Single-Site *β*-Diiminate Zinc Catalysts for the Alternating Copolymerization of CO_2 and Epoxides: Catalyst Synthesis and Unprecedented Polymerization Activity

Ming Cheng, David R. Moore, Joseph J. Reczek, Bradley M. Chamberlain, Emil B. Lobkovsky, and Geoffrey W. Coates*

Contribution from the Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received November 1, 2000. Revised Manuscript Received June 8, 2001

Abstract: Synthetic routes to zinc *β*-diiminate complexes are reported. The synthesis of 11 *β*-diimine [(BDI)-H] ligands, with varying N-aryl substituents and bridging structures, is described. These ligands are converted to (BDI)ZnX complexes (X = OAc, Et, $N(SiMe_3)_2$, Br, Cl, OH, OMe, O^iPr). X-ray structural data revealed that all zinc complexes examined exist as *μ*-X-bridged dimers in the solid state, with the exception of the zinc ethyl and amido complexes which were monomeric. Complexes of the form (BDI)ZnOR (R = alkyl, acyl) and $(BDI)ZnN(SiMe_3)_2$ are highly active catalysts for the alternating copolymerization of epoxides and CO_2. Copolymerizations of cyclohexene oxide (CHO) and CO_2 with (BDI-**1**)ZnX [(BDI-**1**) = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)imino)-2-pentene)] and (BDI-**2**)ZnX [(BDI-**2**) = 2-((2,6-diethylphenyl)-amido)-4-((2,6-diethylphenyl)imino)-2-pentene)], where X = OAc, Et, $N(SiMe_3)_2$, Br, Cl, OH, OMe, O^iPr, were attempted at 50 °C and 100 psi CO_2. Complexes with X = OAc, $N(SiMe_3)_2$, OMe, O^iPr all produced polycarbonate by the alternated insertion of CHO and CO_2 with similar catalytic activities, comparable molecular weights, and narrow molecular weight distributions (MWD ∼ 1.1), indicating the copolymerizations are living. Furthermore, ligand effects were shown to dramatically influence the polymerization activity as minor steric changes accelerated or terminated the polymerization activity.

Introduction

Over the past two decades, a significant amount of research has been directed toward the development of homogeneous, single-site polymerization catalysts. These discrete compounds have the general formula L_nMR, where L_n is an organic ligand set that remains bound to and thus modifies the reactivity of the active metal center (M) throughout the entire chemical reaction, and R is the polymer or initiating group.[1] By carefully tailoring the coordination environment of the metal center, single-site catalysts are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, and the stereochemistry of a polymer in a way that is often impossible using ordinary heterogeneous catalysts. Perhaps most importantly, these defined molecular-based systems allow detailed structural and mechanistic studies to be carried out. Thus, through empirical experiments and theoretical studies, scientists can rapidly evolve new and improved generations of catalysts.

We have recently initiated a program directed toward the synthesis of polymers from renewable resources. Two specific goals of our research are the development of single-site catalysts for (1) the polymerization of lactide and *β*-butyrolactone[2−18] and (2) the copolymerization of CO_2 and epoxides.[8,19−31] The generally accepted mechanisms of these polymerizations are shown in Scheme 1. Metal alkoxides are proposed to be common

---

(1) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252.

(2) For reviews on lactone polymerization, see: (a) Duda, A.; Penczek, S. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; ACS Symposium Series 764; American Chemical Society: Washington, DC, 2000; pp 160−198. (b) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992. (c) Loefgren, A.; Albertsson, A.; Dubois, P.; Jerome, R. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1995**, *C35*, 379−418.

(3) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583−11584.

(4) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229−3238.

(5) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072−4073.

(6) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4686−4692.

(7) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552−1553.

(8) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39−48.

(9) Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2861−2871.

(10) Spassky, N.; Dumas, P.; Le Borgne, A.; Momtaz, A.; Sepulchre, M. *Bull. Soc. Chim. Fr.* **1994**, *131*, 504−514.

(11) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627−2637.

(12) Chisholm, M. H.; Eilerts, N. W. *Chem. Commun.* **1996**, 853−854.

(13) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845−11854.

(14) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53−101.

(15) Beckerle, K.; Hultzsch, K. C.; Okuda, J. *Macromol. Chem. Phys.* **1999**, *200*, 1702−1707.

(16) Chamberlain, B. M.; Sun, Y. P.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G.; Pink, R.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400−2402.

(17) Chamberlain, B. M.; Jazdzewski, B. A.; Pink, R.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2000**, *33*, 3970−3977.

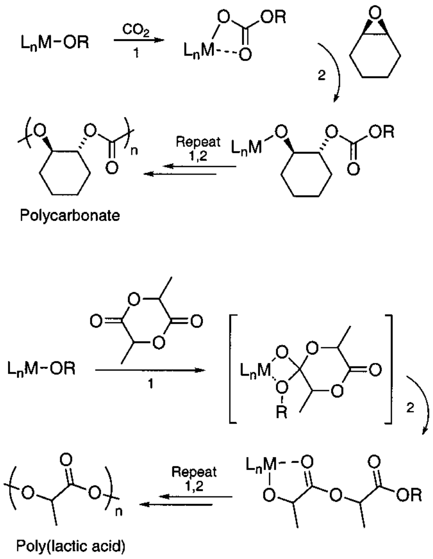
(18) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923−927.

(19) For reviews on the copolymerization of CO_2 with epoxides, see: (a) Super, M.; Beckman, E. J. *Macromol. Symp.* **1998**, *127*, 89−108. (b) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

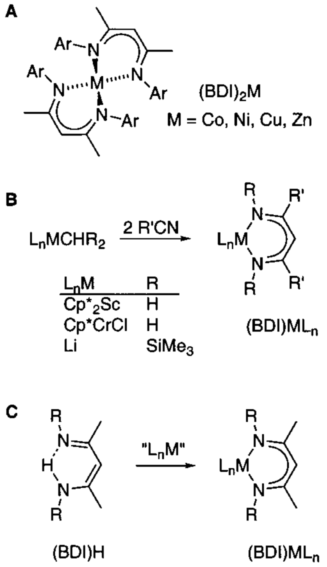
(20) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019.

10.1021/ja003850n CCC: $20.00

Scheme 1. Metal Alkoxides and Carbonates as Catalytic Intermediates in the Synthesis of Aliphatic Polycarbonates and Poly(lactic acid)s



Scheme 2. *β*-Diiminate Complexes



catalytic intermediates to both mechanisms, while metal carbonates are additional intermediates in epoxide/CO_2 copolymerization. Assuming that metal carboxylates would mimic the reactivity of the potentially unstable metal carbonates, we commenced the design and synthesis of well-defined complexes of the form L_nMOR (R = alkyl, acyl). Since zinc compounds exhibit high activities for both lactone polymerizations[3,4,32−37] and CO_2/epoxide reactions,[23−30] we decided to initially investigate the synthesis and application of complexes of the form L_nZnOR. We reasoned the ideal ligands for such complexes would be synthesized easily from readily available starting materials, and systematic ligand variation would allow the investigation of both steric and electronic parameters on the polymerization reaction. Due to the 2+ oxidation state of the metal center, we decided the ligands must be uninegative to accommodate the propagating alkoxide or carbonate. Finally, an η^2-chelating ligand was sought which we anticipated would provide a sterically accessible active site yet confer permanence of the organic surroundings of the metal center. Thus, we centered our research on the synthesis of complexes with *β*-diiminate (BDI) ligands (Scheme 2). Despite several applications of these ligands for the synthesis of $(BDI)_2M$ complexes (M = Co, Ni, Cu, Zn) in the late 1960s (Scheme 2a),[38−40] the ligands were rarely employed in inorganic synthesis[41] until the mid-1980s, when reaction of nitriles with metal alkyls was discovered to form *β*-diiminate ligated complexes in situ (Scheme 2b).[42−47] However, since the mid-1990s a rapidly growing number of papers have been published concerning the formation of *β*-diiminate complexes using preformed BDI ligands (Scheme 2c). Although the vast majority of these papers have emphasized structural aspects of the inorganic chemistry,[48] several have reported the catalytic behavior of these *β*-diiminate complexes in a range of reactions.[49] We recently reported a series of *β*-diiminate complexes for the polymerization of lactide.[4] In this article, we describe the synthesis of a more diverse set of *β*-diiminate zinc complexes and their corresponding catalytic activities for the alternating copolymerization of cyclohexene oxide and carbon dioxide. The zinc complexes reported herein exhibit unprecedented activity yet controlled behavior for the polymerization of cyclohexene oxide (CHO) and CO_2.[20]

---

(21) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007–2008.

(22) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725–727.

(23) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorg. Chem.* **2000**, *39*, 1578–1585.

(24) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577–7579.

(25) Darensbourg, D. J.; Niezgoda, S. A.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 4690–4698.

(26) Darensbourg, D. J.; Zimmer, M. S. *Macromolecules* **1999**, *32*, 2137–2140.

(27) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107–116.

(28) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487–12496.

(29) Super, M. S.; Berluche, E.; Costello, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 368–372.

(30) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009.

(31) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature* **2000**, *405*, 165–168.

(32) Watanabe, Y.; Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1992**, *25*, 1396–1400.

(33) Barakat, I.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *24*, 6542–6545.

(34) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Polym. Bull.* **1991**, *26*, 71–77.

(35) Noltes, J. G.; Verbeek, F.; Overmars, H. G.; Boersma, J. *J. Organomet. Chem.* **1970**, *24*, 257–267.

(36) Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1998**, *199*, 1747–1752.

(37) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Int.* **1998**, *46*, 177–182.

(38) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408–1416.

(39) McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903–1912.

(40) Honeybourne, C. L.; Webb, G. A. *Chem. Commun.* **1968**, 739–740.

(41) For examples, see: (a) Attanasio, D.; Tomlinson, A. A. G.; Alagna, L. *J. Chem. Soc., Chem. Commun.* **1977**, 618–619. (b) Nishida, Y.; Oishi, N.; Kida, S. *Inorg. Chim. Acta* **1979**, *32*, 7–10. (c) Healy, P. C.; Bendall, M. R.; Doddrell, D. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 727–735.

(42) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443–450.

(43) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868–5870.

(44) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570–2577.

(45) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *Chem. Commun.* **1994**, 2637–2638.

(46) Hitchcock, P. B.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Sablong, R.; Tian, S. *J. Chem. Soc., Dalton Trans.* **2000**, 2301–2312.

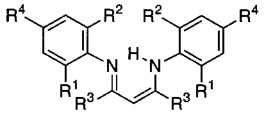
(47) For an example of *β*-diiminate synthesis by the reaction of isonitriles with lithium alkyls, see: Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Chem. Commun.* **1998**, 201–202.

Results and Discussion

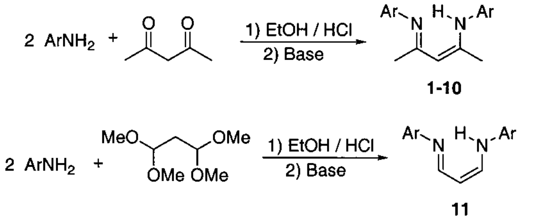
Ligand Synthesis. One of the significant advantages of the β-diiminate ligand design is that the effects of electronic and steric modifications on catalysis can be readily probed by systematic ligand variation. Shown in Scheme 3 are the ligands synthesized in this study. The β-diimines are readily synthesized by refluxing 2 equiv of the desired aniline with 1 equiv of 2,4-pentanedione in acidic ethanol (Scheme 3). Following neutralization, the crystalline ligands are obtained in yields typically approaching 80%. Ligand (BDI-**11**)H, an analogue of (BDI-**1**)H lacking α-methyl substituents, was synthesized by refluxing 2 equiv of the desired aniline with 1 equiv of malonaldehyde bis(dimethyl acetal) in acidic ethanol (Scheme 3).[40]

Synthesis and Structure of Zinc Acetate Complexes. Due to the structural similarity of acetate and carbonate groups, and the presumed mechanistic relevance of the latter as propagating groups in epoxide/CO_2 polymerizations, we have investigated the synthesis of β-diiminate zinc acetate complexes. Deprotonation of (BDI-**1**)H with *n*-BuLi and reaction with zinc acetate gave (BDI-**1**)ZnOAc in 63% isolated yield after removal of LiOAc via filtration and subsequent recrystallization (Scheme 4). Using this procedure, (BDI-**2**)ZnOAc, (BDI-**3**)ZnOAc, and (BDI-**10**)ZnOAc were also synthesized. As an alternate route, the reaction of (BDI)ZnCl with AgOAc was investigated. Deprotonation of (BDI-**1**)H with *n*-BuLi and reaction with zinc chloride or bromide produced (BDI-**1**)ZnX (X = Cl, Br) in quantitative yield after removal of LiX via filtration (Scheme 4). Attempts to convert (BDI-**1**)ZnCl to the acetate complex using AgOAc produced a mixture of unidentified products. One final route that yields β-diiminate zinc acetate complexes is the reaction of β-diiminate zinc amido complexes with acetic acid. (BDI-**1**)H and (BDI-**2**)H each react with $Zn(N(SiMe_3)_2)_2$ to give the corresponding $(BDI)ZnN(SiMe_3)_2$ complexes in quantitative yield. Further reaction of (BDI-**1**)$ZnN(SiMe_3)_2$ with 1 equiv of glacial acetic acid yields (BDI-**1**)ZnOAc in 34% isolated yield following crystallization.

