 3H, Ar), 6.96 (t, 1H, Ar), 6.88 (td, 1H, Ar), 6.38 (t, 1H, Ar), 6.19 (dd, 1H, Ar), 3.43 (septet, 2H, ArC*H*Me$_2$), 1.85 (m, 2H, PC*H*Me$_2$), 1.30 (d, 6H, ArCH*Me*$_2$), 1.23 (d, 6H, ArCH*Me*$_2$), 0.93 (dd, 6H, PCH*Me*$_2$), 0.85 (dd, 6H, PCH*Me*$_2$), –0.16 (s, 3H, ZnCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz) δ –13.82. ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz) δ 164.9 (d, J_{CP} = 7.6, C), 146.8 (s, C), 145.6 (s, C), 133.8 (s, CH), 133.6 (s, CH), 125.3 (s, CH), 124.6 (s, CH), 113.9 (d, J_{CP} = 4.4, CH), 113.3 (d, J_{CP} = 5.3, CH), 106.5 (d, J_{CP} = 38.5, C), 28.9 (s, Ar*C*HMe$_2$), 25.4 (s, ArCH*Me*$_2$), 24.2 (s, ArCH*Me*$_2$), 23.0 (d, J_{CP} = 17.4, P*C*HMe$_2$), 19.7 (d, J_{CP} = 9.1, PCH*Me*$_2$), 18.4 (s, PCH*Me*$_2$), –12.6 (br s, Zn*Me*).

Synthesis of 3a

Solid H[**1a**] (200 mg, 0.52 mmol) was dissolved in diethyl ether (5 mL) and cooled to –35 °C. To this was added a solution of $ZnEt_2$ (0.52 mL, 1.0 M in hexane, 0.52 mmol). The reaction solution was naturally warmed to room temperature and stirred overnight. After being filtered through a pad of Celite, the solution was concentrated to *ca.* 3 mL and cooled to –35 °C to afford a colorless, crystalline solid, which was isolated from the solution and dried *in vacuo*; yield 172 mg (69%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.36–7.40 (m, 4H, Ar), 7.14 (m, 2H, Ar), 6.94–7.08 (m, 9H, Ar), 6.40 (t, 1H, Ar), 6.27 (t, 1H, Ar), 2.23 (s, 6H, Me), 1.35 (t, 3H, ZnCH$_2$CH_3), 0.70 (q, 2H, ZnCH_2CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 Hz) δ –28.93. ^{13}C NMR (C_6D_6, 125.5 MHz) δ 161.6 (J_{CP} = 18.3), 148.9 (J_{CP} = 6.9), 135.2 (J_{CP} = 11.4, CH), 134.4 (CH), 133.9 (J_{CP} = 15.1, CH), 130.8 (J_{CP} = 1.8, CH), 130.8 (J_{CP} = 29.7), 129.7 (J_{CP} = 9.7, CH), 129.6 (CH), 124.4 (CH), 114.9 (J_{CP} = 5.4, CH), 113.1 (J_{CP} = 5.0, CH), 110.3, 109.9, 19.2 (C_6H_3*Me*$_2$), 13.0 (ZnCH$_2$*C*H$_3$), 2.0 (Zn*C*H$_2$). Anal. Calcd. for $C_{28}H_{28}$NPZn: C, 70.80; H, 5.95; N, 2.95. Found: C, 68.19; H, 5.67; N, 2.94.

