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Cationic Organomagnesium Complexes as Highly Active Initiators for the Ring-Opening Polymerization of ε-Caprolactone

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Species of the form $[\mathbf{L}H]^+[BR_4]^-$ (R = pentafluorophenyl, phenyl, **1**) were synthesized by reaction of Brönsted acids with a novel bis-phosphinimine ligand (**L** = 4,6-$(MesN{=}PPh_2)_2$dibenzofuran). Corresponding cationic complexes $[\mathbf{L}Mg^nBu]^+[BR_4]^-$ (**2**) were produced by reaction of $[Mg^nBu_2]$ with $[\mathbf{L}H]^+[BR_4]^-$. Organomagnesium species **2a** and **2b** exhibit extremely high activity as initiators for the polymerization of ε-caprolactone, yielding near-quantitative conversion of monomer to high molecular weight ($> 2.0 \times 10^5$ g/mol) polymer in 4 min at ambient temperature.

Introduction

Polylactones are an important class of biodegradable materials that hold the potential to reduce waste associated with the disposal of conventional plastics.[1] The advancement of polylactone technology, including the development of new homogeneous catalysts for lactone polymerization, is thus an important goal for many researchers, and many excellent reviews are available.[2] Of the commercially viable polylactones (poly(ε-caprolactone), polylactide, and polyglycolide), poly(ε-caprolactone) is particularly attractive, as it is produced from an inexpensive precursor, may be processed under mild conditions (mp ∼60 °C[3]), and is readily degraded by naturally occurring microorganisms.[4]

Magnesium- and zinc-based homogeneous catalyst systems are particularly attractive for lactone polymerization because of their low toxicity and cost paired with high activity. Magnesium catalysts, however, generally exhibit higher activity than more electron-rich zinc analogues.[2a] Therefore, development of sterically and electronically unsaturated magnesium complexes presents an opportunity to achieve even higher levels of polymerization catalytic activity. Catalyst activation by alkide abstraction from organometallic species (which results in a sterically and electronically unsaturated metal center) is well established for olefin polymerization.[5] Only preliminary efforts have been reported for extending similar strategies to lactones.[6]

Herein we describe the synthesis and characterization of a family of cationic organomagnesium complexes that are extremely active initiators for ε-caprolactone polymerization. While some well-characterized examples of formally cationic magnesium complexes have been reported,[7] and a variety of neutral organomagnesium species have been applied to lactone polymerization,[8] to the best of our knowledge the results described herein constitute the first successful use of a cationic organomagnesium species in ε-caprolactone polymerization.

The polymerization of ε-caprolactone using a cationic organomagnesium initiator may conceptually follow either of two mechanisms: coordination−insertion or activated chain-end (Scheme 1).[8b−g,9] Typical organomagnesium catalysts have been shown to polymerize lactones via the former

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(1) (a) Arshady, R. Biodegradable polymers: concepts, criteria, definitions. In *Biodegradable Polymers*; Arshady, R., Eds.; PBM Series 2; Citus Books: London, UK, 2003; pp 1−34. (b) Liebmann-Vinson, A.; Timmins, M. Biodegradable polymers: degradation mechanisms, part 2. In *Biodegradable Polymers*; Arshady, R., Eds.; PBM Series 2; Citus Books: London, UK, 2003; pp 329−372.

(2) (a) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J. *Dalton Trans.* **2009**, 4832–4846. (b) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11–63. (c) Wu, J.; Yu, T.-L.; Chen, C.-T., Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602−626. (d) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176. (e) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215–2224.

(3) Di Maio, E.; Innace, S.; Marrazzo, C.; Narkis, M.; Nicolais, L. *Macromol. Symp.* **2005**, *228*, 219–227.

(4) Shimao, M. *Curr. Opin. Biotechnol.* **2001**, *12*, 242–247.

(5) Chen, E. Y.-X.; Marks, T. *J. Chem. Rev.* **2000**, *100*, 1391–1434.

(6) (a) Haddad, M.; Laghzaoui, M.; Welter, R.; Dagorne, S. *Organometallics* **2009**, *28*, 4584–4592. (b) Dagorne, S.; Le Bideau, F.; Welter, R.; Bellemin-Laponnaz, S.; Maisse-François, A. *Chem.—Eur. J.* **2007**, *13*, 3202–3217. (c) Milione, S.; Grisi, F.; Centore, R.; Tuzi, A. *Organometallics* **2006**, *25*, 266–274. (d) Lewiński, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789–5791. (e) Hannant, M. D.; Schormann, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4071–4073. (f) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J. -B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599–3608.

