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Synthesis and characterization of zinc complexes and reactivity with primary phosphines

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ABSTRACT

Zinc complexes of chelating monoanionic N-donors and neutral diphosphine ligands were synthesized by reaction of diethylzinc with 1,3-diketimine, diazabutadiene, and diphosphine ligand precursors. These complexes were reacted with primary phosphines in an attempt to solicit phosphine dehydrocoupling reactivity. In most cases, insoluble zinc-containing precipitates were formed and ligands were liberated. For the most sterically encumbered complex, $({}^{Dipp}L)ZnEt$ (**3**, ${}^{Dipp}L = [(2,6\text{-}{}^{i}PrC_6H_3)NC(CH_3)]_2CH^-$), a product assigned as the zinc-phosphide $({}^{Dipp}L)ZnPHPh$ (**6**) was observed but could not be isolated as a pure compound. A new, less bulky β-diketiminate complex $({}^{Tol}L)ZnEt$ (**2**, ${}^{Tol}L = [(p\text{-}CH_3C_6H_4)NC(CH_3)]_2CH^-$) was reacted with primary phosphines to give a precipitate and the bis(β-diketiminate)zinc complex $({}^{Tol}L)_2Zn$ (**5**), an apparent product of comproportionation. $({}^{Mes}AI)ZnEt$ (**1**, ${}^{Mes}AI = MesNC(Me)(Et)C(Me){=}NMes$) and **2** were structurally characterized.

1. Introduction

Dehydrocoupling catalysis is a key transformation in the synthesis of main-group materials [1–8]. However, the catalytic dehydrocoupling of phosphines is less developed than related transformations for elements such as silicon or for Lewis acid-base adducts such as amine-boranes [2,4,6–7,9–10]. For phosphine dehydrocoupling, the catalysts that have appeared in the literature primarily use group 4 metals or rhodium [8]. In developing broad synthetic applications for this transformation, it is attractive to use inexpensive metal complexes as catalysts. Earth-abundant, first-row transition metals are considered promising to displace conventional coinage metal complexes in other catalytic transformations [11].

Zinc complexes have shown excellent reactivity in the copolymerization of carbon dioxide with epoxides [12–13]. Though zinc complexes would not be expected to demonstrate the same kinds of reactivity as formally d^8 and d^0 metal complexes, which are demonstrated phosphine dehydrocoupling catalysts [8], the recent report of a tin complex, $Cp^*{}_2SnCl_2$, that is a catalyst for dehydrocoupling prompts the study of alternative metal species [14].

This report outlines efforts to solicit phosphine dehydrocoupling reactivity from a family of $L'ZnEt_2$ and LZnEt (L = monoanionic chelating ligand; L′ = neutral chelating ligand) derivatives. These reactions suggest that the simple zinc complexes reported herein are not viable catalysts due to the formation of insoluble Zn–P products, regardless of the nature of the ancillary ligand.

2. Results and discussion

2.1. Synthesis of zinc complexes

Simple ligands were selected to support zinc complexes as potential catalysts based on prior observation of related zinc complexes in stoichiometric or catalytic transformations. For example, it was expected that β-diketiminate complexes of zinc might afford reactivity with P–H bonds based on copolymerization catalysis [15–16]. Zinc complexes with α-aminoimine ligands have not seen attention in catalysis since their discovery by van Koten and coworkers [17–21], yet these ligands afford tunable steric and electronic parameters in a way that is similar to β-diketiminate ligands. It was also anticipated that neutral ligands, like chelating diphosphines, might promote different reactivites or stability over anionic counterparts.

Reaction of diethylzinc with a mesityl-substitued diazabutadiene in toluene solution gave analytically pure, orange crystals of $({}^{Mes}AI)ZnEt$ (**1**, ${}^{Mes}AI = MesN = C(Me)CEt(Me)NMes$) in 81% yield upon crystallization from pentane (Eq. (1)). Complex 1 is the product of a formal 1,2-insertion of one imine into the Zn–C bond of an ethyl ligand. Diagnostic spectral features of **1** include the imine and amine resonances of the ligand backbone at δ 71.8 and δ 191.1, respectively, in the ^{13}C NMR spectrum. Two methyl