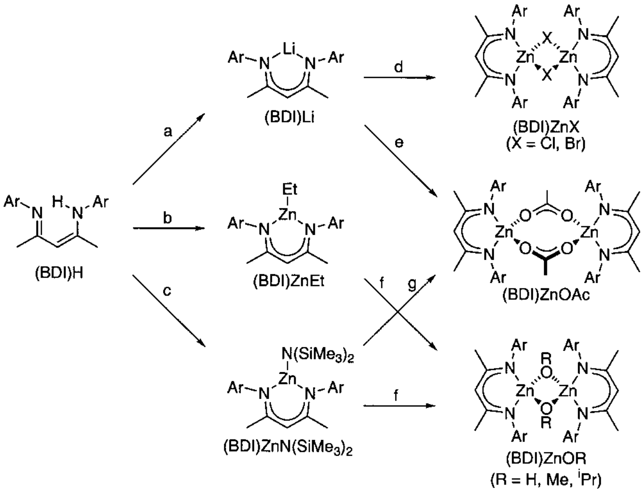
Scheme 3. Synthesis of β-diimine Ligands



Ligand	R^1	R^2	R^3	R^4
(BDI-**1**)H	^{i}Pr	^{i}Pr	Me	H
(BDI-**2**)H	Et	Et	Me	H
(BDI-**3**)H	^{n}Pr	^{n}Pr	Me	H
(BDI-**4**)H	Me	Me	Me	H
(BDI-**5**)H	^{i}Pr	Et	Me	H
(BDI-**6**)H	^{i}Pr	^{n}Pr	Me	H
(BDI-**7**)H	^{i}Pr	Me	Me	H
(BDI-**8**)H	^{i}Pr	H	Me	H
(BDI-**9**)H	Et	^{n}Pr	Me	H
(BDI-**10**)H	Me	Me	Me	Me
(BDI-**11**)H	^{i}Pr	^{i}Pr	H	H



Scheme 4. Synthesis of β-diiminate Zinc Complexes[a]



[a] Conditions: (a) *n*-BuLi; (b) $ZnEt_2$; (c) $Zn(N(SiMe_3)_2)_2$; (d) ZnX_2; (e) $Zn(OAc)_2$; (f) ROH; (g) HOAc).

We have previously reported the molecular structure of (BDI-**1**)ZnOAc which was determined using single-crystal X-ray diffraction.[20] The complex exists as the *syn*−*syn* acetate-bridged dimer in the solid state, with a Zn−Zn separation of 4.24 Å. The six-membered chelate is slightly puckered; the distance of the Zn center from the plane defined by the nitrogen atoms and methine carbon of the chelate is 0.46 Å. The molecular structure of $[(BDI\text{-}\mathbf{2})Zn(\mu\text{-}OAc)]_2$ is shown in Figure 1. In contrast to the *syn*−*syn* acetate geometry of $[(BDI\text{-}\mathbf{1})Zn(\mu\text{-}OAc)]_2$, the bridge is intermediate between *syn*−*syn* and *anti*−*syn* geom-

---

(48) For some recent reports concerning β-diiminate ligated complexes, see the following references. Aluminum: (a) Qian, B. X.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070−3076. (b) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384−9385. (c) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673−8674. (d) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705−706. Boron: (e) Qian, B. X.; Baek, S. W.; Smith, M. R. *Polyhedron* **1999**, *18*, 2405−2414. Barium: (f) Clegg, W.; Coles, S. J.; Cope, E. K.; Mair, F. S. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 796−798. Copper: (g) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270−7271. (h) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 6331−6332. Magnesium: (i) Caro, C. F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 1433−1434. (j) Gibson, V. C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 7120−7121. (k) Bailey, P. J.; Dick, C. M. E.; Fabre, S.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **2000**, *10*, 1655−1661. Rhodium: (l) Budzelaar, P. H. M.; de Gelder, R.; Gal, A. W. *Organometallics* **1998**, *17*, 4121−4123. Samarium and gadolinium: (m) Drees, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 814−818. (n) Drees, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 948−952. Tin: (o) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699−1700. Group IV metals (Ti, Zr, Hf): (p) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *Chem. Commun.* **1994**, 2637−2638. (q) Rahim, M.; Taylor, N. J.; Xin, S. X.; Collins, S. *Organometallics* **1998**, *17*, 1315−1323. (r) Qian, B. X.; Scanlon, W. J.; Smith, M. R.; Motry, D. H. *Organometallics* **1999**, *18*, 1693−1698. (s) Kakaliou, L.; Scanlon, W. J.; Qian, B. X.; Baek, S. W.; Smith, M. R.; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964−5977. Scandium: (t) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947−2949. Uranium: (u) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *J. Organomet. Chem.* **1995**, *488*, 241−248. Ytterbium: (v) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *Chem. Commun.* **1994**, 2691−2692.

(49) For some recent reports concerning the application of β-diiminate ligated complexes in catalysis, see the following references. Ethylene polymerization by zirconium complexes: (a) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203-217. Ethylene polymerization by nickel and palladium complexes: (b) Feldman, J.; McLain, S. J.; Parthasaranthy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516. Ethylene polymerization and ethylene/propylene copolymerization by titanium, chromium, and vanadium complexes: (c) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543. Ethylene polymerization by chromium complexes: (d) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651−1652. Propylene polymerization by titanium complexes: (e) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485−1494. Olefin hydrogenation by rhodium complexes: (f) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753−769. Ethylene polymerization by zirconium complexes: (g) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161−2169. (h) Jin, X.; Novak, B. M. *Macromolecules* **2000**, *33*, 6205−6207.

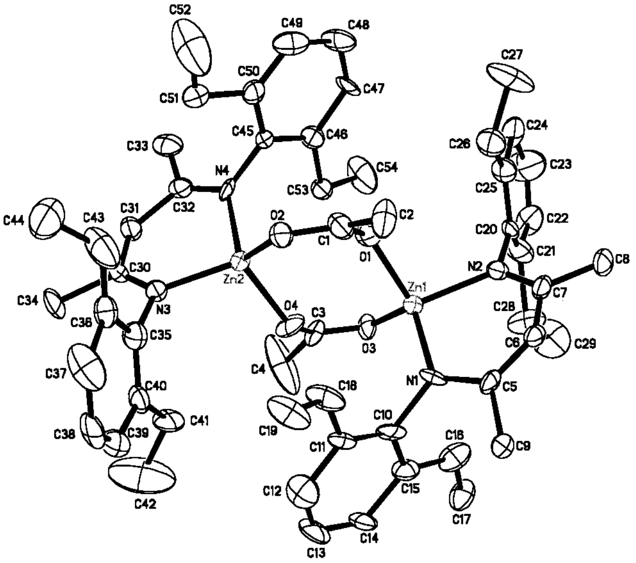


Figure 1. ORTEP drawing of [(BDI-**2**)ZnOAc]$_2$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)−N(1) 1.933(14), Zn(1)−N(2), 2.013(15), Zn(1)−O(1) 1.972(13), Zn(1)−O(3) 1.976(12), C(3)−O(3) 1.22(2), C(1)−O(1) 1.30(3), C(3)−O(4) 1.19(2), N(1)−Zn(1)−N(2) 98.0(6), O(1)−Zn(1)−O(3) 105.2(5), N(1)−Zn(1)−O(1) 119.7(6), N(2)−Zn(1)−O(3) 121.9(6), Zn(1)−O(1)−C(1) 131.3(13), O(3)−C(3)−O(4) 122.5(15).

etries, with a torsional angle for O(2)−C(1)−O(1)−Zn(1) of −95.7°. The complex exhibits a significantly shorter Zn−Zn separation of 3.94 Å, presumably due to the reduced steric constraints of the ligand. The six-membered chelate is again slightly puckered; the distance of Zn(1) from the plane defined by N(1), N(2), and C(6) of the chelate is 0.47 Å. The molecular structures of complexes [(BDI-**3**)Zn(μ-OAc)]$_2$ and [(BDI-**10**)-Zn(μ-OAc)]$_2$ are nearly isostructural with that of [(BDI-**2**)Zn-(μ-OAc)]$_2$. Whereas [(BDI-**1**)Zn(μ-OAc)]$_2$ exists in solution as both a monomer and a dimer in equilibrium (benzene-d_6, 20 °C, 1×10^{-2} M), [(BDI-**2**)Zn(μ-OAc)]$_2$ and [(BDI-**10**)Zn(μ-OAc)]$_2$ exist solely as the dimer under the same conditions.[20] The molecular structure of (BDI-**1**)ZnN(SiMe$_3$)$_2$ has been determined by X-ray diffraction and is shown in Figure 2. The structure reveals that (BDI-**1**)ZnN(SiMe$_3$)$_2$ is a rare example of a neutral, monometallic, nonorganometallic three-coordinate zinc complex.[50] Although the zinc center exhibits a distorted trigonal planar geometry, the ZnN$_3$ core atoms are highly coplanar (sum of angles = 359.74°); the Zn atom is displaced only 0.06 Å from the plane defined by N(1), N(2), and N(3). The six-membered chelate is again slightly puckered; the distance of Zn(1) from the plane defined by N(1), N(2), and C(3) of the chelate is 0.35 Å. Due to steric repulsions, the planes of the phenyl substituents and the bis(trimethylsilyl)amido group are approximately perpendicular to the plane defined by N(1)−N(2)−N(3).

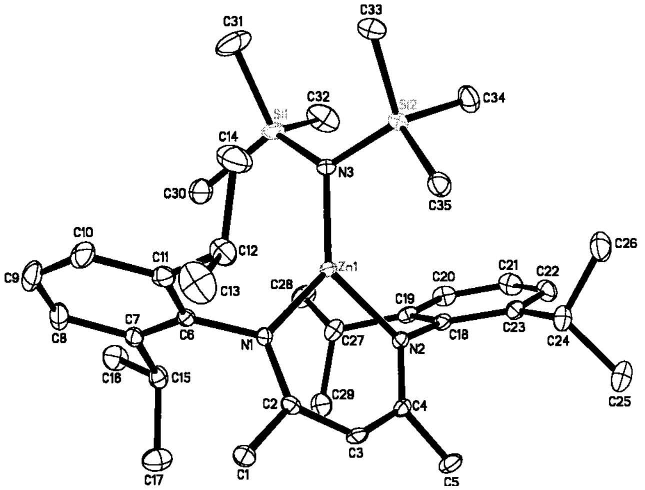
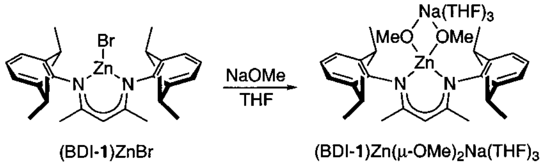


Figure 2. ORTEP drawing of (BDI-**1**)ZnN(SiMe$_3$)$_2$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond distances (Å) and angles (deg): Zn(1)−N(1) 1.949(2), Zn(1)−N(2) 1.986(2), Zn(1)−N(3) 1.896(2), N(1)−Zn(1)−N(2) 98.11(7), N(1)−Zn(1)−N(3) 131.59(7), N(2)−Zn(1)−N(3) 130.04(8), Zn(1)−N(1)−C(6)−C(7) 89.8(2), Zn(1)−N(2)−C(18)−C(23) 110.2(2), N(1)−Zn(1)−N(3)−Si(2) 108.6(1).

Synthesis and Structure of Zinc Alkoxide Complexes. Since metal alkoxides are common catalytic intermediates in both lactone polymerization and epoxide/CO$_2$ polymerization, we have investigated the synthesis of a wide array of β-diiminate zinc alkoxide complexes of the form (BDI)ZnOR. We first attempted a metathesis reaction between NaOMe (3 equiv) and (BDI-**1**)ZnBr. After the THF solution was heated to 50 °C overnight, the reaction mixture was filtered, and an orange, crystalline material was recovered. X-ray analysis of a crystal of this compound revealed that the complex exists as a μ-methoxide-bridged heterobimetallic Na/Zn structure in the solid state (eq 1), although the crystal quality defied acceptable refinement due to partial loss of THF from the lattice. Attempts to form the zinc alkoxide without bound sodium alkoxide by adding only 1 equiv of the NaOMe failed due to low conversion of the starting (BDI)ZnBr derivative. Therefore, we pursued an alternate route. Diethyl zinc reacts with β-diimine ligands in quantitative yield to produce complexes of the formula (BDI)-ZnEt (Scheme 4). Reaction of (BDI)ZnEt with MeOH yields the corresponding (BDI)ZnOMe complexes in high yield;[51] the complexes are obtained in moderate isolated yields (38−72%) following crystallization from saturated solutions (typically toluene) at low temperature (Scheme 4). We have synthesized the methoxide compounds from (BDI)ZnEt complexes ligated by **1**−**5**, **7**, and **11**. We did not attempt the synthesis using (BDI-**10**)ZnEt due to its structural similarity to (BDI-**4**)ZnEt. We could not obtain the corresponding methoxide complex from (BDI-**8**)ZnEt. Due to the lack of steric bulk of the ligand, the product obtained is a bis-ligated complex (BDI-**8**)$_2$Zn (eq 2).[52] Shown in Figure 3 is the molecular structure of (BDI-**8**)$_2$Zn.