(7) (a) Pajerski, A. D.; Squiller, E. P.; Parvez, M.; Whittle, R. R.; Richey, H. G. *Organometallics* **2005**, *24*, 809–814. (b) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* **2004**, *23*, 3296–3302.

(8) Selected examples: (a) Schofield, A. D.; Barros, M. L.; Cushion, M. G.; Schwarz, A. D.; Mountford, P. *Dalton Trans.* **2009**, 85–96. (b) Wang, Z.-X.; Qi, C.-Y. *Organometallics* **2007**, *26*, 2243–2251. (c) Sánchez-Barba, L. F.; Garcés, A.; Fajardo, M.; Alonso-Moreno, C.; Fernández-Baeza, J.; Otero, A.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; López-Solera, M. I. *Organometallics* **2007**, *26*, 6403–6411. (d) Sánchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. (e) Yu, T.-L.; Wu, C.-C.; Chen, C.-C.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Polymer* **2005**, *46*, 5909–5917. (f) Shueh, M.-L.; Wang, Y.-S.; Huang, B.-H.; Kuo, C.-Y.; Lin, C.-C. *Macromolecules* **2004**, *37*, 5155–5162. (g) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854.

(9) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley and Sons: New York, 2004; pp 19−586.

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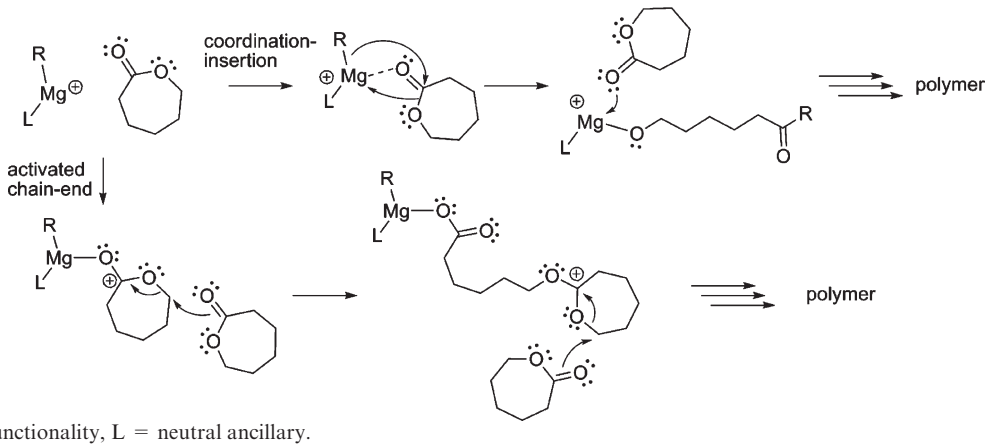
Scheme 1. Possible Mechanisms for the Polymerization of ε-Caprolactone via a Cationic Organomagnesium Initiator: Coordination−Insertion (above) or Activated Chain-End (below)[a]



[a] R = anionic functionality, L = neutral ancillary.

process;[8b−g] however, due to the cationic nature of the complexes in the present study, both mechanisms have been considered.

Since coordination−insertion lactone polymerization presents a scenario in which the catalytic species is intimately connected to the active site of polymerization, it is considered preferable, as it presents greater opportunity for subsequent modulation of the polymerization process by way of ancillary ligand modification. This mechanism requires an anionic initiating group bound to the metal center; thus, an ideal ancillary ligand for an activated magnesium catalyst of the form $[LMgR]^+[A]^-$ (R = alkyl group, A = noncoordinating anion) must be formally neutral and strongly electron donating. Phosphinimines possess such properties and in addition are chemically robust and easily synthesized in a modular manner, while providing a useful ^{31}P NMR handle.[10] In addition, several phosphinimine-containing magnesium complexes have been previously reported.[8b,11]

Synthesis and Characterization. The chelating bis(phosphinimine) architecture employed in the present work was easily produced in high yield (93.9%) by reaction of 4,6-bis(diphenylphosphino)dibenzofuran with 2 equiv of 2,4,6-trimethylphenylazide ($MesN_3$) under standard Staudinger conditions.[12] Single crystals of **L** suitable for X-ray diffraction (Figure 1) were grown from a solution of the compound in a toluene/pentane mixture at ambient temperature.