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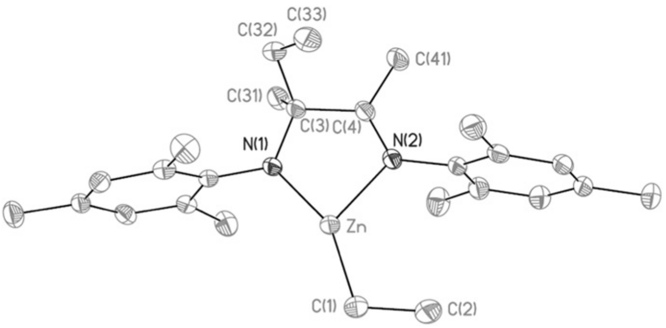
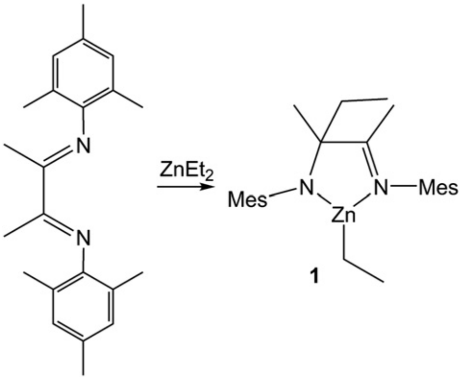


Fig. 1. Molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

resonances were observed in the ^{1}H NMR spectrum of **1** at δ 1.30 and 1.13. The transferred ethyl substituent resonances displayed distinctive coupling and chemical shifts in the ^{1}H NMR spectrum of **1** as well.



(**1**)

Structural characterization by X-ray crystallography confirmed the identity of complex 1. Single crystals of **1** were grown from pentane solution cooled to −30 °C, and the molecular structure is shown in Fig. 1. The three-coordinate zinc is trigonal planar, featuring an imine and amide functionality on the chelating ligand based on C(4)–N(2) = 1.283(2) Å and C(3)–N(1) = 1.466(2) Å, respectively. Selected bond lengths and angles are summarized in Table 1.

Van Koten and coworkers have investigated the use of the diazabutadiene (DAB) bearing alkyl and aryl substituents as ligands precursors for zinc complexes. Interestingly, a formal 1,1-insertion of an imine from a DAB ligand into Zn–C bonds was observed for sterically unencumbered substituents, whereas formal 1,2-insertion products resulted with DABs possessing bulky substituents such as 2,6-diisopropylphenyl [17,21]. It appears that the mesityl substituents possess sufficient bulk to promote the 1,2-insertion product.

Reaction of diethylzinc with one equiv. of para-tolyl substituted 1,3-diketimine in toluene solution gave analytically pure, yellow crystals of ($^{\mathrm{Tol}}$L)ZnEt (**2**, $^{\mathrm{Tol}}$L = [(p-$CH_3C_6H_4$)NC(CH_3)]$_2$CH$^-$) in 78% yield upon crystallization from pentane (Eq. (2)). This procedure was derived from that of ($^{\mathrm{Dipp}}$L)ZnEt (**3**, $^{\mathrm{Dipp}}$L = [(2,6-^{i}PrC_6H_3)NC(CH_3)]$_2$CH$^-$), which was also prepared [22]. Key spectral features in identifying complex **2** include the methine resonance at δ 4.90 and the para-tolyl methyl resonance at δ 2.08 in the ^{1}H NMR spectrum.

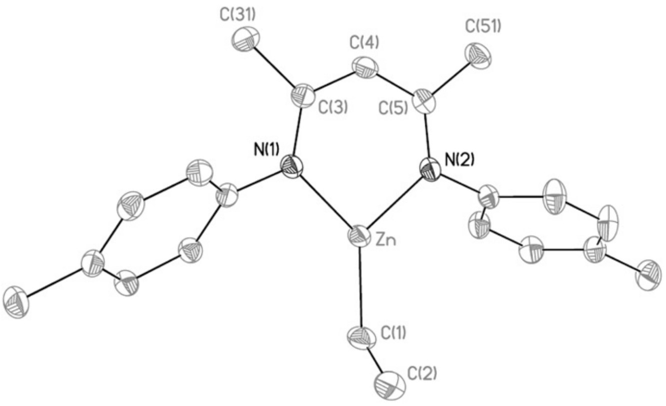
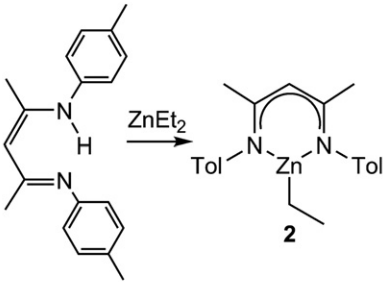


Fig. 2. Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Only one of two of independent molecules in the unit cell are shown.