(1)

---

[50] For examples of such complexes, which are all Lewis-base coordinated bis(aryl chalcogenolato) complexes see: (a) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorg. Chem.* **1998**, *37*, 2852−2853. (b) Chinn, M. S.; Chen, J. Z. *Inorg. Chem.* **1995**, *34*, 6080−6084. (c) Ellison, J. J.; Ruhlandt-Senge, K.; Hope, H. H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 49−54. (d) Bochmann, M.; Bwembya, G. C.; Grinter, R.; Powell, A. K.; Webb, K. J.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. A. *Inorg. Chem.* **1994**, *33*, 2290−2296. (e) Labahn, D.; Bohnen, F. M.; Herbstirmer, R.; Pohl, E.; Stalke, D.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 41−47. (f) Power, P. P.; Shoner, S. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1403−1404. For an exception, see: (g) Pandey, S. K.; Steiner, A.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 5444−5446.

[51] For a recent example where a zinc alkyl complex is reacted with alcohol to form a zinc alkoxide, see: Abufarag, A.; Vahrenkamp, H. *Inorg. Chem.* **1995**, *34*, 3279−3284.

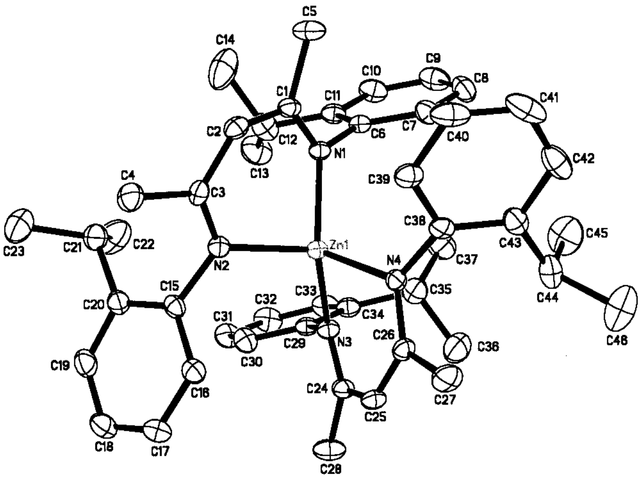
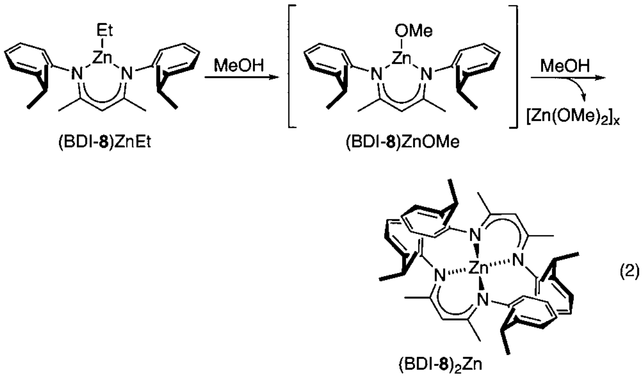


Figure 3. ORTEP drawing of (BDI-**8**)$_2$Zn (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)−N(1) 1.988(3), Zn(1)−N(2) 2.029(3), Zn(1)−N(3) 1.989(3), Zn(1)−N(4) 2.023(3), N(1)−Zn(1)−N(2) 92.87(13), N(1)−Zn(1)−N(3) 135.74(13), N(1)−Zn(1)−N(4) 110.44(12), N(2)−Zn(1)−N(3) 109.80(13), N(2)−Zn(1)−N(4) 117.37(13), N(3)−Zn(1)−N(4) 92.57(13).

The six-membered chelate is significantly puckered; the distance of the distorted tetrahedral Zn atom from the plane defined by N(1), N(2), and C(2) of the chelate is 0.82 Å. We were concerned that such a bis-ligated species might form during a polymerization reaction by the rearrangement of two complexes of the form (BDI)ZnOP to (BDI)$_2$Zn and Zn(OP)$_2$ (P = polymer chain). Therefore, we attempted the thermal degradation of (BDI)ZnOMe complexes. To date, we have not observed the redistribution of such complexes without the addition of excess protic compounds such as alcohols. Due to the general utility of complexes employing BDI-**2** in a range of polymerization reactions, we investigated the synthesis of (BDI-**2**)$_2$Zn. Reaction of (BDI-**2**)Li with 0.5 equiv of Zn(OAc)$_2$ yields a crystalline material that exhibits extremely broad ^{1}H NMR resonances at ambient temperature. X-ray analysis revealed (BDI-**2**)$_2$Zn with a ZnN$_4$ core that is nearly isostructural with (BDI-**8**)$_2$Zn.[53] As anticipated by our molecular modeling studies, we have not been able to synthesize a bis-ligated zinc complex using (BDI-**1**)H.



(2)

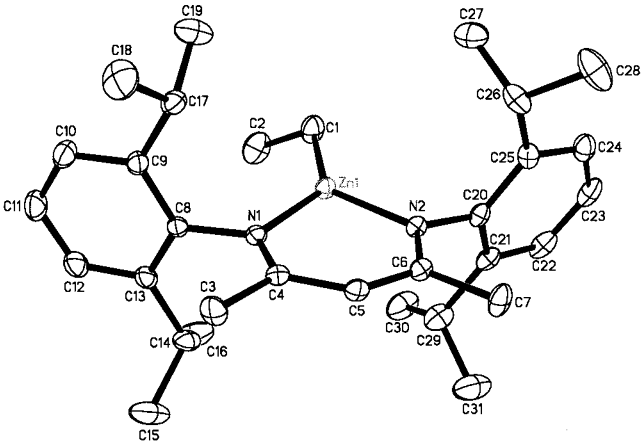


Figure 4. ORTEP drawing of (BDI-**1**)ZnEt (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)−N(1) 1.979(3), Zn(1)−N(2) 1.943(3), Zn(1)−C(1) 1.963(5), N(1)−Zn(1)−N(2) 97.07(12), N(2)−Zn(1)−C(1) 128.99(18), C(1)−Zn(1)−N(1) 133.94(17).

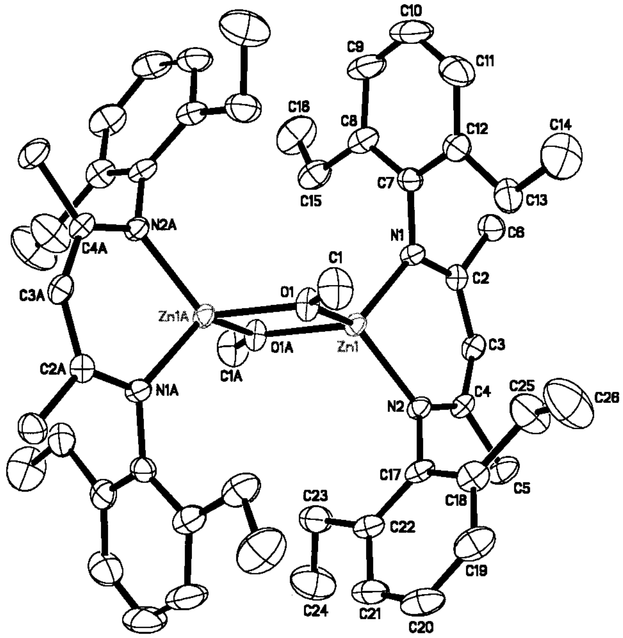


Figure 5. ORTEP drawing of [(BDI-**2**)Zn(μ-OMe)]$_2$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)−N(1) 1.974(3), Zn(1)−N(2) 1.984(2), Zn(1)−O(1) 1.931(2), Zn(1)−O(1A) 1.984(2), N(1)−Zn(1)−N(2) 97.37(11), O(1)−Zn(1)−O(1A) 81.83(9), N(2)−Zn(1)−O(1) 122.07(10), Zn(1)−O(1)−Zn(1A) 98.17(9).

Due to the versatility of (BDI)ZnEt complexes for the synthesis of other complexes, we have determined the molecular structure of (BDI-**1**)ZnEt (Figure 4). In the solid state, the complex is a monomer. The Zn−C distance is 1.96 Å, which is typical of such a bond.[54] The six-membered chelate is essentially planar; the distance of Zn(1) from the plane defined by N(1), N(2), and C(5) of the chelate is 0.13 Å. With the exception of (BDI-**1**)ZnOMe (oil/wax) and (BDI-**3**)ZnOMe (the isopropoxide instead was studied by X-ray analysis, vide infra), we have obtained molecular structures of all methoxide complexes using X-ray diffraction. All of these complexes exist as methoxide-bridged dimers in the solid state, and their core atoms have virtually identical frameworks. The complex [(BDI-**2**)Zn(μ-OMe)]$_2$ is a representative example of this class of compounds (Figure 5). The Zn−Zn separation is 2.96 Å. The six-membered chelate is fairly planar, with a deviation of 0.44 Å from the plane of N(1)−N(2)−C(3). The Zn−O bond lengths of 1.93 and 1.98 Å are within the range expected.[55]

---

(52) Parkin has reported that tris(pyrazolyl)zinc alkyls with less sterically demanding ligands form bis-ligated complexes upon reaction with alcohols. Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288.

(53) See Supporting Information.

(54) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274−288.

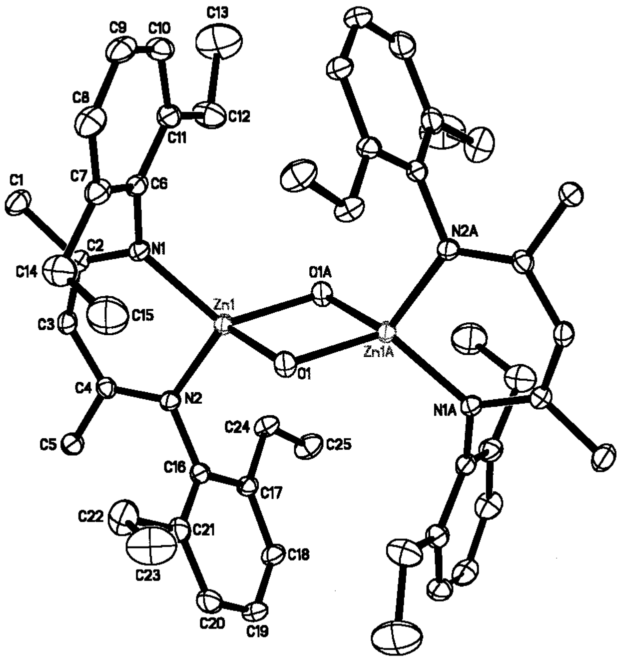


Figure 6. ORTEP drawing of [(BDI-**2**)Zn(μ-OH)]$_2$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)−N(1) 1.9818(15), Zn(1)−N(2) 1.984(2), Zn(1)−O(1) 1.974(2), Zn(1)−O(1A) 1.980(2), N(1)−Zn(1)−N(2) 97.30(6), O(1)−Zn(1)−O(1A) 82.41(8), N(2)−Zn(1)−O(1) 114.18(7), Zn(1)−O(1)−Zn(1A) 97.59(8).