It has been previously demonstrated that direct reaction of neutral organozinc precursors with protonated salts of imines and phosphinimines affords well-defined cationic zinc complexes.[6e,13,14] In an effort to utilize this methodology for the preparation of analogous organomagnesium cations, isolable salts of **L**, $[(\mathbf{L})H]^+[BR_4]^-$ (R = C_6F_5 (**1a**), Ph (**1b**)),

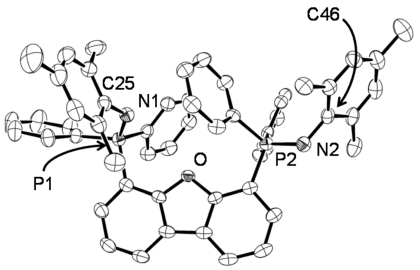
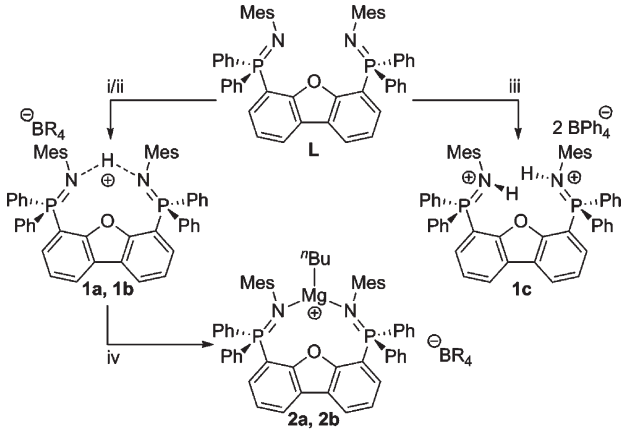


Figure 1. Molecular structure of **L** (50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): P(1)−N(1) 1.549(1), P(2)−N(2) 1.565(1); P(1)−N(1)−C(25) 129.5(1), P(2)−N(2)−C(46) 122.9(1).

Scheme 2. Synthesis of 1a, 1b, and 1c by Protonation of L Using (i) $[HNMe_2Ph][B(C_6F_5)_4]$, (ii) $Na[BPh_4]$ and H_2O, and (iii) 2 $Na[BPh_4]$ and 2 HCl, and Synthesis of Complexes 2a and 2b by Addition of (iv) $[Mg^nBu_2]$



were generated in high yield (**1a**: 80.1%, **1b**: 86.3%) by reaction of **L** with an appropriate Brönsted acid (Scheme 2). The doubly protonated species **1c** was prepared in a parallel fashion in 91.2% yield. Though **1a** and **1b** were not sufficiently crystalline in our hands for single-crystal X-ray diffraction, crystals of **1c** were isolated and the molecular structure was determined (Figure 2). By comparison to the structure of **L** (P1−N1 = 1.549(1) Å), the P−N bonds of **1c** (P1−N1 = 1.639(2) Å) are elongated as a result of protonation of the phosphinimine nitrogen atoms.

(10) (a) Zhu, D.; Budzelaar, P. H. M. *Organometallics* **2008**, *27*, 2699–2705. (b) Courtenay, S.; Walsh, D.; Hawkeswood, S.; Wei, P.; Das, A. K.; Stephan, D. W. *Inorg. Chem.* **2007**, *46*, 3623–3631. (c) Welch, G. C.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 1811–1818.

(11) (a) Ahmed, S. A.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2006**, *25*, 394–402. (b) Wei, P.; Stephan, D. W. *Organometallics* **2003**, *22*, 601–604.

(12) (a) Meyer, J.; Staudinger, H. *Helv. Chim. Acta* **1919**, *2*, 635–646. (b) Alajarin, M.; Lopez-Leonardo, C. L.; Llamas-Lorente, P. L.; Bautista, D. *Synthesis* **2000**, *14*, 2085–2091.

(13) Hannant, M. D.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Inorg. Chim. Acta* **2005**, *358*, 1683–1691.

(14) Wheaton, C. A.; Ireland, B. J.; Hayes, P. G. *Organometallics* **2009**, *28*, 1282–1285.

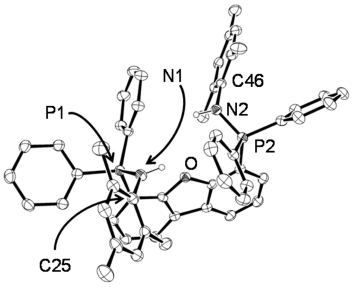


Figure 2. Molecular structure of **1c** (50% probability ellipsoids; BPh_4^-, solvent (acetone), and all H atoms except N−H (calculated) omitted for clarity). Selected bond lengths (Å) and angles (deg): P(1)−N(1) 1.639(2), N(1)−H(1N) 0.894(2); P(1)−N(1)−C(25) 125.6(1).