(**2**)

Single crystals of **2** were grown from cold pentane solution and subjected to an X-ray diffraction study. The molecular structure, shown in Fig. 2, reveals a planar geometry around zinc. There are two independent molecules in the unit cell, differing only in the orientation of the ethyl ligand on zinc. In one molecule (Fig. 2), N(2)–Zn–C(1) = 127.49(8)° and C(1)–Zn–N(1) = 135.26(8)° as compared to the same angles of the other molecule, which are 129.93(8)° and 133.03(8)°, respectively. The remainder of bond lengths and angles are consistent with other β-diketiminate complexes of zinc (Table 2).

A neutral ancillary ligand was also employed. Reaction of diethylzinc with 1,2-bis(dimethylphosphino)ethane (dmpe) in toluene solution gave analytically pure, colorless crystals of (dmpe)ZnEt$_2$ (**4**) in quantitative yield (Eq. (3)). Diagnostic spectral features of **4** include the methylene resonance of the ligand backbone at δ 1.05 in the ^{1}H NMR spectrum and the resonance at δ −43 in the ^{31}P NMR spectrum. Complex 4 is highly similar to the 1,2-

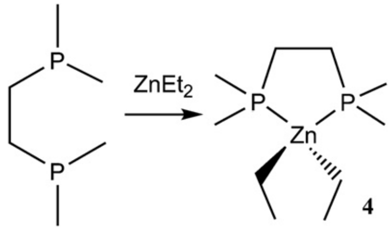
Table 1
Selected bond lengths (Å) and angles (deg) for ($^{\mathrm{Mes}}$AI)ZnEt (**1**).

Zn–C(1)	1.951(2)	N(1)–C(3)	1.466(2)
Zn–N(1)	1.8725(16)	N(2)–C(4)	1.283(2)
Zn–N(2)	2.0950(17)	C(3)–C(4)	1.530(3)
Zn–N(1)–C(3)	117.76(12)	N(1)–Zn–C(1)	154.24(8)
Zn–N(2)–C(4)	112.11(13)	N(2)–Zn–C(1)	123.13(8)
N(1)–C(3)–C(4)	108.67(15)	N(1)–Zn–N(2)	82.62(6)
N(2)–C(4)–C(3)	118.51(17)		

Table 2
Selected bond lengths (Å) and angles (deg) for ($^{\mathrm{Tol}}$L)ZnEt (**2**).

Zn–C(1)	1.970(2)	N(1)–C(3)	1.336(3)
Zn–N(1)	1.9758(17)	N(2)–C(5)	1.326(3)
Zn–N(2)	1.9633(17)		
Zn–N(1)–C(3)	122.31(13)	N(1)–Zn–C(1)	135.26(8)
Zn–N(2)–C(5)	123.07(14)	N(2)–Zn–C(1)	127.49(8)
N(1)–C(3)–C(4)	123.46(19)	N(1)–Zn–N(2)	97.22(7)
N(2)–C(5)–C(4)	123.43(19)		

bis(diphenylphosphino)ethane derivative investigated by Noltes and van den Hurk [23].



(3)

3. Reactions with phosphines

3.1. Attempted catalytic reactions

Initial investigations surrounded complex **4**, which, when reacted with 10 equiv. of phenyl- or cyclohexylphosphine at ambient temperature in benzene-d$_6$, yielded free dmpe and an insoluble, colorless precipitate. Reaction of diethylzinc and phenylphosphine under similar conditions gave the same result. Treatment of **4** with one equiv. each of the same phosphines gave a mixture of dmpe, precipitate, and unreacted **4** as in the attempted catalyst. Precise stoichiometry to decompose **4** with phosphines could not be determined.

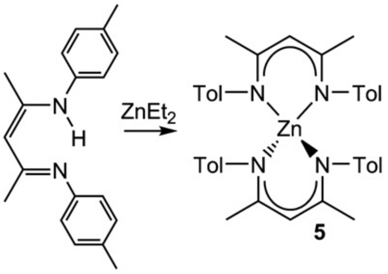
These initial reactions prompted the investigation of zinc complexes supported by monoanionic ancillary ligands to provide greater stability. Reaction of five mol% of complex **1** with phenyl- or cyclohexylphosphine yielded a colorless precipitate that was insoluble in common solvents. Monitoring the reaction by ^{31}P NMR spectroscopy showed little to no conversion to dehydrocoupling products, even upon extended heating.

The aromatized β-diketiminate ligands were targeted as potentially more stable anionic ancillary ligands. Heating benzene-d$_6$ solutions of phenyl- or cyclohexylphosphine with 10 mol % of complex **3** for extended periods resulted in trace quantities of dehydrocoupling products (PHPh)$_2$ and (PCy)$_4$, respectively. The conversions were less than 10% as judged by integration in the ^{1}H and ^{31}P NMR spectra and inconsistent between runs. It was hypothesized that the steric bulk of the diisopropylphenyl substituents was thwarting catalytic reactivity. This hypothesis motivated the preparation of **5**. However, treatment of phenylphosphine with 5 mol % of **2** gave a precipitate, unreacted phosphine as observed in the ^{31}P NMR spectrum, and a complex mixture of products in the ^{1}H NMR spectrum that included an unidentified resonance at δ 4.61. This new resonance was consistent with a new ($^{\mathrm{Tol}}$L)Zn complex, which was initially suspected to be a phosphide derivative. To gain insight into these reactions, they were performed stoichiometrically.