Although these zinc methoxide complexes are excellent polymerization initiators[3,4,20,21] and provide acceptable model compounds for the presumed polymerization intermediates, it is generally accepted that the metal alkoxide that forms during the polymerization of lactide is a secondary alkoxide. In addition, copolymerization of CO$_2$ and cyclohexene or propylene oxides would also be expected to involve a secondary alkoxide. Therefore, we decided to synthesize zinc isopropoxide complexes that would be more suitable mimics of the putative propagating species. Unfortunately, our initial attempt at reacting (BDI-**1**)ZnEt with 2-propanol yielded only a small amount of the desired complex (BDI-**1**)ZnO^{i}Pr. Instead, the alcohol protonated the BDI ligand from the metal rather than the ethyl group. We therefore decided to investigate the reaction of (BDI)ZnN(SiMe$_3$)$_2$ with alcohols to form these model compounds. These amido complexes with ligands **1** and **2** formed the desired isopropoxide complexes in isolated yields of 54 and 67% following crystallization. The molecular structures of (BDI-**1**)ZnO^{i}Pr and (BDI-**2**)ZnO^{i}Pr are virtually isostructural with (BDI-**2**)ZnOMe.[3,53] (BDI-**2**)ZnN(SiMe$_3$)$_2$ also reacts cleanly with water to produce (BDI-**2**)ZnOH in quantitative yield. The molecular structure of (BDI-**2**)ZnOH is shown in Figure 6; it is a hydroxo-bridged dimer in the solid state, with a framework that is essentially the same as that of (BDI-**2**)ZnOMe. The Zn−O bond distances of 1.98 and 1.97 Å are within the range expected for such bonds.[54,56,57] This zinc hydroxide complex provides a potential model compound for enzymes such as carbonic anhydrase or liver alcohol dehydrase.[57−59]

Alternating Copolymerization of Cyclohexene Oxide and Carbon Dioxide. Several zinc complexes have been reported to catalyze the alternating copolymerization of cyclohexene oxide and carbon dioxide, but polymerizations were on the order of days, and the variability of the catalytic precursors was limited.[24,28,29] We have recently reported that under the mild conditions of 50 °C and 100 psi CO$_2$,[20] we have successfully synthesized polycarbonate with carbonate linkages exceeding 95% in only 2 h with (BDI-**1**)ZnOAc. Furthermore, the detailed study of ligand design has provided many avenues of exploration, including the tuning of steric bulk of the ligand, as well as the initiating groups of the complex. It is well documented that ligand sterics influence catalytic activity in many systems.[60−63] From these ligand and complex variations, we have seen remarkable differences in polymerization results, indicating that minor ligand changes heavily influence the polymerization activity.

Table 1. Effect on Initiating Group: (BDI)ZnX Copolymerization of CHO/CO$_2$[a]

complex	TON[b]	TOF[c] (h^{-1})	carbonate linkages (%)[d]	M_n (kg/mol)[e]	M_w/M_n[e]
[(BDI-**1**)ZnOAc]$_2$	494	247	96	31.0	1.11
[(BDI-**1**)ZnOMe]$_2$	449	224	95	19.1	1.07
(BDI-**1**)ZnN(SiMe$_3$)$_2$	438	219	95	21.0	1.09
[(BDI-**1**)ZnO^{i}Pr]$_2$	436	218	94	25.2	1.08
(BDI-**1**)ZnEt	0	0			
[(BDI-**1**)ZnCl]$_2$	0	0			
[(BDI-**1**)ZnBr]$_2$	0	0			
[(BDI-**2**)ZnOAc]$_2$	470	235	96	22.0	1.12
[(BDI-**2**)ZnOMe]$_2$	477	239	96	23.7	1.14
(BDI-**2**)ZnN(SiMe$_3$)$_2$	386	193	98	25.3	1.12
[(BDI-**2**)ZnOH]$_2$	0	0			

[a] All reactions were performed in neat cyclohexene oxide with [monomer]:[Zn] = 1000:1 at 50 °C for 2 h. [b] Mole of CHO consumed per mole of zinc. [c] Mole of CHO consumed per mole of zinc per hour. [d] Calculated by integration of methine resonances in ^{1}H NMR of polymer (CDCl$_3$, 300 MHz). [e] Determined by gel permeation chromatography, calibrated with polystyrene standards in tetrahydrofuran.

In Table 1 we report the copolymerization data of (BDI-**1**)ZnX complexes with several initiating groups, including X = OAc, OMe, O^{i}Pr, N(SiMe$_3$)$_2$, Et, Cl, and Br. The polymerization behaviors of (BDI-**1**)ZnX, where X = OAc, OMe, O^{i}Pr, and N(SiMe$_3$)$_2$, are remarkably similar, suggesting identical propagating species following initiation. The resulting polycarbonates possess greater than 94% carbonate linkages and have narrow molecular weight distributions, consistent with rapid initiation and the lack of chain termination or transcarbonation (a living polymerization). All polymers produced are atactic, as determined by ^{13}C NMR,[21,30] and contain only *trans*-cyclohexane linkages in the main chain,[20,21] consistent with backside attack of the epoxide during enchainment. However, when X = Et, Cl, or Br, no polymerization activity is observed. None of these groups mimic the propagating polymer chain, and due to their lack of reactivity with cyclohexene oxide and CO$_2$, they do not serve as viable initiators. In addition, the polymerizations using (BDI-**2**)ZnX (X = OAc, OMe, and N(SiMe$_3$)$_2$) have been investigated. Polycarbonates with greater than 96% carbonate linkages are achieved with similar rates, number-average molecular weights, and low molecular weight distributions. Finally, the turnover frequencies are again very similar.

---

(55) Melnik, M.; Györyová, K.; Skorsepa, J.; Holloway, C. E. *J. Coord. Chem.* **1995**, *35*, 179−279.

(56) Bergquist, C.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 422−423.

(57) Bergquist, C.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 6322−6323.

(58) Lipscomb, W. N.; Strater, N. *Chem. Rev.* **1996**, *96*, 2375−2433.

(59) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239−2314.

(60) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143−7144.

(61) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049−4050.

(62) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(63) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665.

Table 2. Effect on Ligand: (BDI)ZnOR Copolymerization of CHO/CO_2[a]

complex	time (h)	TON[b]	TOF[c](h^{-1})	g poly/(g Zn•h)	carbonate linkages (%)[d]	M_n (kg/mol)[e]	M_w/M_n[e]
[(BDI-**1**)ZnOAc]$_2$	2	494	247	536	96	31.0	1.11
[(BDI-**1**)ZnOMe]$_2$	2	449	224	486	95	19.1	1.07
[(BDI-**2**)ZnOAc]$_2$	2	470	235	510	96	22.0	1.12
[(BDI-**2**)ZnOMe]$_2$	2	477	239	518	96	23.7	1.14
[(BDI-**3**)ZnOAc]$_2$	24	0	0	0			
[(BDI-**3**)ZnOMe]$_2$	24	0	0	0			
[(BDI-**3**)ZnO^{i}Pr]$_2$	24	0	0	0			
[(BDI-**4**)ZnOMe]$_2$	24	0	0	0			
[(BDI-**5**)ZnOMe]$_2$	2	515	257	558	99	32.1	1.14
(BDI-**6**)ZnN($SiMe_3$)$_2$	2	364	182	396	97	39.4	1.09
[(BDI-**7**)ZnOMe]$_2$	2	418	209	454	94	17.0	1.21
(BDI-**8**)$_2$Zn	24	0	0	0			
[(BDI-**9**)ZnO^{i}Pr]$_2$	5	265	53	115	93	14.8	1.10
[(BDI-**10**)ZnOAc]$_2$	24	0	0	0			
[(BDI-**11**)ZnOMe]$_2$	11	461	42	91	87	19.7	1.21

[a] All reactions were performed in neat cyclohexene oxide with [monomer]:[Zn] = 1000:1 at 50 °C for 2 h. [b] Mole of CHO consumed per mole of zinc. [c] Mole of CHO consumed per mole of zinc per hour. [d] Calculated by integration of methine resonances in ^{1}H NMR of polymer ($CDCl_3$, 300 MHz). [e] Determined by gel-permeation chromatography, calibrated with polystyrene standards in tetrahydrofuran.

However, (BDI-**2**)ZnOH exhibits no catalytic activity in the copolymerization. ^{1}H NMR studies in benzene-d_6 have shown that the β-diiminate ligand is produced when (BDI-**2**)ZnOH is exposed to 100 psi CO_2 in toluene at 50 °C. Presumably, insertion of carbon dioxide results in a carbonic acid intermediate which then undergoes a facile proton exchange to produce ligand and zinc aggregates. It is thereby concluded that the acetate, methoxide, isopropoxide, and bis(trimethylsilyl)amido groups are all adequate initiators for the alternating copolymerization of cyclohexene oxide and carbon dioxide.

A more comprehensive study of ligand effects was undertaken to better understand the geometric requirements of the ligands of these β-diimine complexes. Ligands with varying steric bulk in the ortho positions of the anilines were examined. While (BDI-**1**) and (BDI-**2**) complexes exhibited high activities, [(BDI-**3**)ZnX]$_2$ (X = OAc, OMe, and O^{i}Pr), [(BDI-**4**)ZnOMe]$_2$, and [(BDI-**10**)ZnOAc]$_2$ demonstrated *no polymerization activity* over 1 day at 100 psi CO_2 and 50 °C in neat cyclohexene oxide. It is believed that the dimeric structures of [(BDI-**4**)ZnOMe]$_2$ and [(BDI-**10**)ZnOAc]$_2$ are highly stable and do not equilibrate to the monomeric structures because they lack the steric bulk of BDI-**1** and BDI-**2** which serves to destabilize the dimers. Presumably, these stable dimers are not able to react with monomers via either monometallic or bimetallic transition states. The inability of the (BDI-**3**)ZnOR complexes to polymerize CHO and CO_2 remains a conundrum given their similarity to (BDI-**2**)ZnOR complexes (Table 2). We hypothesize that the additional steric bulk of *n*-propyl groups significantly hinders the approach of monomers to the active site. To eliminate the unlikely possibility of a side reaction involving the *n*-propyl complexes, mixed ligands were synthesized and used in the copolymerization. A 54:46 cis/trans mixture of (BDI-**6**)ZnN($SiMe_3$)$_2$ showed significant activity over the course of 2 h, producing polycarbonate with 97% carbonate linkages, a low molecular weight distribution of 1.09, and a turnover frequency of 182 h^{-1}. Interestingly, the narrow MWD indicates that either the cis and trans isomers, which cannot isomerize on the polymerization time scale, exhibit identical rates, or exchange of polymer chains between these diastereomers occurs on a time scale much more rapid than chain formation. Furthermore, a cis/trans mixture of (BDI-**9**)ZnO^{i}Pr copolymerized CHO and CO_2 in 5 h to make polycarbonate with 93% carbonate linkages, a molecular weight distribution of 1.10, and a turnover frequency of 53 h^{-1}. The existence of steric bulk is paramount in the above complexes. As the substituents proceed from *n*-propyl to ethyl to isopropyl, activity increases.

The optimal ligand geometry occurs with BDI-**5**, which possesses the mixed isopropyl and ethyl ortho N-aryl substituents in the β-diimine ligand. When [(BDI-**5**)ZnOMe]$_2$, crystallized as the μ-methoxide-bridged dimer where the isopropyl substituents adopt a cis geometry,[53] was exposed to copolymerization conditions of 50 °C and 100 psi CO_2 for 2 h, polycarbonate was produced with a low molecular weight distribution of 1.14 and a turnover frequency of 257 h^{-1}. In accordance with the complexes bearing *n*-propyl substituents, a similar result occurs with the isopropyl-substituted β-diiminate zinc complexes. As the steric bulk is diminished, the catalytic activity suffers and eventually disappears. [(BDI-**7**)ZnOMe]$_2$, again crystallized as the cis isomer, is an active catalyst for the polymerization and produces polycarbonate with 97% carbonate linkages in 2 h with a turnover frequency of 209 h^{-1}. With no substituent in one ortho position of the aromatic ring, (BDI-**8**)$_2$Zn exists as a bis-ligate (Figure 3), which possesses no viable initiating group. Consequently, no polymerization activity is observed. We are currently investigating the effects of various other mixed ligand geometries and will report on this in due time.

Steric considerations on the backbone of the β-diiminate zinc complexes also prominently influence the polymerization activity. [(BDI-**11**)ZnOMe]$_2$ polymerizes CHO and CO_2 over the course of 11 h to yield polycarbonate with 87% carbonate linkages, a molecular weight distribution of 1.21, and a turnover frequency of 42 h^{-1}. As evidenced in the olefin polymerization chemistry of Brookhart,[60−64] restricted rotation of the aniline is imperative for facilitating catalytic activity. We hypothesize that entrance of the cyclohexene oxide monomer is hindered by the motion of the aromatic rings.[65]

Enchainment Steps of the Alternating Copolymerization of CHO and CO_2. We are currently investigating the intricate mechanistic details of the alternating copolymerization of cyclohexene oxide and carbon dioxide. NMR studies show that acetate complexes of the form (BDI)ZnOAc reversibly react with cyclohexene oxide to open the strained three-membered epoxide ring to form a zinc alkoxide intermediate. Carbon dioxide subsequently inserts into the zinc−alkoxide bond to

---

(64) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268.

(65) Reetz, M. T.; Haderlein, G.; Angermund, K. *J. Am. Chem. Soc.* **2000**, *122*, 996−997.

make a zinc carbonate species which will continue in the same catalytic cycle to make polycarbonate (Scheme 1). The zinc alkoxide complexes of the form (BDI)ZnOR insert carbon dioxide into the Zn−O bond and consequently react with cyclohexene oxide to continue the catalytic cycle. The (BDI)ZnN$(SiMe_3)_2$ complexes are converted cleanly to [(BDI)ZnOSiMe$_3$]$_2$ species in the presence of CO_2; presumably CO_2 inserts into the Zn−N bond, followed by migration of a $SiMe_3$ group to oxygen and extrusion of trimethylsilylisocyanate.[21,66] The mechanism of polymerization using these complexes is currently under investigation, and more details will be reported soon.