Synthesis of 3c

To a solution of H[**1c**] (100 mg, 0.32 mmol) in diethyl ether (6 mL) at –35 °C was added $ZnEt_2$ (0.32 mL, 1.0 M in hexanes, 0.32 mmol). The reaction mixture was naturally warmed to room temperature and stirred overnight. A reaction aliquot was taken and examined by ^{31}P{^{1}H} NMR spectroscopy which showed the quantitative formation of **3c**. The diethyl ether solution was filtered through a pad of Celite, which was further washed with diethyl ether (2 mL × 2) until the washings became colorless. The diethyl ether filtrate and washings were combined, concentrated under reduced pressure, and cooled to –35 °C to afford the product as yellow crystals suitable for X-ray diffraction analysis; yield 86 mg (66%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.21 (d, 2H, Ar), 7.06 (t, 1H, Ar), 6.96 (t, 1H, Ar), 6.90 (t, 1H, Ar), 6.42 (t, 1H, Ar), 6.22 (dd, 1H, Ar), 2.30 (s, 6H, Ar*C*H$_3$), 1.84 (m, 2H, C*H*Me$_2$), 1.40 (t, 3H, ZnCH$_2$CH_3), 0.91 (dd, 6H, CH*Me*$_2$), 0.82 (dd, 6H, CH*Me*$_2$), 0.66 (q, 2H, ZnCH_2). ^{31}P{^{1}H} NMR (C_6D_6, 202.3 MHz) δ –12.94. ^{31}P{^{1}H} NMR (diethyl ether, 80.95 MHz) δ –12.58. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.2 (d, J_{CP} = 15.6, C), 149.5 (d, J_{CP} = 6.4, C), 134.9 (s, C), 134.0 (s, CH), 133.7 (s, CH), 129.5 (s, CH), 124.1 (s, CH), 113.4 (d, J_{CP} = 5.0, CH), 112.6 (d, J_{CP} = 5.0, CH), 106.9 (d, J_{CP} = 36.7, C), 23.0 (d, J_{CP} = 16.1, *C*HMe$_2$), 19.9 (d, J_{CP} = 9.7, CH*Me*$_2$), 19.3 (s, Ar*C*H$_3$), 18.5 (d, J_{CP} = 2.3, CH*Me*$_2$), 13.1 (s, ZnCH$_2$*C*H$_3$), 1.5 (d, $^{2}J_{CP}$ = 36.7, Zn*C*H$_2$CH$_3$). Anal. Calcd for $C_{22}H_{32}$NPZn: C, 64.92; H, 7.93; N, 3.44. Found: C, 65.05; H, 7.94; N, 2.99.

Synthesis of 3d

To a solution of H[**1d**] (118 mg, 0.32 mmol) in diethyl ether (2 mL) at –35 °C was added $ZnEt_2$ (0.32 mL, 1 M in toluene, 0.32 mmol). The reaction mixture was naturally warmed to room temperature and stirred for 2 h. Removal of all volatiles under reduced pressure afforded the product as yellow oil; yield 144 mg (98%). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.29 (m, 3H, Ar), 6.96 (td, 1H, Ar), 6.90 (td, 1H, Ar), 6.39 (t, 1H, Ar), 6.19 (dd, 1H, Ar), 3.42 (septet, 2H, ArC*H*Me$_2$), 1.85 (m, 2H, PC*H*Me$_2$), 1.41 (td, 3H, ZnCH$_2$CH_3), 1.30 (d, 6H, ArCH*Me*$_2$), 1.23 (d, 6H, ArCH*Me*$_2$), 0.96 (dd, 6H,

PCHMe_2), 0.86 (dd, 6H, PCHMe_2), 0.66 (q, 2H, ZnCH_2CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz) δ −13.23. ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz) δ 164.8 (d, J_{CP} = 15.1, C), 147.0 (d, J_{CP} = 6.8, C), 145.5 (s, C), 133.8 (s, CH), 133.6 (s, CH), 125.3 (s, CH), 124.5 (s, CH), 113.8 (d, J_{CP} = 4.5, CH), 113.4 (d, J_{CP} = 5.3, CH), 106.6 (d, J_{CP} = 36.2, C), 28.9 (s, *C*HMe$_2$), 25.2 (s, CH*Me*$_2$), 24.2 (s, CH*Me*$_2$), 23.1 (d, J_{CP} = 16.6, P*C*HMe$_2$), 19.8 (d, J_{CP} = 9.8, PCH*Me*$_2$), 18.5 (s, PCH*Me*$_2$), 13.2 (s, ZnCH$_2$*C*H$_3$), 1.5 (d, J_{CP} = 37.0, Zn*C*H$_2$CH$_3$).