3.2. Stoichiometric reactions with phosphines

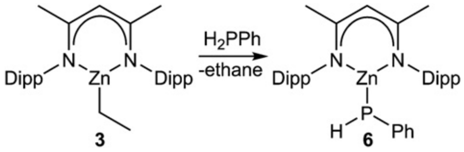
Treatment of complex **2** with one equiv. of phenylphosphine in benzene-d$_6$ showed loss of the ethyl ligand on zinc and complete consumption of phenylphosphine. A new product was formed in low conversion featuring the same δ 4.61 resonance in the ^{1}H NMR spectrum as observed in the catalytic reaction. A precipitate was also formed, and like the precipitate from the catalytic reactions, it was insoluble in common solvents. Attempts to run this reaction at larger scales gave the compound with the resonance at δ 4.61 of low purity and unreliable yield.

Working under the hypothesis that this new compound was in fact the bis(β-diketiminate) complex, a toluene solution of diethylzinc was added to p-tolyl 1,3-diketimine in toluene to give analytically pure, colorless crystals of ($^{\mathrm{Tol}}$L)$_2$Zn (**5**) in 84% yield upon consecutive crystallization from Et$_2$O then pentane (Eq. (4)). Beside the diagnostic resonance at δ 4.61, methyl resonances were observed at δ 2.08 and δ 1.77 in the ^{1}H NMR spectrum. Order of addition was key in this transformation as addition of 1,3-diketimine to a solution of diethylzinc gave a mixture of complexes **2** and **5**.



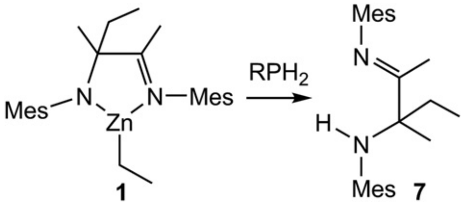
(4)

Some indication of a new phosphide complex came from the reaction of **3** with five equiv. of phenylphosphine in toluene solution (Eq (5)). The zinc-containing product was assigned to be ($^{\mathrm{Dipp}}$L)ZnPHPh (**6**) based on spectroscopic data. In particular, a new ^{31}P NMR resonance at δ −152 as well as a PH doublet ($J_{\mathrm{PH}} = 211$ Hz) at δ 4.92 in the ^{1}H NMR spectrum were observed. Unfortunately, the optimum yield for complex 6 was obtained under these conditions, and all other reactions and subsequent attempts to purify 6 could not separate it from unreacted **3**.



(5)

Treatment of complex **1** with phenyl- or cyclohexylphosphine in toluene solution afforded analytically pure, colorless crystals of the amine-substituted imine product (**7**) upon filtration through silica and crystallization from pentane in greater than 92% yield (Eq. (6)). The insoluble byproduct of the reaction, presumed to be Zn–P containing, could not be identified. Formation of **7** was also observed upon reaction of an NMR sample of 1 with water. Important spectral features of **7** include the aryl resonances around δ 6.8 and the methylene resonances at δ 2.01 and δ 1.48 in the ^{1}H NMR spectrum. Isolation of **7** allowed for the positive identification of the same complex in attempted catalytic reactions involving **1**. Formation of **7** is consistent with the reactivity observed by Van Koten and coworkers for alcoholysis reactions of related Zn complexes [17].



(6)

In nearly every reaction described, the formation of an insoluble precipitate was observed. Because some reactions led to the clean liberation of ancillary ligands such as the formation of **7** (vide supra), it is suspected that a zinc phosphinidene may have been formed analogously to known zinc imido complexes [24,25]. Efforts to isolate any putative phosphinidene complex by dissolution in a wide variety of solvents as well as conducting some of these reactions in alternative solvents (e.g., THF, a là Powers magnesium imide [26]) have not produced a clean products. Thus, we have accrued no evidence to support the formation of a zinc phosphinidene but no evidence to discount it either.