The species **L**, **1a**, **1b**, and **1c** all display C_{2v} symmetry in solution, as indicated by a single ^{31}P NMR resonance each at δ −17.6 (**L**), 10.1 (**1a**, **1b**), and 28.1 (**1c**). Both **1a** and **1b** exhibit a broad ^1H NMR resonance at δ 5.7 attributed to the N−H proton, whereas the analogous resonance of **1c** appears as a doublet at δ 8.1 ($^2J_{PH} = 9.7$ Hz). The molecular symmetry established spectroscopically suggests that the N−H protons of **1a** and **1b** are rapidly exchanging between the two nitrogen atoms on the NMR time scale. At temperatures as low as −80 °C, NMR experiments were unable to show the C_s symmetric species; however, a rapid proton exchange process is corroborated by the chemical shift of the ^{31}P NMR resonances for **1a** and **1b**, which are intermediate between those observed for **1c** and **L**.

Treatment of **1a** or **1b** with 1 equiv of di-*n*-butylmagnesium resulted in loss of *n*-butane and concomitant formation of **2a** or **2b**, respectively (Scheme 2). The remaining *n*-butyl group was well resolved by ^1H NMR spectroscopy, giving rise to diagnostic resonances at δ 1.38−1.32 (CH_2CH_2), 0.99 (CH_3), and −0.13 ($MgCH_2$) in each case. C_{2v} symmetry was preserved, and a large downfield shift in the ^{31}P NMR resonance (δ −17.6 to 23.0 for **2a**, δ −17.6 to 23.2 for **2b**) was observed upon coordination of **L** to the magnesium center. This observation is consistent with the behavior of a closely related mono-phosphinimine ligand upon coordination to zinc[14] and with other phosphinimines upon coordination to magnesium.[8b,11] Complexes **2a** and **2b** were isolated as thermally stable, air-sensitive solids in good yield (**2a**: 73%, **2b**: 91%). Notably, complexes **2a** and **2b** were prepared in 55% and 74% overall yields, respectively, from 4,6-bis-(diphenylphosphino)dibenzofuran.

The structure of **2b** was confirmed by a single-crystal X-ray diffraction study (Figure 3). The ligand is κ^2-bound to Mg (Mg−N 2.078(5), 2.086(5) Å; Mg−C 2.13(1) Å), resulting in trigonal-planar geometry about magnesium (sum of angles = 360.0°). No noteworthy cation−anion interactions were observed (shortest $Mg-C_{anion}$ contact = 6.3 Å).

Though **2a** eluded exhaustive crystallization efforts, the weakly coordinating nature of $B(C_6F_5)_4^-$ has been well established.[15] Furthermore, the ^1H, ^{31}P, and ^{13}C NMR spectral properties of $[Mg^nBu]^+$ in **2a** and **2b** are virtually identical, suggesting minimal interaction with the BR_4^- counterions. Likewise, the ^{11}B NMR resonances of **2a** and **2b** were observed upfield of 0 ppm (δ −15.8 for **2a**, δ −5.6 for **2b**) and the ^{19}F $\Delta\delta_{mp}$ of **2a** was 3.8 ppm.[16] Thus, it is reasonable to suggest that both **2a** and **2b** are best described as extremely weakly interacting ion pairs, and although anions can have a significant effect on polymerization,[17] that does not appear to be the case here.

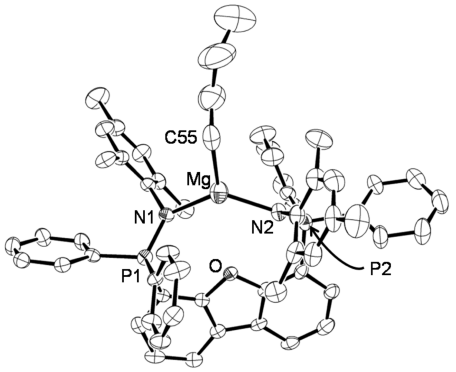


Figure 3. Molecular structure of **2b** (30% probability ellipsoids; BPh_4^- and H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): P(1)−N(1) 1.602(5), P(2)−N(2) 1.601(5), Mg−N(1) 2.086(6), Mg−N(2) 2.077(5), Mg−C(55) 2.13(1); P(1)−N(1)−Mg 129.6(3), P(2)−N(2)−Mg 130.7(3), N(1)−Mg−N(2) 132.6(2), N(1)−Mg−C(55) 115.0(3), N(2)−Mg−C-(55) 112.3(3).