Synthesis of 4a

To a diethyl ether solution (3 mL) of H[**1a**] (100 mg, 0.26 mmol) at −35 °C was added ZnMe$_2$ (0.065 mL, 2.0 M in toluene, 0.13 mmol). The solution was stirred at room temperature overnight and filtered through a pad of Celite, which was further washed with diethyl ether (2 mL × 2) until the washings became colorless. The filtrates were combined, concentrated under reduced pressure to *ca.* 4 mL, and cooled to −35 °C to afford the product as a yellow solid; yield 91 mg (84%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.32 (m, 8H, Ar), 7.06 (m, 2H, Ar), 6.95–7.00 (m, 12H, Ar), 6.72–6.87 (m, 4H, Ar), 6.71 (m, 4H, Ar), 6.27 (t, 2H, Ar), 6.21 (m, 2H, Ar), 1.96 (s, 6H, C*H*$_3$), 1.82 (s, 6H, C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz) δ −28.63. ^{31}P{^{1}H} NMR (THF, 202.5 MHz) δ −29.39. ^{13}C NMR (C_6D_6, 125.7 MHz) δ 163.1 (J_{CP} = 19.9), 163.1, 137.3, 136.1 (CH), 135.7, 134.1 (CH), 133.9 (CH), 133.8 (CH), 130.3 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 114.2 (CH, J_{CP} = 19.9), 109.5 (J_{CP} = 44.5), 109.5, 19.5 (Me), 19.0 (Me).

Synthesis of 4d

Solid Zn(OAc)$_2$ (18 mg, 0.2 mmol) was suspended in THF (1 mL) and cooled to −35 °C. To this was added a pre-chilled solution of **5d** (93 mg, 0.2 mmol) in THF (4 mL) at −35 °C. The reaction mixture was stirred at room temperature for 6 h and evaporated to dryness under reduced pressure. The solid residue was triturated with pentane (2 mL × 2) and diethyl ether (6 mL) was added. The ether solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure. Pentane (1 mL) was added. The pentane solution was cooled to −35 °C to afford the product as pale yellow crystals suitable for X-ray diffraction analysis; yield 68 mg (69%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.18 (m, 6H, Ar), 6.86 (t, 2H, Ar), 6.78 (t, 2H, Ar), 6.34 (t, 2H, Ar), 6.16 (t, 2H, Ar), 3.94 (septet, 2H, ArC*H*Me$_2$), 3.51 (septet, 2H, ArC*H*Me$_2$), 2.32 (septet of doublets, 2H, PC*H*Me$_2$), 1.93 (septet of doublets, 2H, PC*H*Me$_2$), 1.34 (d, 6H, CH*Me*$_2$), 1.25 (m, 12H, CH*Me*$_2$), 1.05 (dd, 6H, CH*Me*$_2$), 0.97 (d, 6H, CH*Me*$_2$), 0.94 (d, 6H, CH*Me*$_2$), 0.86 (m, 6H, CH*Me*$_2$), 0.34 (dd, 6H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz) δ −12.55. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 165.5 (t, J_{CP} = 17.4, C), 150.3 (s, C), 148.4 (s, C), 145.6 (s, C), 132.4 (d, J_{CP} = 22.9, CH), 128.7 (s, CH), 125.2 (s, CH), 125.1 (s, CH), 124.6 (s, CH), 120.8 (d, J_{CP} = 102.9, C), 118.5 (t, J_{CP} = 3.0, CH), 113.2 (t, J_{CP} = 4.5, CH), 28.7 (s, Ar*C*HMe$_2$), 28.39 (s, Ar*C*HMe$_2$), 28.37 (s, CH*Me*$_2$), 25.6 (s, CH*Me*$_2$), 25.34 (t, J_{CP} = 11.7, P*C*HMe$_2$), 25.33 (s, CH*Me*$_2$), 23.3 (s, CH*Me*$_2$), 21.8 (t, J_{CP} = 6.9, PCH*Me*$_2$), 20.2 (t, J_{CP} = 7.3, PCH*Me*$_2$), 19.9 (t, J_{CP} = 15.6, P*C*HMe$_2$), 18.4 (br s, CH*Me*$_2$), 17.8 (br s, CH*Me*$_2$). Anal. Calcd for $C_{48}H_{70}N_2P_2Zn$: C, 71.83; H, 8.80; N, 3.49. Found: C, 71.52; H, 8.71; N, 3.35.