4. Conclusion

In this study, three new zinc ethyl complexes **1**, **2**, and **4** were prepared, and complexes **1** and **2** were structurally characterized. These and other zinc complexes were tested for catalytic reactivity in the dehydrocoupling of phosphines. Unfortunately, these reactions demonstrate that the complexes selected for this study are ineffective catalysts for the dehydrocoupling of primary phosphines. Given that different types of ancillary ligands were explored, it appears that the formation of insoluble Zn–P products is the main problem in these reactions. These difficulties are further compounded by the comproportionation of complex **2** to bis(β-diketiminate) complex **5**. However, the isolation of complex 6, though impure, suggests that Zn–P σ-bonds can be stabilized and that other systems may provide catalytic activity.

5. Experimental Section

5.1. General considerations

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk or high vacuum techniques and/or in an M. Braun glovebox. Dry, oxygen-free solvents were employed throughout. All NMR spectra were collected in benzene-d_6 that was purchased from Cambridge Isotope Laboratories, degassed, and dried over NaK alloy. Elemental analyses were collected using an Elementar VarioMICRO micro-analyzer. Infrared spectra were collected on a Bruker Alpha FT-IR spectrometer using an ATR head. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on a Bruker ARX 500 MHz NMR spectrometer (^{1}H, 500.1 HMz; ^{31}P, 202.4 MHz; ^{13}C, 125.8 MHz) and are reported with reference to residual solvent resonances (C_6HD_5 δ 7.16 and δ 128.0). 1,4-Bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene, para-tolyl 1,3-diketimine (^{Tol}LH), and (^{Dipp}L)ZnEt (**3**, ^{Dipp}L = [(2,6-^{i}PrC_6H_3)NC(CH_3)]$_2$CH$^-$) were prepared according to literature protocols, and toluidine•HCl was prepared using the method reported by Barton and Young [22,27–29].

5.2. Synthetic procedures

(^{Mes}AI)ZnEt (**1**). To a stirring solution of diethylzinc (2.5 mL, 1.5 M in toluene), a solution of diazabutadiene (1.1 g, 3.5 mmol) in toluene (10 mL) was added dropwise at ambient temperature causing an immediate color change to deep red. The solution was stirred for an additional 10 min then dried under reduced pressure The resulting oil was dissolved in minimal pentane and cooled to −30 °C yielding **1** as an orange solid (1.1 g, 2.5 mmol, 81%). ^{1}H NMR: δ 7.05 (s, $C_6H_2(CH_3)_3$, 2 H), 6.73 (s, $C_6H_2(CH_3)_3$, 1 H), 6.72 (s, $C_6H_2(CH_3)_3$, 1 H), 2.49 (s, CH_3, 3 H), 2.46 (s, CH_3, 3 H), 2.29 (s, CH_3, 3 H), 2.12 (s, CH_3, 3 H), 2.00 (s, CH_3, 3 H), 1.94 (s, CH_3, 3 H), 1.79 (m, CH_2, 1 H), 1.33 (s, CH_3, 3 H), 1.31 (m, CH_2, 1 H), 1.20 (t, $ZnCH_2CH_3$, 3 H, J = 8.1 Hz), 1.13 (s, CH_3, 3 H), 0.92 (t, CH_3, 3 H, J = 7.3 Hz), 0.51 (q, $ZnCH_2CH_3$, 2 H, J = 8.1 Hz). ^{13}C{^{1}H} NMR: δ 191.1 (s, N=C), 149.5 (s, Mes), 143.2 (s, Mes), 134.4 (s, Mes), 130.9 (s, Mes), 130.1 (s, Mes), 129.7 (s, Mes), 127.4 (s, Mes), 127.3 (s, Mes), 71.8 (s, NC), 25.1 (s, CH_2), 22.0 (s, CH_3), 20.9 (s, CH_3), 20.8 (s, CH_3), 19.0 (s, CH_3), 18.0 (s, CH_3), 16.4 (s, CH_3), 12.2 (S, CH_3), 10.0 (s, $ZnCH_2CH_3$), −1.7 (s, $ZnCH_2CH_3$). IR: 2919 w, 2139 m, 1549 m, 1528 m, 1397 s, 1365 s, 1276 m, 1197 m, 1173 m, 1016 w, 859 w, 807 m, 763 m, 748 w, 711 m, 694 w, 626 m, 584 m, 571 w, 554 m, 432 m, 417 w. Anal. Calcd. for $C_{26}H_{38}N_2Zn$: C, 70.33; H, 8.63; N, 6.31. Found: C, 70.38; H, 8.31; N, 6.45.