Conclusions

We have developed several synthetic routes to important classes of zinc-based β-diiminate complexes. The zinc alkoxide, acetate, and bis(trimethylsilyl)amide complexes are all excellent catalysts for the copolymerization of CO_2 and epoxides. By varying the ligand geometries of the β-diimines, we are able to tailor the catalytic behavior of the zinc complexes and thereby effect drastic changes in the copolymerization activities. To our knowledge, these complexes exhibit the highest reported activities for this type of polymerization; in addition, they offer unprecedented opportunities for control of molecular weight as well as stereochemistry.[20,21] The well-defined nature of the complexes presents an excellent opportunity to study the mechanism of the polymerization steps in detail, which is the current focus of our research. The zinc alkoxide complexes serve an additional role as a highly promising class of lactone polymerization catalysts. These versatile complexes polymerize (*S*,*S*)-lactide to isotactic PLA, *rac*-lactide to heterotactic PLA, and *meso*-lactide to syndiotactic PLA.[3,4] In addition, these catalysts show unprecedented reaction rates and control the molecular weight of the resultant PLA. Given the easily tailored ligand architecture of the BDI ligand platform, we anticipate that catalysts bearing these ligands will open many new opportunities in polymer synthesis.

Experimental Section

(A) General Procedures. All reactions with air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk line techniques. NMR spectra were recorded on a Bruker AF300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) and a Varian VXR-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer and referenced versus residual solvent shifts. Gel permeation chromatography (GPC) analyses were carried out using a Waters instrument (M510 pump, U6K injector) equipped with Waters UV486 and Milton Roy differential refractive index detectors and four 5-μm PL Gel columns (Polymer Laboratories; 100 Å, 500 Å, 1000 Å, and Mixed C porosities) in series. The GPC columns were eluted with tetrahydrofuran at 45 °C at 1 mL/min and were calibrated using 23 monodisperse polystyrene standards. High-resolution mass spectra were obtained at the Mass Spectrometry Facility at Cornell University; the ionization method is given in parentheses.

Tetrahydrofuran, toluene, C_6D_6, and toluene-d_8 were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride and chloroform were distilled from phosphorus pentoxide under nitrogen. Hexanes and pentane were distilled from calcium hydride under nitrogen. CD_2Cl_2 was stored over 4 Å molecular sieves. All chemicals were purchased from Aldrich except where noted. Carbon dioxide (Matheson Research Purity Grade, 99.995%) was used as received. Cyclohexene oxide (CHO) was distilled from calcium hydride under vacuum following three freeze−pump−thaw cycles and stored in a sealed flask in a drybox.

(B) X-ray Crystallography. Suitable crystals of each sample were attached to a glass fiber with heavy-weight oil and mounted in the Siemens SMART system (Mo Kα, $\lambda = 0.71073$ Å) for data collection at 173(2) K. Initial sets of cell constants for each sample were calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrixes from 248 reflections. In each case, final cell constants were calculated from a set of no less than 5000 strong reflections from the actual data collections. For each sample, a randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω.

Space groups for each sample were determined on the basis of systematic absences and intensity statistics. In each case, successful direct-methods solutions were calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were then performed to locate the remainder of the non-hydrogen atoms. For each sample, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters.

Complete drawings and full details of the X-ray structure determinations, including tables of bond lengths and angles, atomic positional parameters, and final thermal parameters for the complexes, are provided in the Supporting Information.

(C) Synthesis of Ligand Precursors. *N*-Allyl-2-isopropylaniline. Sodium carbonate (17.7 g, 167 mmol) was dissolved in water (120 mL) and combined with 2-isopropylaniline (15.03 g, 111.2 mmol), which was dissolved in $CHCl_3$ (250 mL). This was stirred vigorously, and the mixture was warmed to 40 °C in an oil bath. Allyl bromide (5.38 g, 44.5 mmol) was then added dropwise via syringe over a 5 h period. The mixture was heated for 10 h at 80 °C before separating the organic phase. The organic phase was washed with brine (2 × 50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed in vacuo to leave a light brown oil. The product was purified by flash chromatography on a silica gel column using ether/pentane (1:24) as eluant to produce a light yellow oil (4.34 g, 56% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25 (2H, m, ArH), 6.89 (1H, t, ArH), 6.75 (1H, d, $J = 8.0$ Hz, ArH), 6.11 (1H, m, $CH_2C\mathit{H}{=}CH_2$), 5.35 (2H, m, $CH_2CH{=}C\mathit{H}_2$), 3.92 (3H, m, NH + $C\mathit{H}_2CH{=}CH_2$), 3.00 (1H, septet, $J = 7.0$ Hz, $C\mathit{H}Me_2$), 1.39 (6H, d, $J = 7.0$ Hz, $CH\mathit{Me}_2$).

2-Allyl-6-isopropylaniline. This synthesis was based on a literature preparation.[67] *N*-Allyl-2-isopropylaniline (4.34 g, 24.7 mmol) was dissolved in xylenes (80 mL) and loaded with anhydrous zinc chloride (3.65 g, 27.2 mmol). The suspension was heated at reflux for 6 h under N_2 to effect an aza-Claisen rearrangement. The product was purified by flash chromatography on a silica gel column using ether/pentane (3:17) to afford a light yellow oil (2.93 g, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (1H, d, $J = 7.5$ Hz, ArH), 7.04 (1H, d, $J = 7.0$ Hz, ArH), 6.87 (1H, t, $J = 7.5$ Hz, ArH), 6.07 (1H, m, $CH_2C\mathit{H}{=}CH_2$), 5.23 (2H, m, $CH_2CH{=}C\mathit{H}_2$), 3.82 (2H, b, NH_2), 3.43 (2H, d, $J = 6.0$ Hz, $C\mathit{H}_2CH{=}CH_2$), 3.00 (1H, septet, $J = 7.0$ Hz, $C\mathit{H}Me_2$), 1.37 (6H, d, $J = 7.0$ Hz, $CH\mathit{Me}_2$).

2-Isopropyl-6-*n*-propylaniline. 2-Allyl-6-isopropylaniline (2.93 g, 16.7 mmol) was dissolved in ethanol (20 mL) in a Fischer Porter bottle equipped with a pressure fitting rated to 100 psi and charged with 10% palladium on carbon (0.100 g). The reactor was pressured with 100 psi H_2 and stirred at room temperature, with periodic refilling of H_2, until the pressure remained constant. The reactor contents were filtered over Celite, and the solvent was removed in vacuo to leave a light yellow oil as the desired product in quantitative yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.18 (1H, d, $J = 7.5$ Hz, ArH), 7.07 (1H, d, $J = 7.5$ Hz, ArH), 6.75 (1H, t, $J = 7.5$ Hz, ArH), 3.76 (2H, b, NH_2), 2.94 (1H, septet, $J = 7.0$ Hz, $C\mathit{H}Me_2$), 2.51 (2H, t, $J = 7.5$ Hz, $C\mathit{H}_2CH_2CH_3$), 1.70 (2H, sextet, $J = 7.5$ Hz, $CH_2C\mathit{H}_2CH_3$), 1.30 (6H, d, $J = 7.0$ Hz, $CH\mathit{Me}_2$), 1.00 (3H, t, $J = 7.25$, $CH_2CH_2C\mathit{H}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 141.41, 132.68, 127.27, 126.92, 123.41, 118.67, 34.36, 28.22, 22.83, 22.26, 14.74.

---

[66] Sita, L. R.; Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912−10913.

[67] Arresta, M.; Greco, R. *Met.-Org. Chem.* **1979**, *9*, 377−390.

2-Ethyl-6-*n*-propylaniline. 2-*n*-Propylaniline (9.5 g, 70 mmol) was added to a stainless steel high-pressure reactor equipped with a pressure fitting rated to 2000 psi. Al (−200 mesh) powder (0.206 g, 6.87 mmol) and $AlCl_3$ (0.690 g, 5.18 mmol) were added sequentially, causing the release of gas. The high-pressure reactor was charged with 1000 psi ethylene at 70 °C and heated to 280 °C. The reaction was allowed to proceed for 2 h, and then the reactor was cooled to room temperature. The reaction was quenched with 6 M NaOH and extracted into diethyl ether, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo to leave a brown oil. The product (5.7 g, 50% yield) was distilled at 140−148 °C (350 mTorr). ^1H NMR ($CDCl_3$, 300 MHz): δ 6.9 (3H, m, ArH), 3.66 (2H, b, NH_2), 2.60 (4H, m, CH_2CH_3 + $CH_2CH_2CH_3$), 1.72 (2H, sextet, $CH_2CH_2CH_3$, 1.35 (3H, t, J = 7.0 Hz, CH_2CH_3), 1.08 (3H, t, J = 7.0 Hz, $CH_2CH_2CH_3$).

(D) Ligand Synthesis. β-Diimine ligands **1**−**10** were prepared using the procedure reported by Feldman and co-workers for the synthesis of (BDI-**1**).[49b] The preparation of ligand (BDI-**3**)H was recently reported.[4]

(BDI-2)H. The crude material was recrystallized from ethanol to give colorless block-shape crystals (62% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 12.16 (1H, b, NH), 7.05 (6H, b, ArH), 4.86 (1H, s, β-CH), 2.53 (8H, m, J = 7.5 Hz, CH_2CH_3), 1.68 (6H, s, α-Me), 1.16 (12H, t, J = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.00, 142.41, 137.92, 125.92, 124.73, 93.44, 24.70, 20.63, 14.48. HRMS (EI): *m*/*z* 362.2718 (M^+, $C_{25}H_{34}N_2$ requires 362.2722).

(BDI-4)H. The crude material was recrystallized from methanol at −4 °C to give colorless fine crystals (53% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 12.20 (1H, b, NH), 7.00 (6H, s, ArH), 4.88 (1H, s, β-CH), 2.59 (12H, s, *o*-CH_3), 1.69 (6H, s, α-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.81, 143.76, 132.15, 127.77, 124.28, 93.40, 20.35, 18.40. HRMS (EI): *m*/*z* 306.2096 (M^+, $C_{21}H_{26}N_2$ requires 306.2096).

(BDI-5)H. The crude material was recrystallized from methanol to give colorless block-shape crystals (50% yield). ^{13}C NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although the isomers could not be detected by ^1H NMR. ^1H NMR ($CDCl_3$, 300 MHz): δ 12.15 (1H, b, NH), 7.15 (6H, m, ArH), 4.86 (1H, s, β-CH), 3.12 (2H, m, $CHMe_2$), 2.52 (4H, m, CH_2CH_3), 1.69 (6H, s, α-Me), 1.16 (18H, m, $CHMe_2$ and CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.11, 161.10, 142.55, 142.49, 141.56, 137.81, 137.76, 125.60, 124.91, 123.21, 123.17, 93.32, 28.12, 28.04, 24.79, 24.70, 24.20, 24.12, 23.15, 23.12, 20.67, 14.35, 14.31. HRMS (EI): *m*/*z* 390.3039 (M^+, $C_{27}H_{38}N_2$ requires 390.3035).

(BDI-6)H. Using the preparation for (BDI-**1**)H, it was difficult to obtain pure, crystalline (BDI-**6**)H. Therefore, a modified procedure was used. 2-Isopropyl-6-*n*-propylaniline (1.787 g, 10.08 mmol) and 2,4-pentanedione (0.482 g, 4.81 mmol) were dissolved in absolute ethanol (10 mL). Concentrated hydrochloric acid (0.42 mL, 5.2 mmol) was added via syringe. The solution was refluxed for 67 h, at which point the solvent was removed in vacuo to leave a light brown solid. The solid was redissolved in a minimal amount of ethanol, and diethyl ether was added to precipitate a flocculent white solid. The solid was neutralized with saturated sodium carbonate solution (2 × 50 mL) and extracted into diethyl ether. The organic layer was washed with brine (2 × 50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed in vacuo to leave a light brown oil which crystallized upon standing (0.716 g, 36% yield). ^{13}C NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although the isomers could not be detected by ^1H NMR. ^1H NMR (C_6D_6, 300 MHz): δ 12.37 (1H, b, NH), 7.06 (6H, b, ArH), 4.83 (1H, s, β-CH), 3.27 (2H, m, J = 6.8 Hz, $CHMe_2$), 2.53 (4H, m, $CH_2CH_2CH_3$), 1.78−1.46 (12H, b, $CH_2CH_2CH_3$ + α-Me), 1.22 (6H, t, J = 7.3 Hz, $CH_2CH_2CH_3$), 1.13 (6H, d, J = 7.0 Hz, CH*Me*Me), 0.91 (6H, m, CHMe*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 161.26, 142.85, 142.30, 136.61, 127.09, 127.00, 125.38, 123.81, 123.75, 94.37, 94.31, 34.70, 34.49, 28.49, 28.44, 24.37, 23.62, 23.49, 23.33, 20.73, 14.57. HRMS (EI): *m*/*z* 418.3358 (M^+, $C_{29}H_{42}N_2$ requires 418.3348).