Table 1. Polymerization of ε-Caprolactone by Initiators 2a and 2b

initiator	temp (°C)	initiator conc (mM)	initiator loading	conversion after 4 min
2a	23	4.2	0.77%	95%
2b	23	4.4	0.77%	90%
2b	23	0.37	0.19%	75%
2b	0	2.1	0.56%	73%

Polymerization of ε-Caprolactone. Preliminary examination of **2a** and **2b** in the ring-opening polymerization of ε-caprolactone revealed remarkably high activity. Investigations were conducted at initiator concentrations of approximately 4 mM (0.77 mol % relative to the lactone monomer) in benzene-d_6. In both cases, ^1H NMR spectroscopy indicated >90% conversion of ε-caprolactone to poly-(ε-caprolactone) in 4 min at ambient temperature (Table 1).

As the BR_4^- anions were established to be extremely weakly coordinating, they were not expected to substantially influence the polymerization process. Indeed, similar activity was observed for **2a** and **2b** at 23 °C (Table 1). Hence, subsequent reactions focused on the less expensive initiator **2b**. Notably, **2b** maintains impressive activity at reduced concentrations (0.37 mM) and loading (0.19%). Likewise, high activity and a linear relationship between ln[monomer] and time (pseudo-first-order kinetics) were observed at 0 °C. In fact, **2b** was active at temperatures as low as −40 °C; however, at temperatures less than 0 °C the exceedingly high viscosity of the reaction mixture rendered it difficult to achieve complete conversion.

The polymerization of ε-caprolactone by **2a** and **2b** was studied by NMR spectroscopy in an attempt to elucidate the operative polymerization mechanism (Scheme 1). *In situ* examination of the polymerization process indicated cleavage of the Mg−C bond in both cases (evidenced by

(15) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066–2090.

(16) (a) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672–2674. (b) Drewitt, M. J.; Niedermann, M.; Kumar, R.; Baird, M. C. *Inorg. Chim. Acta* **2002**, *335*, 43–51.

(17) Roberts, J. A. S.; Chen, M.-C.; Seyam, A. M.; Li, L.; Zuccaccia, C.; Stahl, N. G.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 12713–12733.

Table 2. GPC Results for Poly(ε-caprolactone) Produced Using Initiator 2b: Weight Average (M_w), Number Average (M_n), and Corresponding PDI (M_w/M_n) Values

batch	M_w	M_n	PDI (M_w/M_n)
1	1.9×10^5	1.2×10^5	1.6
2	2.1×10^5	1.3×10^5	1.5

disappearance of a characteristic Mg−CH_2 resonance at δ −0.13 in the ^{1}H NMR spectrum), and while the methylene resonances could not be detected due to overlapping polymer signals, the *n*-butyl−CH_3 resonance is clearly visible at δ 0.86 in the ^{1}H NMR spectrum. However, this same *n*-butyl resonance could not be detected in the spectra of isolated oligomer samples (generated using 10 mol % **2b**), clearly demonstrating that the polymer does not bear an *n*-butyl end group. Corroboration of these results via MALDI-ToF mass spectrometry was not successful despite an exhaustive examination of a variety of polymer samples.[7b,18] Thus, while the ultimate fate of the initiator is unknown, the absence of an *n*-butyl end group on isolated oligo(ε-caprolactone) samples suggests that lactone polymerizaton occurs via an activated chain-end process (Scheme 1).

Poly(ε-caprolactone) samples produced using **2b** (0.24%, 23 °C) possessed average molecular weights (M_w) as high as 2×10^5 g/mol and PDIs 1.6 or less, as determined by GPC analysis (Table 2).[2a] The average molecular weights of the polymers were higher than expected (i.e., a controlled polymerization utilizing 0.24 mol % initiator would be expected to afford polymer with a molecular weight of 4.8×10^4 g/mol), which may be attributed to slow initiation relative to propagation in the polymerization process, and therefore only moderate initiator efficiency. A relatively slow initiation step is also consistent with the observed polydispersity values. This could occur in the context of an activated chain-end mechanism, whereby the cationic chain end may be less stable and more reactive than the initiating cationic magnesium species.

Conclusion

Cationic organomagnesium species (**2a** and **2b**), prepared by treating di-*n*-butylmagnesium with novel species **1a** and **1b**, respectively, have demonstrated exceptionally high activity for the polymerization of ε-caprolactone. The observed results are extremely promising, and future generations of this initiator will be designed in hopes of maintaining high activity while giving enhanced molecular weight control.