Synthesis of 5c

To a solution of H[**1c**] (500 mg, 1.6 mmol) in THF (5 mL) at −35 °C was added *n*-BuLi (1.00 mL, 1.6 M in hexane, 1.6 mmol). The reaction mixture was naturally warmed to room temperature and stirred for 3 h. All volatiles were removed *in vacuo*. The red viscous residue was triturated with pentane (10 mL) to yield a yellow solid. The yellow solid was isolated from the orange solution, washed with pentane (5 mL × 2), and dried *in vacuo*; yield 718 mg (99%). Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.27 (d, 2H, Ar), 7.19 (t, 1H, Ar), 7.09 (t, 1H, Ar), 6.99 (t, 1H, Ar), 6.44 (t, 1H, Ar), 6.25 (t, 1H, Ar), 3.37 (br s, 8H, OCH_2CH$_2$), 2.39 (s, 6H, ArCH_3), 2.13 (m, 2H, C*H*Me$_2$), 1.27 (br s, 8H, OCH$_2$CH_2), 1.21 (m, 6H, CH*Me*$_2$), 1.17 (m, 6H, CH*Me*$_2$). ^{7}Li{^{1}H} NMR (C_6D_6, 194 MHz) δ 1.41 ($\Delta\nu_{1/2}$ = 29.4). ^{7}Li{^{1}H} NMR (toluene-d_8, −30 °C, 194 MHz) δ −3.65 (d, $^1J_{LiP}$ = 45.6). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ −7.90 ($\Delta\nu_{1/2}$ = 29). ^{31}P{^{1}H} NMR (THF, 81 MHz) δ −8.84. ^{31}P{^{1}H} NMR (toluene-d_8, −30 °C, 202 MHz) δ −10.89 (1 : 1 : 1 : 1 q, $^1J_{LiP}$ = 45.6). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 165.2 (d, J_{CP} = 21.4, C), 155.6 (s, C), 134.1 (s, C), 133.6 (d, J_{CP} = 2.5, CH), 131.9 (s, CH), 128.9 (s, CH), 120.2 (s, CH), 112.6 (s, CH), 112.1 (d, J_{CP} = 11.3, C), 108.8 (s, CH), 68.5 (s, O*C*H$_2$CH$_2$), 25.8 (s, OCH$_2$*C*H$_2$), 24.0 (br s, *C*HMe$_2$), 21.0 (d, J_{CP} = 14.3, CH*Me*$_2$), 20.3 (d, J_{CP} = 9.2, CH*Me*$_2$), 19.9 (s, Ar*C*H$_3$). Anal. Calcd for $C_{28}H_{43}LiNO_2P$: C, 72.52; H, 9.35; N, 3.02. Found: C, 72.01; H, 9.27; N, 3.19.