(^{Tol}L)ZnEt (2). To a stirring solution of diethylzinc (3.6 mL, 1.5 M in toluene), a solution of ^{Tol}LH (0.52 g, 1.9 mmol) in toluene (10 mL) was added dropwise at ambient temperature causing an immediate color change to orange. The solution was stirred for 18 h then dried under reduced pressure. The residue was extracted into minimal pentane, and the solution was filtered then cooled to −30 °C yielding **2** as yellow crystals (0.54 g, 1.5 mmol, 78%). ^{1}H NMR: δ 6.92 (d, $C_6H_4CH_3$, 4 H, J = 7.9 Hz), 6.74 (d, $C_6H_4CH_3$, 4 H, J = 8.2 Hz), 4.90 (s, CH, 1 H), 2.08 (s, CH_3, 6 H), 1.83 (s, CH_3, 6 H), 1.14 (t, CH_3, 3 H, J = 8.1 Hz), 0.40 (q, CH_2, 2 H, J = 8.1 Hz). ^{13}C{^{1}H} NMR: δ 166.2 (s, C=CH), 147.9 (s, tol), 133.6 (s, tol), 129.7 (s, tol), 124.7 (s, tol), 97.0 (H_3CC=$CHCCH_3$), 23.2 (s, CH_3), 20.8 (s, CH_3), 12.7 (s, CH_2), −1.8 (s, CH_3). IR: 2919 w, 1548 m, 1499 s, 1394 s, 1275 m, 1196 m, 1015 m, 937 w, 859 m, 805 m, 747 w, 626 w, 530 m, 500 w. Anal. Calcd. for $C_{21}H_{26}N_2Zn$: C, 67.83; H, 7.05; N, 7.53. Found: C, 68.12; H, 7.24; N, 7.64.

(dmpe)$ZnEt_2$ (4). To a stirring solution of diethylzinc (4.0 mL, 1.5 mL in toluene), a solution of dmpe (1.0 mL, 6.0 mmol) in toluene (2 mL) was added dropwise. The solution was stirred for 15 h and dried under reduced pressure yielding **4** as a colorless crystalline solid (1.63 g, 5.9 mmol, 99%). ^{1}H NMR: δ 1.62 (t, $ZnCH_2CH_3$, 6 H, J = 8.1 Hz), 1.05 (m, PCH_2, 4 H), 0.72 (br. s, $P(CH_3)_2$, 12 H), 0.52 (q, $ZnCH_2CH_3$, 4 H, J = 8.1 Hz). ^{13}C{^{1}H} NMR: δ 26.8 (t, PCH_2, J_{PC} = 6.6 Hz), 14.7 (s, CH_3), 11.8 (br. s, PCH_3), 2.4 (s, $ZnCH_2CH_3$). ^{31}P NMR (202.4 MHz): δ −42.96 (s). IR: 2835 s, 1423 s, 1297 m, 1281 m, 1180 w, 1096 m, 989 w, 939 s, 887 s, 860 m, 720 s, 590 s, 484 s, 444 s. Anal. Calcd. for $C_{10}H_{26}P_2Zn$: C, 43.89; H, 9.58. Found: C, 43.39; H, 9.02.

(^{Tol}L)$_2$Zn (5). To a stirring solution of **2** (0.51 g, 1.4 mmol) in toluene (10 mL), diethylzinc (3.6 mL, 1.5 M in toluene) was added dropwise yielding an immediate color change to yellow. The solution was stirred for 18 h and dried under reduced pressure. The crude product was then dissolved in minimal ether, and the solution was then cooled to −30 °C. The resulting solid was then dissolved in minimal pentane, the solution filtered, and then cooled to −30 °C to afford 5 as colorless crystals (0.48 g, 0.77 mmol, 84%). ^{1}H NMR: δ 6.97 (d, $C_6H_4CH_3$, 8 H, J = 8.1 Hz), 6.81 (d, $C_6H_4CH_3$, 8 H, J = 8.2 Hz), 4.61 (s, CH, 2 H), 2.13 (s, $C_6H_4CH_3$, 12 H), 1.77 (s, CH_3, 12 H). ^{13}C{^{1}H} NMR: δ 165.8 (s, C=CH), 148.3 (s, tol), 132.2 (s, tol), 129.0 (s, tol), 124.6 (s, tol), 95.8 (s, C=CH), 22.9 (s, CH_3), 20.6 (s, CH_3). IR: 3017 w, 2918 w, 2860 w, 1548 m, 1499 m, 1394 s, 1276 s, 1196 s, 1105 w, 1015 m, 938 m, 860 w, 806 m, 747 m, 626 m, 531 m, 500 w. Anal. Calcd. for $C_{38}H_{42}N_4Zn$: C, 73.59; H, 6.83; N, 9.03. Found: C, 73.39; H, 7.30; N, 9.02.