(BDI-7)H. The crude material was recrystallized from methanol to give colorless block-shape crystals (85% yield).^{13}C and ^1H NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although assignment of the shifts was not possible. ^1H NMR ($CDCl_3$, 300 MHz): δ 12.20 (2H, b, NH), 7.12 (2H, m, ArH), 7.04 (4H, m, ArH), 4.88 (1H, s, β-CH), 3.12 (2H, m, $CHMe_2$), 2.16 (3H, s, *o*-Me), 2.15 (3H, s, *o*-Me), 1.71 (3H, s, α-Me), 1.70 (3H, s, α-Me), 1.21 (3H, d, J = 7.0 Hz, CH*Me*Me), 1.20 (3H, d, J = 7.0 Hz, CH*Me*Me), 1.11 (6H, d, J = 7.0 Hz, CHMe*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.05, 161.00, 142.68, 142.45, 142.30, 142.27, 132.10, 132.00, 127.56, 124.74, 124.71, 123.25, 123.20, 93.39, 93.32, 28.22, 28.15, 24.12, 24.00, 23.15, 22.86, 20.54, 20.51, 18.62, 18.49. HRMS (EI): *m*/*z* 362.2720 (M^+, $C_{25}H_{34}N_2$ requires 362.2722).

(BDI-8)H. The crude material was recrystallized from ethanol to give colorless crystals of the ligand as a cis/trans mixture (46% yield).^{13}C NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although the isomers could not be detected by ^1H NMR. ^1H NMR ($CDCl_3$, 300 MHz): δ 12.85 (1H, b, NH), 7.16 (2H, m, ArH), 7.00 (4H, m, ArH), 6.83 (2H, m, ArH), 4.86 (1H, s, β-CH), 3.34 (2H, m, J = 6.5 Hz, $CHMe_2$), 1.75 (6H, s, α-Me), 1.12 (12H, d, J = 6.5 Hz, $CHMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.12, 160.02, 143.48, 142.46, 141.64, 140.77, 125.83, 125.53, 125.16, 124.19, 123.87, 123.06, 123.01, 94.79, 28.30, 28.24, 28.05, 24.23, 23.27, 23.23, 22.98, 20.86, 20.76. HRMS (EI): *m*/*z* 334.2407 (M^+, $C_{23}H_{30}N_2$ requires 334.2409).

(BDI-9)H. 2-Ethyl-6-*n*-propylaniline (2.295 g, 14.06 mmol) and 2,4-pentanedione (0.690 g, 6.90 mmol) were dissolved in absolute ethanol (7 mL). Concentrated hydrochloric acid (0.60 mL, 7.38 mmol) was added via syringe. The solution was refluxed for 91.5 h, at which point the solvent was removed in vacuo to leave a brown waxy solid. Diethyl ether was added to precipitate a white powder. The solid was neutralized with saturated sodium carbonate solution (2 × 50 mL) and extracted into diethyl ether. The organic layer was washed with brine (2 × 50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed in vacuo to leave a light yellow oil (0.582 g, 22% yield). The ^1H NMR of this compound was broad, presumably due to a mixture of cis and trans isomers. ^1H NMR (C_6D_6, 300 MHz): δ 12.32 (1H, b, NH), 7.07 (6H, b, ArH), 4.84 (1H, b, β-CH), 2.86−2.32 (8H, b, CH_2CH_3 + $CH_2CH_2CH_3$), 1.82 (2H, bm, $CH_2CH_2CH_3$), 1.59 (8H, b, $CH_2CH_2CH_3$ + α-Me), 1.19 (6H, b, CH_2CH_3), 0.89 (6H, b, $CH_2CH_2CH_3$). HRMS (EI): *m*/*z* 390.3033 (M^+, $C_{27}H_{38}N_2$ requires 390.3035).

(BDI-10)H. The crude material was recrystallized from methanol to give light brown block-shape crystals (59% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 12.14 (1H, b, NH), 6.85 (4H, s, ArH), 4.85 (1H, s, β-CH), 2.25 (6H, s, *p*-CH_3), 2.11 (12H, s, *o*-CH_3), 1.68 (12H, s, α-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.99, 141.18, 133.53, 131.83, 128.46, 93.32, 20.88, 20.33, 18.33. HRMS (EI): *m*/*z* 334.2407 (M^+, $C_{23}H_{30}N_2$ requires 334.2409).

(BDI-11)H. This ligand was prepared using the standard β-diimine ligand preparation[49b] except that malonaldehyde bis(dimethyl acetal) replaced 2,4-pentadione as the starting material.[40] The desired product was recrystallized from CH_2Cl_2/hexanes to give colorless, fine crystals (45% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 11.62 (1H, b, NH), 7.24 (2H, d, α-CH), 7.12 (6H, b, ArH), 4.83 (1H, t, β-CH), 3.37 (4H, m, J = 7.0 Hz, $CHMe_2$), 1.18 (24H, d, J = 7.0 Hz, $CHMe_2$).$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.67, 143.70, 141.78, 125.22, 123.23, 91.44, 28.25, 23.67. HRMS (EI): *m*/*z* 390.3030 (M^+, $C_{27}H_{38}N_2$ requires 390.3035).

(E) Complex Synthesis. The preparations of (BDI-**3**)$ZnN(SiMe_3)_2$ and (BDI-**3**)ZnO^iPr have been described previously.[4]

General Procedure for [(BDI)Zn(*μ*-OAc)]$_2$. To a solution of (BDI-**1**)H (0.535 g, 1.28 mmol) in THF (10 mL) was slowly added *n*-BuLi (1.6 M in hexane, 0.88 mL, 1.41 mmol) at 0 °C. After being stirred for 5 min at 0 °C, the solution was cannulated into a solution of zinc acetate (0.240 g, 1.41 mmol) in THF (15 mL). After being stirred overnight at room temperature, the suspension was filtered over a frit, and the clear solution was dried in vacuo.

[(BDI-1)Zn(*μ*-OAc)]$_2$. The light yellow solid was recrystallized from methylene chloride at −20 °C to give light yellow block-shape crystals (0.436 g, 63% yield). ^1H NMR (25 mg of complex in 0.55 mL of C_6D_6, 300 MHz, "M", (2.2) denotes monomer, "D", (2.3) denotes dimer): δ 7.11 (18H, M + D, m, ArH), 4.93 (1H, s, β-CH, M), 4.64 (2H, s, β-CH, D), 3.29 (12H, m, $CHMe_2$, M + D), 1.73 (6H, s, OC(O)Me, D), 1.67 (6H, s, α-Me, M), 1.55 (12H, s, α-Me, D), 1.41 (12H, d, J = 6.4 Hz, CH*Me*Me, M), 1.31 (3H, s, OC(O)Me, M), 1.19 (24H, d, J = 7.0 Hz, CH*Me*Me, D), 1.14 (24H, d, J = 7.0 Hz, CHMe*Me*, D), 0.87

(12H, d, J = 6.4 Hz, CHMe*Me*, M). X-ray analysis of the crystals revealed that the complex exists as a μ,η^2-acetate-bridged dimer in the solid state (see Supporting Information).

[(BDI-2)Zn(μ-OAc)]$_2$. The crude material was dissolved in 20 mL of toluene, and the insoluble precipitate was filtered over a frit. The clear solution was concentrated and then recrystallized at −30 °C to give light yellow block-shape crystals (48% yield). ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.05 (6H, m, ArH), 4.66 (1H, s, β-CH), 2.51 (8H, q, J = 7.5 Hz, C*H*$_2$CH$_3$), 1.60 (3H, s, OC(O)C*H*$_3$), 1.53 (6H, s, α-Me), 1.15 (12H, t, J = 7.5 Hz, CH$_2$C*H*$_3$). X-ray analysis of the crystals revealed that the complex exists as a μ,η^2-acetate-bridged dimer in the solid state (see Supporting Information).

[(BDI-3)Zn(μ-OAc)]$_2$. The crude material was dissolved in 20 mL of toluene, and the insoluble precipitate was filtered over a frit and Celite to leave a light bluish-green solution. The solvent was removed in vacuo to leave a waxy solid. This solid was dissolved in hexane and subsequently filtered over a frit and Celite to remove more insoluble precipitate. The clear solution was concentrated and then recrystallized at −20 °C to give clear block-shape crystals (19% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.05 (6H, m, ArH), 4.70 (1H, b, β-CH), 2.55 (4H, m, J = 7.5 Hz, C*H*$_2$CH$_2$CH$_3$), 2.41 (4H, b, C*H*$_2$CH$_2$CH$_3$), 1.58 (17H, m, OC(O)C*H*$_3$) + CH$_2$C*H*$_2$CH$_3$ + α-Me), 1.01 (12H, t, J = 7.5 Hz, CH$_2$CH$_2$C*H*$_3$). X-ray analysis of the crystals revealed that the complex exists as a μ,η^2-acetate-bridged dimer in the solid state (see Supporting Information).

[(BDI-10)Zn(μ-OAc)]$_2$. The crude material was dissolved in 20 mL of methylene chloride, and the insoluble precipitate was filtered over a frit. The clear solution was concentrated to 5 mL and then recrystallized at 5 °C to give light yellow block-shape crystals (46% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.81 (4H, s, ArH), 4.71 (1H, s, β-CH), 2.31 (6H, s, *p*-CH$_3$), 2.09 (12H, s, *o*-CH$_3$), 1.73 (3H, s, OC(O)CH$_3$), 1.53 (6H, s, α-Me). X-ray analysis of the crystals revealed that the complex exists as a μ,η^2-acetate-bridged dimer in the solid state (see Supporting Information).

[(BDI-1)ZnBr]$_2$. To a solution of (BDI-**1**)H (0.487 g, 1.16 mmol) in THF (10 mL) was slowly added *n*-BuLi (1.6 M in hexanes, 0.80 mL, 1.28 mmol) at 0 °C. After being stirred for 5 min at 0 °C, the solution was cannulated to a solution of zinc bromide (0.270 g, 1.18 mmol) in THF (5 mL). After being stirred overnight at room temperature, the clear solution was dried in vacuo to yield a colorless solid. Toluene (20 mL) was added, and the resultant suspension was filtered over a medium frit. Removal of solvent in vacuo gave a quantitative yield (0.654 g) of the desired compound. ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.12 (6H, m, ArH), 4.82 (1H, s, β-CH), 3.71 (4H, m, C*H*Me$_2$), 1.76 (6H, s, α-Me), 1.54 (12H, d, J = 7.0 Hz, CH*Me*Me), 1.25 (12H, d, J = 7.0 Hz, CHMe*Me*).

[(BDI-1)ZnCl]$_2$. To a solution of (BDI-**1**)H (2.42 g, 5.77 mmol) in THF (20 mL) was slowly added *n*-BuLi (1.6M in hexanes, 3.6 mL, 5.76 mmol) at 0 °C. After being stirred for 5 min at 0 °C, the solution was cannulated to a solution of zinc chloride (0.785 g, 5.75 mmol) in THF (5 mL). After being stirred overnight at room temperature, the clear solution was dried in vacuo to yield a colorless solid. Toluene (30 mL) was added, and the resultant suspension was filtered over a pad of Celite on a medium frit. Removal of solvent in vacuo gave a pale yellow solid in 96% yield (2.88 g). ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.08 (6H, m, ArH), 4.84 (1H, s, β-CH), 3.61 (4H, b, J = 7.0 Hz, CHMe$_2$), 1.77 (6H, s, α-Me), 1.52 (12H, d, J = 6.9 Hz, CH*Me*Me), 1.21 (12H, d, J = 7.0 Hz, CHMe*Me*). The compound crystallized from toluene as a microcrystalline white solid. Attempts to obtain a single crystal for X-ray structural studies were not successful.

(BDI-1)ZnN(SiMe$_3$)$_2$. A solution of (BDI-**1**)H (3.04 g, 7.29 mmol) in toluene (15 mL) was added into zinc bis(trimethylsilyl)amide (3.0 mL, 7.2 mmol) in toluene (5 mL) at room temperature. After being stirred for 6 days at 80 °C, the clear, yellow-green solution was dried in vacuo, giving the desired compound in quantitative yield (4.64 g). The light yellow solid was recrystallized from toluene (10 mL) at −30 °C to give colorless block-shape crystals (3.52 g, 76% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (6H, m, ArH), 4.85 (1H, s, β-CH), 3.24 (4H, m, J = 7.0 Hz, C*H*Me$_2$), 1.66 (6H, s, α-Me), 1.37 (12H, d, J = 7.0 Hz, CH*Me*Me), 1.12 (12H, d, J = 7.0 Hz, CHMe*Me*), −0.01 (18H, s, C*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 169.65, 144.85, 142.23, 126.33, 124.39, 95.73, 28.94, 24.85, 24.67, 24.63, 5.67. X-ray analysis of the crystals revealed that the complex exists as mononuclear species in the solid state (see Supporting Information).