Synthesis of 5d

Method 1: To a solution of *N*-(2-bromophenyl)-2,6-diisopropylaniline (1.00 g, 3.01 mmol) in diethyl ether (20 mL) at −35 °C was added *n*-BuLi (3.8 mL, 1.6 M in hexane, 6.02 mmol, 2 equiv.). The reaction solution was naturally warmed to room temperature with stirring. After being stirred at room temperature for 1 h, the reaction mixture was cooled to −35 °C again and chlorodiisopropylphosphine (459 mg, 3.01 mmol) was added. The reaction solution was stirred at room temperature overnight and filtered through a pad of Celite, which was further washed with diethyl ether (5 mL × 2). The filtrate and washings were combined and dimethoxyethane (271 mg, 3.01 mmol) was added. The solution was concentrated under reduced pressure to *ca.* 2 mL and cooled to −35 °C to afford the product as pale yellow crystals suitable for X-ray diffraction analysis; yield 711 mg (51%). **Method 2**: Direct deprotonation of H[**1d**] with 1 equiv. of *n*-BuLi in DME at −35 °C gave quantitative formation of **5d** as indicated by ^{31}P{^{1}H} NMR. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.34 (d, 2H, Ar), 7.18 (m, 2H, Ar), 7.11 (td, 1H, Ar), 7.03 (td, 1H, Ar), 6.38 (t, 1H, Ar), 6.13 (dd, 1H, Ar), 3.64 (septet, 2H, ArC*H*Me$_2$), 2.87 (s, 6H, OMe), 2.69 (s, 4H, OCH$_2$), 2.09 (m, 2H, PC*H*Me$_2$), 1.34 (d, 6H, ArCH*Me*$_2$), 1.27 (d, 6H, ArCH*Me*$_2$), 1.21 (dd, 6H, PCH*Me*$_2$), 1.14 (dd, 6H, PCH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 203 MHz) δ −7.29 (q, $^1J_{PLi}$ = 49). ^{31}P{^{1}H} NMR (Et_2O, 81 MHz) δ −8.15. ^{7}Li{^{1}H} NMR (C_6D_6, 194 MHz) δ 1.63 (d, $^1J_{PLi}$ = 49). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 167.2 (d, J_{CP} = 21, C), 153.0 (d, J_{CP} = 2.3, C), 144.9 (s, C), 133.4 (d, J_{CP} = 2.8, CH), 131.4 (s, CH), 124.1 (s, CH), 121.6 (s, CH), 114.1 (d, J_{CP} = 5.0, CH), 111.7 (d, J_{CP} = 12.4, C), 108.7 (d, J_{CP} = 2.8, CH), 70.3 (s, OCH$_2$), 59.3 (s, OCH$_3$), 28.3 (s, CH), 25.9 (s, CH$_3$), 25.0 (s, CH$_3$), 24.1 (s, CH), 21.1 (d, J_{CP} = 15.2, CH$_3$), 20.4

(d, $J_{CP} = 8.7$, CH_3). Anal. Calcd for $C_{28}H_{45}LiNO_2P$: C, 72.21; H, 9.75; N, 3.01. Found: C, 67.51; H, 8.25; N, 2.15.

Synthesis of 6c

To a solution of H[**1c**] (200 mg, 0.64 mmol) in THF (6 mL) was added $ZnCl_2$ (1.28 mL, 0.5 M in THF, 0.64 mmol) at room temperature. The reaction solution was stirred at room temperature for 2 h and evaporated to dryness under reduced pressure. The solid residue was gently washed with diethyl ether (2 mL × 2) and dried *in vacuo* to afford the product as an off-white solid; yield 205 mg (71%). ^{1}H NMR (C_6D_6, 500 MHz) δ 6.99 (m, 3H, Ar and NH), 6.89 (t, 1H, Ar), 6.80 (t, 1H, Ar), 6.54 (m, 2H, Ar), 6.38 (dd, 1H, Ar), 2.30 (s, 6H, ArCH_3), 2.25 (m, 2H, C*H*Me$_2$), 1.31 (dd, 6H, CH*Me*$_2$), 0.93 (dd, 6H, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz) δ −7.73 ($\Delta\nu_{1/2} = 65$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 151.9 (d, $J_{CP} = 9.2$, C), 138.7 (s, C), 135.6 (s, C), 134.4 (s, CH), 133.3 (s, CH), 129.7 (s, CH), 126.4 (s, CH), 120.2 (d, $J_{CP} = 6.4$, CH), 117.2 (d, $J_{CP} = 5.5$, CH), 110.6 (d, $J_{CP} = 5.4$, C), 24.2 (d, $^1J_{CP} = 22.0$, *C*HMe$_2$), 19.38 (s, CH*Me*$_2$), 19.35 (s, CH*Me*$_2$), 17.8 (s, Ar*C*H$_3$).