(^{Dipp}L)ZnPHPh (**6**). A PTFE-valved reaction tube was charged with 3 (137 mg, 0.267 mmol), approximately five equiv. of $PhPH_2$ (146 mg, 1.327 mmol), and 5 mL of toluene. The vessel was sealed and the pale orange solution was heated at 70 °C for 8 h. The volatile materials were removed under reduced pressure, and the resultant yellow oil was dissolved in minimal Et_2O. The solution was filtered then cooled to −30 °C to yield 161 mg of a colorless crystalline solid that contained 6 (>80%) and starting 3. Data for 6 ^{1}H NMR: δ 7.09 (d, Ar, 2 H, J = 8 Hz), 6.73–6.63 (m, Ar, 9 H) 4.91 (s, CH, 1 H), 4.92 (d, PH, 1 H, J_{PH} = 211) 3.11 (sept. CH, 2 H), 1.67 (s, CH_3, 6 H), 1.55 (d, CH_3, J = 7 Hz), 1.11 (d, CH_3, J = 7 Hz). ^{31}P NMR: δ −152.3 (s).

Table 3
Crystal data and structure refinement parameters for **1** and **2**.

	1	**2**
Formula	$C_{26}H_{38}N_2Zn$	$C_{42}H_{52}N_4Zn_2$
M	444.00	743.62
Cryst syst	Monoclinic	Monoclinic
Color	Colorless	Colorless
a/Å	7.9835(8)	12.2791(7)
b/Å	23.309(2)	22.4735(13)
c/Å	13.0485(13)	13.9929(8)
α/deg	90.00	90.00
β/deg	94.6350(10)	99.0660(10)
γ/deg	90.00	90.00
Unit cell vol/$Å^3$	2420.2(4)	3813.2(4)
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
θ range/deg	2.35 to 29.25	2.40 to 29.14
μ/mm^{-1}	1.029	1.292
N	30283	47641
N_{ind}	6383	10054
R_{int}	0.0261	0.0222
R_1[a] $(I > 2\sigma(I))$	0.0379	0.0373
wR_2[b] $(I > 2\sigma(I))$	0.1058	0.1077
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e $Å^3$	0.559; −0.509	0.687; −0.625
GoF on R_1	1.050	1.085

[a] $R_1 = |F_o| - |F_c|/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

(E)-N-(3-(mesitylamino)-3-methylpentan-2-ylidene)-mesitylaniline (**7**).

Method A- Reaction with phenylphosphine. To a stirring solution of **1** (0.10 g, 0.23 mmol) in toluene (2.0 mL), phenylphosphine (0.02 mL, 0.23 mmol) was added dropwise causing the immediate formation of colorless precipitate. The resulting orange solution was allowed to stir for 18 h, filtered through silica, and the filtrate was dried under reduced pressure yielding **7** as a colorless solid (0.075 g, 0.21 mmol, 94%).

Method B- Reaction with cyclohexylphosphine. To a stirring solution of **1** (0.13 g, 0.23 mmol) in toluene (2.0 mL), cyclohexylphosphine (0.02 mL, 0.23 mmol) was added dropwise and allowed to stir for 18 h. The resulting orange oil was filtered through silica and the filtrate was dried under reduced pressure yielding **7** as a yellow solid (0.072 g, 0.21 mmol, 92%).

Method C- Reaction with water. A solution of **1** (0.01 g, 0.02 mmol) in benzene-d_6 (0.7 mL) was removed from the glovebox. The cap was removed and the sample was exposed to air. The reaction gave the organic product based on ^1H NMR spectroscopy.

^1H NMR: δ 6.85 (s, $C_6H_2(CH_3)_3$, 2 H), 6.83 (s, $C_6H_2(CH_3)_3$, 2H), 5.47 (s, NH, 1 H), 2.41 (s, $C_6H_2(CH_3)_3$, 6 H), 2.21 (d, $C_6H_2(CH_3)_3$, 3 H), 2.20 (s, $C_6H_2(CH_3)_3$, 3 H), 2.08 (s, $C_6H_2(CH_3)_3$, 3 H), 2.00 (m, CCH_2CH_3, 1 H), 1.97 (s, $C_6H_2(CH_3)_3$, 3 H), 1.49 (m, CCH_2CH_3, 1 H), 1.41 (s, $N{=}CCH_3$, 3 H), 1.06 (s, $HNCCH_3$, 3 H), 1.04 (t, CCH_2CH_3, 3 H, $J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR: δ 174.9 (s, N=C), 146.3 (s, Mes), 142.6 (s, Mes), 135.0 (s, Mes), 132.0 (s, Mes), 129.8 (s, Mes), 129.3 (s, Mes), 126.1 (s, Mes), 125.0 (s, Mes), 65.1 (s, HNC), 32.5 (s, CH_2), 24.5 (s, CH_3), 20.9 (s, CH_3), 20.8 (s, CH_3), 18.8 (s, CH_3), 18.2 (s, CH_3), 15.5 (s, CH_3), 9.2 (s, CH_3). IR: 3314 s (ν_{NH}), 2971 m, 2950 m, 2916 m, 2855 m, 1646 s (ν_{CN}), 1470 s, 1446 m, 1301 w, 1227 s, 1182 m, 1147 m, 1121 m, 849 s, 788 s, 727 m, 670 m, 565 m, 463 m. Anal. Calcd. for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.05; H, 9.70; N, 7.65.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα, $\lambda = 0.71073$ Å) at 125 K. Suitable crystals of each complex **1** and **2** were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.14) [30]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. Crystal data and refinement details are presented in Table 3.