Experimental Section

General Procedures. All manipulations of air-sensitive materials and reagents were conducted using high-vacuum techniques[19] under a purified argon atmosphere or in a glovebox (MBraun Labmaster 130). Proteo solvents were purified using an MBraun solvent purification system (MB-SPS), stored in Teflon-sealed glass vessels over appropriate drying agents, and vacuum transferred directly to reaction vessels. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents, vacuum transferred, and stored under an inert atmosphere prior to use. ε-Caprolactone was dried over CaH_2, distilled, and stored under an inert atmosphere prior to use. All other materials were obtained in high purity (Sigma-Aldrich) and used without additional purification. NMR spectra (^{1}H (300.13 MHz), ^{13}C{^{1}H} (75.47 MHz), ^{31}P{^{1}H} (121.48 MHz), ^{19}F (282.42 MHz), and ^{11}B (96.29 MHz)) were collected using a Bruker Avance II NMR spectrometer equipped with a variable-temperature unit. Spectra were collected at ambient temperature unless otherwise noted and referenced to residual proteo solvent resonances (^{1}H), solvent ^{13}C resonances (^{13}C{^{1}H}), or an external standard (triphenylphosphine (^{31}P{^{1}H}), trifluorotoluene (^{19}F), or boron trifluoride diethyl etherate (^{11}B)) depending on the nucleus of interest. ^{1}H and ^{13}C NMR peak assignments were facilitated by DEPT-45, DEPT-90, DEPT-135, COSY, and HSQC experiments. X-ray crystal structures were collected using a Bruker AXS SMART APEX II single-crystal X-ray diffractometer (Mo Kα (λ = 0.71073 Å)). Elemental analyses were performed using an Elementar Vario Microcube.

Synthesis of 4,6-(PPh_2)$_2$dibenzofuran. The ligand precursor 4,6-(PPh_2)$_2$dibenzofuran was prepared as described by Kranenburg et al.[20] with several modifications. A 250 mL round-bottom flask was charged with 2.6869 g (15.974 mmol) of dibenzofuran, to which 100 mL of diethyl ether was added by vacuum transfer at −78 °C. Tetramethylethylenediamine (TMEDA) was injected slowly (7.2 mL, 5.6 g, 48 mmol), and the suspension was allowed to warm to ambient temperature over approximately 20 min. The dibenzofuran fully dissolved to afford a light yellow solution. This solution was cooled back to −78 °C, and a solution of *sec*-butyllithium (35 mL at 1.4 mol/L in heptane, 49 mmol) was added dropwise. The reaction mixture was stirred for 2 h, producing a light green suspension, which became dark green upon slow warming to ambient temperature. The reaction mixture was stirred for an additional 6 h and then cooled to −78 °C. Beginning 9 h after the initial injection of *sec*-butyllithium, 9.0 mL (11 g, 50 mmol) of neat chlorodiphenylphosphine was injected rapidly. An immediate color change from green to white was noted. The reaction mixture was gradually warmed back to ambient temperature and stirred for an additional 14 h, during which a light brown suspension formed. The solvent was removed *in vacuo*. All subsequent manipulations were performed under aerobic conditions. The resulting light brown oil was dissolved in 80 mL of dichloromethane and quenched with 50 mL of distilled water. The aqueous phase was removed, and the organic phase was washed with three subsequent 50 mL fractions of distilled water. The organic phase was dried thoroughly *in vacuo*, and the resultant light brown oily solid was washed five times with 50 mL fractions of pentane. During each washing procedure, the mixture was sonicated and vigorously stirred for approximately 5 min prior to filtration. The resultant white solid was dried thoroughly *in vacuo*, affording 6.06 g (11.3 mmol, 70.9%) of the desired product. ^{1}H and ^{31}P{^{1}H} NMR spectra matched published results.[19] ^{31}P{^{1}H} NMR (chloroform-*d*): δ −16.8 (s). ^{1}H NMR (chloroform-*d*): δ 7.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, dbf-C$_{1/9}H$), 7.35−7.20 (ov m, 22H, dbf-C$_{3/7}H$ + *o*-PPh_2 + *m*-PPh_2 + *p*-PPh_2), 7.10 (m, 2H dbf-C$_{2/8}H$).

Synthesis of 4,6-(MesN=PPh_2)$_2$dibenzofuran (L). A 500 mL Teflon-sealed glass reaction vessel was charged with 5.7732 g (10.760 mmol) of 4,6-(PPh_2)$_2$dibenzofuran. The precursor dissolved fully in 110 mL of toluene, and then excess neat 2,4,6-trimethylphenylazide (mesityl azide, $MesN_3$)[21] (4.255 g, 26.39 mmol) was added. Evolution of a colorless gas was noted within

(18) Fontaine, F.-G. Personal communication. High molecular weight poly(ε-caprolactone) has proven impossible for the Fontaine group to observe by MALDI-ToF mass spectrometry.

(19) Burger, B. J.; Bercaw J. E. Vacuum line techniques for handling air-sensitive organometallic compounds. In *Experimental Organometallic Chemistry. A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington DC, 1987; pp 79−98.