Synthesis of 7c

To a solution of **6c** (112 mg, 0.25 mmol) in THF (6 mL) was added *n*-BuLi (0.1 mL, 2.5 M in hexane, 0.25 mmol) at −35 °C. The reaction solution was stirred at room temperature for 2 h and evaporated to dryness under reduced pressure. Pentane (8 mL) was added. The pentane solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure to afford the product as pale yellow oil; yield 80 mg (73%). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.20 (m, 2H, Ar), 7.05 (t, 1H, Ar), 6.93 (m, 2H, Ar), 6.40 (t, 1H, Ar), 6.15 (t, 1H, Ar), 2.27 (s, 6H, ArCH_3), 1.87 (m, 2H, C*H*Me$_2$), 1.69 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.94 (m, 9H, CH*Me*$_2$ mixed with CH_3), 0.82 (dd, 6H, CH*Me*$_2$), 0.73 (m, 2H, ZnCH_2). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz) δ −14.43. ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz) δ 163.1 (d, $J_{CP} = 14.71$, *C*), 149.7 (s, *C*), 135.1 (br s, *C*), 134.0 (s, *C*H), 133.7 (s, *C*H), 129.3 (s, *C*H), 124.1 (s, *C*H), 113.3 (br s, *C*), 112.7 (s, *C*H), 112.6 (s, *C*H), 30.1 (s, *C*H$_2$), 23.1 (d, $J_{CP} = 18.4$, P*C*H), 19.8 (d, $J_{CP} = 7.4$, PCH*Me*$_2$), 19.3 (s, *C*H$_3$), 18.4 (s, *C*H$_3$), 15.2 (br s, *C*H$_2$), 14.7 (s, *C*H$_3$), 1.8 (br s, Zn*C*H$_2$).

Catalytic ROP of ε-CL

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

Acknowledgements

We thank the National Science Council of Taiwan for financial support (NSC 96-2628-M-110-007-MY3, 96-2738-M-110-001, and 96-2918-I-110-011), 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 elemental analysis, Ms Chao-Lien Ho (NSYSU), Ms Mei-Yueh Chien (NCHU) and Ms Ru-Rong Wu (NCKU) for assistance with NMR, and the National Center for High-performance Computing (NCHC) for accesses to chemical databases.