Appendix. Supplementary material

Crystallographic data for complexes **1** and **2**, CCDC 843858 and 843859, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] T.J. Clark, K. Lee, I. Manners, Chem. Eur. J. 12 (2006) 8634–8648.
[2] J.Y. Corey, Adv. Organomet. Chem. 51 (2004) 1–52.
[3] F. Gauvin, J.F. Harrod, H.G. Woo, Adv. Organomet. Chem. 42 (1998) 363–405.
[4] J.F. Harrod, Y. Mu, E. Samuel, Polyhedron 10 (1991) 1239–1245.
[5] C.A. Jaska, A. Bartole-Scott, I. Manners, Dalton Trans. (2003) 4015–4021.
[6] A. Staubitz, A.P.M. Robertson, M.E. Sloan, I. Manners, Chem. Rev. 110 (2010) 4023–4078.
[7] T.D. Tilley, Acc. Chem. Res. 26 (1993) 22–29.
[8] R. Waterman, Curr. Org. Chem. 12 (2008) 1322–1339.
[9] T.D. Tilley, Comments Inorg. Chem. 10 (1990) 37–51.
[10] C.W. Hamilton, R.T. Baker, A. Staubitz, I. Manners, Chem. Soc. Rev. 38 (2009) 279–293.
[11] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice. Oxford University Press, Oxford, 1998.
[12] G. Coates, S. Allen, H. Ajiro, Discrete catalysts for stereoselective epoxide polymerization, in: Stereoselective Polymerization with Single-Site Catalysts. CRC Press, 2007, pp. 627–644.
[13] C.A. Wheaton, P.G. Hayes, B.J. Ireland, Dalton Trans. (2009) 4832–4846.
[14] V. Naseri, R.J. Less, R.E. Mulvey, M. McPartlin, D.S. Wright, Chem. Comm. 46 (2010) 5000–5002.
[15] D.J. Mindiola, Acc. Chem. Res. 39 (2006) 813–821.
[16] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031–3065.
[17] J.M. Klerks, J.T.B.H. Jastrzebski, G. van Koten, K. Vrieze, J. Organomet. Chem. 224 (1982) 107–119.
[18] G. van Koten, K. Vrieze, Recueil Des Travaux Chimiques Des Pays-Bas 100 (1981) 129–142.
[19] G. van Koten, K. Vrieze, Adv. Organomet. Chem. 21 (1982) 151–239.
[20] K. Vrieze, G. van Koten, Inorg. Chim. Acta 100 (1985) 79–96.
[21] E. Wissing, K. Vangorp, J. Boersma, G. van Koten, Inorg. Chim. Acta 220 (1994) 55–61.
[22] R. Eberhardt, M. Allmendinger, G.A. Luinstra, B. Rieger, Organometallics 22 (2002) 211–214.
[23] J.G. Noltes, J.W.G. van den Hurk, J. Organomet. Chem. 1 (1964) 377–383.
[24] M. Westerhausen, T. Bollwein, A. Pfitzner, T. Nilges, H.-J. Deiseroth, Inorg. Chim. Acta 312 (2001) 239–244.
[25] M. Westerhausen, A.N. Kneifel, A. Kalisch, Angew. Chem. Int. Ed. 44 (2005) 96–98.
[26] T. Hascall, K. Ruhlandt-Senge, P.P. Power, Angew. Chem. Int. Ed. Eng. 33 (1994) 356–357.
[27] A.D. Barton, L. Young, J. Am. Chem. Soc. 65 (1943) 294–295.
[28] J.E. Parks, R.H. Holm, Inorg. Chem. 7 (1968) 1408–1416.
[29] H.A. Zhong, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 124 (2002) 1378–1399.
[30] G.M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr. 64 (2008) 112–122.