(20) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081–3089.

(21) Murata, S.; Abe, S.; Tomioka, H. *J. Org. Chem.* **1997**, *62*, 3055–3061.

5 min, and the solution was stirred at ambient temperature, with occasional venting, for 60 min. The temperature was then gradually raised to 65 °C, and the solution was stirred for 16 h, over which time the color changed from yellow to light brown. An additional 0.459 g (2.85 mmol) of neat $MesN_3$ was added, and the reaction mixture was allowed to stir at 65 °C until the ^{31}P NMR spectrum of crude reaction mixture aliquots indicated that the reaction had reached completion (approximately 2 additional h). The solution was cooled to ambient temperature and transferred to a 100 mL round-bottom flask in two fractions of approximately 60 mL each. The solvent was removed *in vacuo* between fractions and after the full volume had been transferred, yielding an oily yellow solid. All subsequent manipulations were conducted under aerobic conditions. The product was washed five times with 50 mL fractions of hexane. During each washing procedure, the mixture was sonicated and vigorously stirred for approximately 5 min prior to filtration. The product was collected as a white powder and dried *in vacuo*. Total yield was 93.9% (8.10 g, 10.1 mmol). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −17.6 (s). ^1H NMR (benzene-d_6): δ 7.82 (dd, J = 12 Hz, J = 9.2 Hz, 2H, dbf-$C_{1/9}H$), 7.71−7.60 (m, 8H, *o*-PPh_2), 7.57 (m, 2H, dbf-$C_{3/7}H$), 7.02−6.82 (br ov m, 18H, dbf-$C_{2/8}H$ + *m*-PPh_2 + *p*-PPh_2 + *m*-Mes), 2.27 (s, 6H, *p*-Mes), 1.93 (s, 12H, *o*-Mes). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 157.0 (s, dbf-quaternary), 145.2 (s, dbf-quaternary), 133.0 (s, *p*-Mes (CCH_3)), 132.7 (d, $^3J_{CP}$ = 7.5 Hz, *m*-PPh_2), 132.0 (d, $^2J_{CP}$ = 10.6 Hz, *o*-PPh_2), 131.9 (d, $^1J_{CP}$ = 50.6 Hz, dbf-$C_{4/6}$), 131.3 (s, dbf-$C_{1/9}$), 129.0 (s, dbf-$C_{2/8}$), 128.6 (s, *m*-Mes), 127.0 (d, $^3J_{CP}$ = 3.0 Hz, *o*-Mes (CCH_3)), 124.5 (d, $^2J_{CP}$ = 6.8 Hz, *ipso*-Mes), 124.0 (s, *p*-PPh_2), 123.1 (d, $^2J_{CP}$ = 9.8 Hz, dbf-$C_{3/7}$), 121.5 (d, $^1J_{CP}$ = 93.6 Hz, *ipso*-PPh_2), 21.1 (s, *o*-Mes (CCH_3)), 21.0 (s, *p*-Mes (CCH_3)). Anal. Calcd (%) for $C_{54}H_{48}N_2OP_2$: C, 80.76; H, 6.04; N, 3.48. Found: C, 80.46; H, 6.03; N, 3.49.