(BDI-2)ZnN(SiMe$_3$)$_2$. A solution of (BDI-**2**)H (0.369 g, 1.02 mmol) in toluene (5 mL) was added to zinc bis(trimethylsilyl)amide (0.42 mL, 1.0 mmol) in toluene (5 mL) at room temperature. After being stirred for 20 h at 80 °C, the clear, yellow solution was dried in vacuo, giving the desired compound in quantitative yield (0.593 g). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.11 (6H, b, ArH), 4.87 (1H, s, β-CH), 2.73 (4H, m, J = 7.5 Hz, C*H*$_2$CH$_3$), 2.60 (4H, m, J = 7.5 Hz, C*H*$_2$CH$_3$), 1.58 (6H, s, α-Me), 1.21 (12H, t, J = 7.5 Hz, CH$_2$C*H*$_3$), −0.03 (18H, s, C*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 169.21, 145.86, 136.99, 125.99, 125.85, 95.62, 24.79, 23.43, 13.59, 5.17.

(BDI-6)ZnN(SiMe$_3$)$_2$. A solution of (BDI-**6**)H (0.349 g, 0.834 mmol) in toluene (5 mL) was added to zinc bis(trimethylsilyl)amide (0.337 mL, 0.835 mmol) in toluene (5 mL) at room temperature. After being stirred for 70.5 h at 90 °C, the clear, yellow solution was dried in vacuo, giving the desired compound in quantitative yield (0.593 g). The product was crystallized from hexanes at −20 °C. The ^{1}H NMR showed a 54:46 ratio of the cis:trans products, although only the amido shifts could be assigned. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.11 (12H, b, ArH), 4.91 (1H, s, β-CH), 4.84 (1H, s, β-CH), 3.39 (2H, m, J = 6.9 Hz, C*H*Me$_2$), 3.20 (2H, m, J = 6.9 Hz, C*H*Me$_2$), 2.83−2.32 (8H, m, C*H*$_2$CH$_2$CH$_3$), 1.81−1.50 (20H, b, CH$_2$C*H*$_2$CH$_3$ + α-Me), 1.44 (6H, d, J = 6.8 Hz, CH*Me*Me), 1.32 (6H, d, J = 6.9 Hz, CHMe*Me*), 1.12 (12H, m, CH*Me*$_2$), 0.95 (12H, m, CH$_2$CH$_2$C*H*$_3$), 0.10 (9H, s, C*H*$_3$, cis), −0.01 (18H, s, C*H*$_3$, trans), −0.11 (9H, s, C*H*$_3$, cis).

(BDI-9)ZnN(SiMe$_3$)$_2$. A solution of (BDI-**9**)H (0.503 g, 1.29 mmol) in toluene (3 mL) was added to zinc bis(trimethylsilyl)amide (0.515 mL, 1.28 mmol) in toluene (3 mL) at room temperature. After being stirred for 48 h at 90 °C, the clear, yellow solution was dried in vacuo, giving the desired compound in quantitative yield (0.79 g). The oily product could not be crystallized from any common solvents. The ^{1}H NMR showed a 43:57 ratio of the cis:trans products, although only the amido shifts could be assigned. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.11 (6H, b, ArH), 7.03 (6H, b, ArH), 4.87 (2H, b, β-CH), 2.60 (16H, m, C*H*$_2$CH$_2$CH$_3$ + C*H*$_2$CH$_3$), 1.64 (16H, m, CH$_2$C*H*$_2$CH$_3$ + α-Me), 1.21 (16H, m CH$_2$C*H*$_2$CH$_3$ + CH$_2$C*H*$_3$), 0.99 (12H, m, CH$_2$CH$_2$C*H*$_3$), 0.10 (9H, s, C*H*$_3$, cis), −0.01 (18H, s, C*H*$_3$, trans), −0.10 (9H, s, C*H*$_3$, cis).

[(BDI-1)Zn(μ-OAc)]$_2$. To a solution of (BDI-**1**)ZnN(SiMe$_3$)$_2$ (0.467 g, 0.726 mmol) in toluene (10 mL) was added glacial acetic acid (41 μL, 0.72 mmol). After the solution was stirred at 20 °C for 18 h, volatiles were removed in vacuo, and the resultant solid was recrystallized from CH$_2$Cl$_2$ (10 mL), giving 0.132 g of [(BDI-**1**)Zn(μ-OAc)]$_2$ (34% isolated yield). The ^{1}H NMR matched that reported above.

[(BDI-1)Zn(μ-OMe)$_2$Na(THF)$_3$]. A solution of (BDI-**1**)ZnBr (0.653 g, 1.16 mmol) in THF (10 mL) was slowly added to NaOMe (0.266 g, 4.68 mmol) at room temperature. After the solution was stirred at 50 °C overnight, the precipitate was filtered over a frit. The clear solution was concentrated and then recrystallized at −30 °C to afford an orange block-shape solid (0.31 g, 34%). ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.04 (6H, m, ArH), 4.66 (1H, s, β-CH), 3.55 (12H, m, α-CH$_2$ + C*H*Me$_2$), 3.37 (6H, s, OCH$_3$), 1.68 (H, s, α-Me), 1.46 (8H, m, β-CH$_2$), 1.31 (12H, d, J = 7.0 Hz, CH*Me*Me), 1.23 (12H, d, J = 7.0 Hz, CHMe*Me*). X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged structure in the solid state, although the crystal quality defied acceptable refinement.

General Procedure for (BDI)ZnEt. To a solution of diethyl zinc (0.61 mL, 5.95 mmol) in toluene (10 mL) was slowly added (BDI-**1**)H (0.501 g, 1.196 mmol) in toluene (10 mL) at 0 °C. After being stirred overnight at 80 °C, the clear solution was dried in vacuo, giving a quantitative yield of the desired compound as light yellow oil.

(BDI-1)ZnEt. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.07 (6H, m, ArH), 4.98 (1H, s, β-CH), 3.18 (4H, m, C*H*Me$_2$), 1.69 (6H, s, α-Me), 1.25 (12H, d, J = 7.0 Hz, CH*Me*Me), 1.14 (12H, d, J = 7.0 Hz, CHMe*Me*), 0.89 (3H, t, J = 8.0 Hz, CH$_2$C*H*$_3$), 0.24 (2H, q, J = 8.0 Hz, C*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 167.03, 144.67, 141.17, 125.61, 123.46, 95.03, 28.16, 23.88, 23.14, 22.93, 11.74, −1.53. Upon standing for several days in a glovebox at room temperature, large, colorless crystals formed. X-ray analysis of the crystals revealed that the complex exists as a monomer in the solid state (see Supporting Information).

(BDI-2)ZnEt. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.04 (6H, b, ArH), 4.92 (1H, s, β-CH), 2.60 (4H, m, $J = 7.5$ Hz, CH_2CH_3), 2.45 (4H, m, $J = 7.5$ Hz, CH_2CH_3), 1.62 (6H, s, α-Me), 1.16 (12H, t, $J = 7.5$ Hz, CH_2CH_3), 0.95 (3H, t, $J = 8.0$ Hz, CH_2CH_3), 0.25 (2H, q, $J = 8.0$ Hz, CH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 167.00, 146.83, 136.93, 126.74, 125.38, 95.42, 25.19, 22.99, 14.57, 12.12, −1.98.

(BDI-3)ZnEt. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.04 (6H, b, ArH), 4.92 (1H, s, β-CH), 2.65 (4H, m, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 2.45 (4H, m, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 1.68 (14H, m, $CH_2CH_2CH_3$ + α-Me), 1.16 (15H, t, $J = 7.5$ Hz, $CH_2CH_3 + CH_2CH_2CH_3$), 0.26 (2H, q, $J = 8.0$ Hz, CH_2CH_3).

(BDI-4)ZnEt. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.96 (6H, b, ArH), 4.91 (1H, s, β-CH), 2.10 (12H, s, *o*-CH_3), 1.56 (6H, s, α-Me), 0.97 (3H, t, $J = 8.0$ Hz, CH_2CH_3), 0.25 (2H, q, $J = 8.0$ Hz, CH_2CH_3).

(BDI-5)ZnEt. ^{1}H NMR spectroscopic analysis revealed only one set of peaks which we have tentatively assigned to the cis isomer since only the cis isomer of [(BDI-**5**)ZnOMe]$_2$ is formed from (BDI-**5**)ZnEt (vide infra). ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.05 (6H, b, ArH), 4.94 (1H, s, β-CH), 3.16 (2H, m, $CHMe_2$), 2.60 (2H, m, CH_2CH_3), 2.46 (2H, m, CH_2CH_3), 1.66 (6H, s, α-Me), 1.21 (18H, m, $CHMe_2$ + CH_2CH_3), 0.85 (3H, t, $J = 8.0$ Hz, CH_2CH_3), 0.16 (2H, q, $J = 8.0$ Hz, CH_2CH_3).

(BDI-6)ZnEt. ^{1}H NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although assignment of the shifts was not possible.^{1}H NMR (C_6D_6, 300 MHz): δ 7.01−7.14 (12H, m, ArH), 4.94 (1H, s, β-CH), 4.93 (1H, s, β-CH), 3.18 (4H, m, $J = 7.0$ Hz, $CHMe_2$), 2.52 (8H, m, $CH_2CH_2CH_3$), 1.67 (20H, b, α-Me + $CH_2CH_2CH_3$), 1.26 (6H, d, $J = 7.0$ Hz, CHMeMe), 1.24 (6H, d, $J = 7.0$ Hz, CHMeMe), 1.18 (6H, d, $J = 7.0$ Hz, CHMeMe), 1.14 (6H, d, $J = 7.0$ Hz, CHMeMe), 0.95 (18H, m, $CH_2CH_2CH_3 + CH_2CH_3$), 0.24 (4H, q, $J = 8.0$ Hz, CH_2CH_3).

(BDI-7)ZnEt. ^{1}H NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers, although assignment of the shifts was not possible.^{1}H NMR (C_6D_6, 300 MHz): δ 7.07 (12H, m, ArH), 4.95 (1H, s, β-CH), 4.94 (1H, s, β-CH), 3.16 (4H, m, $CHMe_2$), 2.13 (12H, s, *o*-Me), 1.62 (12H, s, α-Me), 1.20 (12H, d, $J = 7.0$ Hz, CHMeMe), 1.14 (12H, d, $J = 7.0$ Hz, CHMeMe), 0.95 (6H, t, $J = 8.0$ Hz, CH_2CH_3), 0.24 (4H, q, $J = 8.0$ Hz, CH_2CH_3).

(BDI-8)ZnEt. ^{1}H NMR spectroscopic analysis revealed an approximately 1:1 mixture of the cis and trans isomers, although assignment of the shifts was not possible. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.17 (4H, m, ArH), 7.00 (8H, m, ArH), 6.78 (4H, m, ArH), 4.95 (1H, s, β-CH), 4.89 (1H, s, β-CH), 3.19 (4H, m, $CHMe_2$), 1.72 (6H, s, α-Me), 1.69 (6H, s, α-Me), 1.19 (12H, m, CHMeMe), 1.11 (12H, m, CHMeMe), 1.02 (3H, m, CH_2CH_3), 0.97 (3H, m, CH_2CH_3), 0.35 (2H, m, CH_2CH_3), 0.28 (2H, m, CH_2CH_3).

(BDI-11)ZnEt. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.19 (2H, d, α-H), 7.12 (6H, b, ArH), 4.81 (1H, t, β-CH), 3.28 (4H, m, $CHMe_2$), 1.22 (12H, d, $J = 7.0$ Hz, CHMeMe), 1.14 (12H, d, $J = 7.0$ Hz, CHMeMe), 1.05 (3H, t, $J = 8.0$ Hz, CH_2CH_3), 0.42 (2H, q, $J = 8.0$ Hz, CH_2CH_3).

General Procedure for [(BDI)Zn(μ-OMe)]$_2$. To a solution of (BDI-**2**)ZnEt (1.35 g, 2.97 mmol, 1 equiv) in toluene (10 mL) was added methanol (0.13 mL, 3.20 mmol, 1.1 equiv) at room temperature. After being stirred for 1 h at room temperature, the clear solution was dried in vacuo. This procedure is used throughout unless otherwise noted.

[(BDI-1)Zn(μ-OMe)]$_2$. Instead of the normal 1.1 equiv of methanol, 5 equiv was added, and the clear solution was dried in vacuo after being stirred for 1 h at room temperature, giving a quantitative yield of the desired compound as a colorless oily solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (6H, m, ArH), 4.87 (1H, s, β-CH), 3.30 (3H, s, OCH_3), 2.97 (4H, m, $CHMe_2$), 1.53 (6H, s, α-Me), 1.20 (12H, d, $J = 6.5$ Hz, CHMeMe), 1.16 (12H, d, $J = 6.5$ Hz, CHMeMe). Despite several attempts, X-ray diffraction quality crystals of this compound were not obtained.