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35 Crystal data for **2c**: $C_{21}H_{30}NPZn$, $M = 392.62$, monoclinic, space group $P2_1/c$, $a = 14.6479(5)$ Å, $b = 8.9972(3)$ Å, $c = 15.6842(6)$ Å, $\beta = 94.579(2)°$, $V = 2060.42(13)$ Å^3, $T = 200(2)$ K, $Z = 4$,μ(Mo-Kα) = 1.272 mm^{-1}, 11 371 reflections measured, 3730 unique ($R_{int} = 0.0662$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0556, wR_2 [$I > 2\sigma(I)$] = 0.1508, R_1 (all data) = 0.0713, wR_2 (all data) = 0.1725, GOF (on F^2) = 1.142, CCDC 773056. **2d**: $C_{25}H_{38}NPZn$, $M = 448.90$, monoclinic, space group $P2_1/n$, $a = 12.5895(3)$ Å, $b = 13.6322(4)$ Å, $c = 12.7248(4)$ Å, $\beta = 90.0190(10)°$, $V = 2527.11(12)$ Å^3, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.045 mm^{-1}, 13 704 reflections measured, 4207 unique ($R_{int} = 0.0740$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0583, wR_2 [$I > 2\sigma(I)$] = 0.1461, R_1 (all data) = 0.0979, wR_2 (all data) = 0.1910, GOF (on F^2) = 1.203, CCDC 773057. **3c**: $C_{22}H_{32}NPZn$, $M = 406.83$, triclinic, space group $P1$, $a = 8.6210(2)$ Å, $b = 9.1959(2)$ Å, $c = 14.8726(4)$ Å, $\alpha = 106.0720(10)°$, $\beta = 91.3470(10)°$, $\gamma = 106.9420(10)°$, $V = 1076.83(4)$ Å^3, $T = 200(2)$ K, $Z = 2$, μ(Mo-Kα) = 1.219 mm^{-1}, 13 672 reflections measured, 3796 unique ($R_{int} = 0.0469$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0344, wR_2 [$I > 2\sigma(I)$] = 0.0887, R_1 (all data) = 0.0437, wR_2 (all data) = 0.0949, GOF (on F^2) = 1.099, CCDC 773058. **4d**: $C_{48}H_{70}N_2P_2Zn$, $M = 802.37$, monoclinic, space group $P2_1/c$, $a = 14.6308(2)$ Å, $b = 21.8029(4)$ Å, $c = 15.9501(3)$ Å, $\beta = 90.8220(10)°$, $V = 5087.46(15)$ Å^3, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.575 mm^{-1}, 30 751 reflections measured, 8884 unique ($R_{int} = 0.0771$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0599, wR_2 [$I > 2\sigma(I)$] = 0.1766, R_1 (all data) = 0.0982, wR_2 (all data) = 0.2112, GOF (on F^2) = 0.758, CCDC 773059. **5c**: $C_{28}H_{43}LiNO_2P$, $M = 463.54$, triclinic, space group $P1$, $a = 9.2124(3)$ Å, $b = 9.3766(3)$ Å, $c = 18.2449(7)$ Å, $\alpha = 77.7120(10)°$, $\beta = 78.2640(10)°$, $\gamma = 67.232(2)°$, $V = 1407.04(8)$ Å^3, $T = 200(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.120 mm^{-1}, 18 628 reflections measured, 5025 unique ($R_{int} = 0.0964$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0937, wR_2 [$I > 2\sigma(I)$] = 0.2116, R_1 (all data) = 0.1706, wR_2 (all data) = 0.2776, GOF (on F^2) = 1.081, CCDC 773060. **5d**: $C_{28}H_{45}LiNO_2P$, $M = 465.56$, orthorhombic, space group $Pbn2_1$, $a = 10.7145(3)$ Å, $b = 15.3867(5)$ Å, $c = 17.6868(6)$ Å, $V = 2915.86(16)$ Å^3, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.116 mm^{-1}, 13 751 reflections measured, 4376 unique ($R_{int} = 0.0533$) which were used in allcalculations. Final R_1 [$I > 2\sigma(I)$] = 0.0837, wR_2 [$I > 2\sigma(I)$] = 0.1914, R_1 (all data) = 0.1159, wR_2 (all data) = 0.2194, GOF (on F^2) = 1.163, CCDC 773061. **6c**: $C_{40}H_{56}Cl_4N_2P_2Zn_2$, $M = 899.35$, monoclinic, space group $P2_1/c$, $a = 9.2599(4)$ Å, $b = 12.7189(7)$ Å, $c = 17.0867(9)$ Å, $\beta = 90.465(2)°$, $V = 2170.55(18)$ Å^3, $T = 200(2)$ K, $Z = 2$, μ(Mo-Kα) = 1.455 mm^{-1}, 13 719 reflections measured, 3792 unique ($R_{int} = 0.1073$) which were used in all calculations. Final R_1 [$I > 2\sigma(I)$] = 0.0895, wR_2 [$I > 2\sigma(I)$] = 0.2023, R_1 (all data) = 0.1543, wR_2 (all data) = 0.2427, GOF (on F^2) = 1.146, CCDC 773062.

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