[(BDI-2)Zn(μ-OMe)]$_2$. The crude material was recrystallized from toluene at −30 °C to give colorless block-shape crystals (0.98 g, 72%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.09 (6H, m, ArH), 4.64 (1H, s, β-CH), 3.53 (3H, s, OCH_3), 2.55 (4H, m, $J = 7.5$ Hz, CH_2CH_3), 2.20 (4H, m, $J = 7.5$ Hz, CH_2CH_3), 1.41 (6H, s, α-Me), 1.13 (12H, t, $J = 7.5$ Hz, CH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 168.32, 147.48, 137.12, 126.12, 124.67, 94.34, 55.42, 23.62, 13.95. X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged dimer in the solid state (see Supporting Information).

[(BDI-3)Zn(μ-OMe)]$_2$. To a solution of (BDI-**3**)ZnEt (0.475 g, 0.928 mmol, 1 equiv) in toluene (7 mL) was added methanol (0.040 mL, 0.988 mmol, 1.06 equiv) at room temperature. After being stirred for 1 h at room temperature, the clear solution was dried in vacuo (^{1}H NMR shows only 25% conversion). Excess methanol (0.20 mL, 4.9 mmol, 5.3 equiv) was then added at room temperature. After being stirred for 1.5 h at room temperature, the clear solution was dried in vacuo (^{1}H NMR shows 100% conversion and decomposition to the ligand) and then recrystallized from hexane at −20 °C to give clear block crystals (0.070 g, 15%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.05 (6H, m, ArH), 4.64 (1H, s, β-CH), 3.65 (3H, s, OCH_3), 2.59 (4H, m, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 2.12 (4H, m, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 1.61 (8H, sextet, $J = 7.5$ Hz, $CH_2CH_2CH_3$), 1.45 (6H, s, α-Me), 1.00 (12H, t, $J = 7.5$ Hz, $CH_2CH_2CH_3$).

[(BDI-4)Zn(μ-OMe)]$_2$. The conversion was quantitative. The colorless solid was recrystallized from toluene at 5 °C to give colorless block-shape crystals (52% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.01 (6H, b, ArH), 4.65 (1H, s, β-CH), 3.59 (3H, s, OCH_3), 1.99 (12H, s, *o*-CH_3), 1.39 (6H, s, α-Me). X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged dimer in the solid state (see Supporting Information).

[(BDI-5)Zn(μ-OMe)]$_2$. To a solution of (BDI-**5**)ZnEt (0.528 g, 1.09 mmol) in toluene (10 mL) was added methanol (0.15 mL, 3.4 mmol, 3.4 equiv) at room temperature. After being stirred for 1 h at room temperature, the suspension was filtered over a frit, and the clear solution was dried in vacuo and then recrystallized from toluene at −30 °C to give colorless needle-shape crystals (0.201 g, 38%). ^{1}H NMR (toluene-d_8, 300 MHz): δ 7.07 (6H, b, ArH), 4.94 (1H, s, β-CH), 3.28 (3H, s, OCH_3), 2.97 (2H, m, $CHMe_2$), 2.46 (2H, m, $CHHCH_3$), 2.35 (2H, m, $CHHCH_3$), 1.56 (6H, s, α-Me), 1.20 (18H, m, $CHMe_2$ and CH_2CH_3). X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged dimer in the solid state, where the ligand adopts a cis geometry and the dimer is of C_{2h} symmetry (see Supporting Information).

[(BDI-7)Zn(μ-OMe)]$_2$. The crude material was recrystallized from toluene at −30 °C to give colorless needle-shape crystals (49% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.08 (6H, m, ArH), 4.56 (1H, s, β-CH), 3.65 (3H, s, OCH_3), 3.41 (2H, m, $CHMe_2$), 1.75 (6H, s, *o*-Me), 1.45 (6H, s, α-Me), 1.35 (6H, d, $J = 7.0$ Hz, CHMeMe), 1.28 (6H, d, $J = 7.0$ Hz, CHMeMe). X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged dimer in the solid state, where the ligand adopts a cis geometry and the dimer is of C_{2h} symmetry (see Supporting Information).

[(BDI-11)Zn(μ-OMe)]$_2$. The crude material was recrystallized from toluene at −30 °C to give colorless block-shape crystals (59% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.16 (2H, d, α-H), 7.06 (6H, m, ArH), 4.40 (1H, t, β-CH), 3.64 (3H, s, OCH_3), 3.31 (4H, m, $CHMe_2$), 1.13 (12H, d, $J = 7.0$ Hz, CHMeMe), 0.91 (12H, d, $J = 7.0$ Hz, CHMeMe). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 163.69, 142.28, 125.61, 125.45, 123.38, 88.30, 55.61, 27.94, 25.31, 22.62. X-ray analysis of the crystals revealed that the complex exists as a μ-methoxide-bridged dimer in the solid state (see Supporting Information).

(BDI-8)$_2$Zn. Refer to the general synthetic procedure for [(BDI)-Zn(μ-OMe)]$_2$. After being stirred for 1 h at room temperature, the suspension was filtered over a frit. The clear solution was dried in vacuo and then recrystallized from pentane at 5 °C to give light yellow block-shaped crystals (41%). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.80−7.60 (16H, m, ArH), 4.71 (2H, s, β-CH), 3.24 (2H, m, $J = 7.0$ Hz, $CHMe_2$), 2.75 (2H, m, $J = 7.0$ Hz, $CHMe_2$), 1.82 (6H, s, α-Me), 1.41 (6H, s, α-Me), 1.29 (6H, d, $J = 7.0$ Hz, CHMeMe), 1.12 (6H, d, $J = 7.0$ Hz, CHMeMe), 0.94 (6H, d, $J = 7.0$ Hz, CHMeMe), 0.43 (6H, d, $J = 7.0$ Hz, CHMeMe). X-ray analysis of the crystals revealed that the complex exists as a bis-ligated structure in the solid state, where the ligand adopts a cis geometry (see Supporting Information).

(BDI-2)$_2$Zn. Refer to the synthetic procedure for [(BDI-**2**)Zn(μ-OAc)]$_2$; however, 0.5 equiv of Zn(OAc)$_2$ is used. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.98 (12H, b, ArH), 4.74 (2H, s, β-CH), 3.11 (2H, b, CH_2CH_3), 2.55 (2H, b, CH_2CH_3), 2.15 (2H, b, CH_2CH_3), 1.85 (2H, b, CH_2CH_3), 1.60 (8H, b, CH_2CH_3), 1.26 (12H, b, α-Me), 1.26 (12H, b,

CH_2CH_3), 0.88 (12H, b, CH_2CH_3). X-ray analysis of the crystals revealed that the complex exists as a bis-ligated structure in the solid state (see Supporting Information).

[(BDI-1)Zn(μ-O^{i}Pr)]$_2$. 2-Propanol (49 μL, 0.64 mmol) was added to a solution of (BDI-**1**)ZnN$(SiMe_3)_2$ (0.411 g, 0.638 mmol) in toluene (6 mL) at room temperature. After being stirred for 6 h at room temperature, the colorless solution was dried in vacuo. The colorless solid was recrystallized from toluene (2 mL) at −30 °C to give colorless block-shape crystals (0.165 g, 54% yield). X-ray suitable crystals were grown from hexanes (15 mL) at 5 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.08 (6H, m, ArH), 4.90 (1H, s, β-CH), 3.86 (1H, m, *J* = 5.9 Hz, OC*H*Me$_2$), 3.16 (4H, m, *J* = 7.0 Hz, C*H*Me$_2$), 1.63 (6H, s, α-Me), 1.37 (12H, d, *J* = 7.0 Hz, CH*Me*Me), 1.15 (12H, d, *J* = 7.0 Hz, CHMe*Me*), 0.90 (6H, d, *J* = 5.9 Hz, OCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 169.52, 143.79, 141.67, 126.45, 123.92, 94.89, 66.70, 29.66, 28.64, 24.40, 23.48, 23.36. X-ray analysis of the crystals revealed that the complex exists as a μ-isopropoxide-bridged dimer in the solid state (see Supporting Information).

[(BDI-2)Zn(μ-O^{i}Pr)]$_2$. 2-Propanol (58 μL, 0.76 mmol) was added to a solution of (BDI-**2**)ZnN$(SiMe_3)_2$ (0.449 g, 0.764 mmol) in toluene (6 mL) at room temperature. The clear solution turned cloudy instantaneously. After being stirred at room temperature for 10 min, the slurry was dried in vacuo. The colorless solid was recrystallized from toluene (10 mL) at 5 °C to give colorless block-shape crystals (0.25 g, 67% yield). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.11 (6H, b, ArH), 4.74 (1H, s, β-CH), 3.46 (1H, m, *J* = 5.9 Hz, OC*H*Me$_2$), 2.45 (4H, m, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.94 (4H, m, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.41 (6H, s, α-Me), 0.98 (12H, t, *J* = 7.5 Hz, CH$_2$C*H*$_3$), 0.81 (6H, d, *J* = 5.9 Hz, OCH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ 167.51, 147.72, 137.61, 125.52, 124.42, 94.78, 65.04, 27.79, 23.53, 23.49, 13.60.

[(BDI-9)ZnO^{i}Pr]$_2$. 2-Propanol (35 μL, 0.46 mmol) was added to a solution of (BDI-**9**)ZnN$(SiMe_3)_2$ (0.25 g, 0.41 mmol) in toluene (3 mL) at room temperature. After being stirred for 1.5 h at room temperature, the solution was dried in vacuo to leave a white solid, which was recrystallized from hexanes (2 mL) at −20 °C to give feathery white crystals (0.14 g, 68% yield). The ^{1}H NMR of this complex was unusually complicated at room temperature, which we believe results from cis and trans stereoisomers and multiple mixed dimers. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.17 (6H, m, ArH), 4.77 (1H, m, β-CH), 3.78 (1H, m, OC*H*Me$_2$), 2.64 (8H, m, C*H*$_2$CH$_2$CH$_3$ + C*H*$_2$CH$_3$), 1.56 (4H, m, CH$_2$C*H*$_2$CH$_3$), 1.46 (6H, m, α-Me), 1.15 (12H, m, CH$_2$C*H*$_3$ + OCH*Me*$_2$), 0.95 (6H, m, CH$_2$CH$_2$C*H*$_3$).

[(BDI-2)Zn(μ-OH)]$_2$. Degassed H_2O (19 μL, 1.1 mmol) was added to (BDI-**2**)ZnN$(SiMe_3)_2$ (0.560 g, 0.954 mmol) in toluene (5 mL) at room temperature. After being stirred at room temperature for 10 min, the slurry was dried in vacuo, giving the desired compound in quantitative yield. The crude material was recrystallized from toluene (10 mL) at room temperature to give colorless block-shape crystals. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.07 (2H, b, ArH), 6.91 (4H, b, ArH), 4.70 (1H, s, β-CH), 2.45 (4H, m, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 2.26 (4H, m, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.39 (6H, s, α-Me), 1.08 (12H, t, *J* = 7.5 Hz, CH$_2$C*H*$_3$), −0.14 (1H, s, OH). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 168.03, 147.04, 136.90, 126.38, 124.78, 94.03, 23.85, 23.62, 14.06. X-ray analysis of the crystals revealed that the complex exists as a μ-hydroxide-bridged dimer in the solid state (see Supporting Information).

(F) Representative Procedure for Polymer Synthesis. In a drybox, [(BDI-**1**)ZnOAc]$_2$ (20 mg, 3.7×10^{-5} mol), cyclohexene oxide (3.8 mL, 3.7 g, 3.8×10^{-2} mol), and a magnetic stir bar were placed in a 60 mL Fischer−Porter bottle. The vessel was pressurized to 100 psi with CO_2, and the mixture was allowed to stir at the desired temperature for the necessary reaction time. After a small sample of the crude material was removed for characterization, the product was dissolved in 5 mL of methylene chloride, and the polymer was precipitated from 20 mL of methanol. The product was then dried in vacuo to constant weight.

Acknowledgment. This work was generously supported by the NSF (Career Award CHE-9875261). We thank the Cornell University Center for Biotechnology, a New York State Center for Advanced Technology, supported by the New York State Science and Technology Foundation and industrial partners, for partial support of this research. This work made use of the Cornell Center for Materials Research Shared Experimental Facilities, supported through the National Science Foundation Materials Research Science and Engineering Centers program (DMR-0079992), and the Cornell Chemistry Department X-ray Facility (supported by the NSF; CHE-9700441). G.W.C. gratefully acknowledges a Camille and Henry Dreyfus New Faculty Award, a Research Corporation Research Innovation Award, an Alfred P. Sloan Research Fellowship, an Arnold and Mabel Beckman Foundation Young Investigator Award, a Camille Dreyfus Teacher-Scholar Award, a David and Lucile Packard Foundation Fellowship in Science and Engineering, a 3M Untenured Faculty Grant, and a Union Carbide Innovation Recognition Award.

Supporting Information Available: Crystal structure data for all complexes (PDF). This material is free of charge via the Internet at http://pubs.acs.org.

JA003850N