Synthesis of [H-4,6-(MesN=PPh_2)$_2$dibenzofuran][$B(C_6F_5)_4$] (1a). A 50 mL round-bottom flask was charged with 0.2710 g (0.3375 mmol) of **L**, 0.2659 g (0.3319 mmol) of [$HNMe_2Ph$]-[$B(C_6F_5)_4$], and 10 mL of benzene. The solution was stirred for 10 min, and the benzene was removed *in vacuo*, affording an oily, light yellow solid containing the desired product and Me_2NPh. The flask was attached to a swivel frit apparatus, and the solid was washed three times with 10 mL portions of pentane. During each washing procedure, the mixture was sonicated and stirred for several minutes before filtration. The resultant light yellow solid was dried *in vacuo* for 20 h. A total of 0.3945 g (0.2660 mmol) of [H-4,6-(MesN=PPh_2)$_2$dbf][$B(C_6F_5)_4$] was recovered as an analytically pure, light yellow solid (80.1% yield). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 10.1 (s). $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 9.4 (s). ^1H NMR (chloroform-*d*): δ 8.30 (d, $^3J_{HH}$ = 6.0 Hz, 2H, dbf-$C_{1/9}H$), 7.57−7.21 (br ov m, 24H, dbf-$C_{2/8}H$ + dbf-$C_{3/7}H$ + *o*-PPh_2 + *m*-PPh_2 + *p*-PPh_2), 6.58 (s, 4H, *m*-Mes), 5.72 (br s, 1H, N*H*), 2.17 (s, 6H, *p*-Mes), 1.55 (s, 12H, *o*-Mes). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 157.2 (s, dbf-quaternary), 134.6 (d, $^3J_{CP}$ = 5.3 Hz, dbf-$C_{2/8}$), 134.0 (s), 133.4 (s), 132.6 (d, $^2J_{CP}$ = 10.6 Hz, *o*-PPh_2), 131.2 (s), 130.0 (s, *p*-PPh_2), 129.8 (s, *m*-PPh_2), 129.5 (s, *m*-Mes), 127.1 (s, dbf-$C_{1/9}$), 125.4 (s), 124.0 (s), 123.3 (s), 20.8 (s, *p*-Mes (CCH_3)), 20.1 (s, *o*-Mes (CCH_3)). $B(C_6F_5)_4^-$ resonances not reported. *ipso*-PPh_2 not observed. ^{19}F NMR (benzene-d_6): δ −130.8 (br d, $^3J_{FF}$ = 11 Hz, 8F, *o*-C_6F_5), −161.7 (t, $^3J_{FF}$ = 22 Hz, 4F, *p*-C_6F_5), −165.5 (m, 8F, *m*-C_6F_5). ^{11}B NMR (chloroform-*d*): δ −16.7 (br s). Anal. Calcd (%) for $C_{78}H_{49}BF_{20}N_2OP_2$: C, 63.17; H, 3.34; N, 1.89. Found: C, 63.34; H, 3.37; N, 1.95.

Synthesis of [H-4,6-(MesN=PPh_2)$_2$dibenzofuran][BPh_4] (1b). Under aerobic conditions, two solutions—one containing 1.0531 g (1.3115 mmol) of previously prepared **L** in 125 mL of benzene, the other containing 0.4418 g (1.291 mmol) of $NaBPh_4$ in 75 mL of distilled water—were prepared. The aqueous solution was added to the organic solution in a 500 mL round-bottom flask, and the mixture was stirred vigorously for 25 min. The organic layer was decanted and washed with three 50 mL portions of distilled water. The organic layer was then thoroughly dried *in vacuo* for 14 h, yielding the desired product as an analytically pure, light yellow solid in high yield (1.2508 g, 1.1136 mmol, 86.26%). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 10.1 (s). $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 9.5 (s). ^1H NMR (chloroform-*d*): δ 8.14 (d, $^3J_{HH}$ = 6.3 Hz, 2H, dbf-$C_{1/9}H$), 7.46−7.31 (ov m, 24H, dbf-$C_{2/8}H$ + dbf-$C_{3/7}H$ + *o*-PPh_2 + *p*-PPh_2 + *o*-BPh_4^-), 7.30−7.19 (m, 8H, *m*-PPh_2), 6.95 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.1 Hz, 8H, *m*-BPh_4^-), 6.82 (t, $^3J_{HH}$ = 7.4 Hz, 4H, *p*-BPh_4^-), 6.58 (s, 4H, *m*-Mes), 5.69 (br s, 1H, N*H*), 2.18 (s, 6H, *p*-Mes), 1.56 (s, 12H, *o*-Mes). $^{13}C\{^1H\}$ NMR (chloroform-*d*): δ 164.4 (1:1:1:1 q, $^1J_{CB}$ = 49.1 Hz, *ipso*-BPh_4^-), 157.0 (s, dbf-quaternary), 136.5 (s, *m*-BPh_4^-), 134.5 (s), 133.9 (s, dbf-$C_{2/8}$), 133.6 (s), 132.5 (d, $^2J_{CP}$ = 9.8 Hz, *o*-PPh_2), 131.2 (s), 129.6 (s, *p*-PPh_2), 129.3 (s, *m*-PPh_2), 128.5 (s, *m*-Mes), 127.4 (s, dbf-$C_{1/9}$), 125.5 (s, *o*-BPh_4^-), 125.1 (s) 124.2 (d, $^2J_{CP}$ = 6.0 Hz, dbf-$C_{3/7}$), 123.4 (s), 121.6 (s, *p*-BPh_4^-), 20.8 (s, *o*-Mes (CCH_3)), 20.2 (s, *p*-Mes (CCH_3)). *ipso*-PPh_2 not observed. ^{11}B NMR (chloroform-*d*): δ −6.5 (br s). Anal. Calcd (%) for $C_{78}H_{69}BN_2OP_2$: C, 83.39; H, 6.20; N, 2.49. Found: C, 83.24; H, 6.11; N, 2.51.

Synthesis of [H_2-4,6-(MesN=PPh_2)$_2$dibenzofuran][BPh_4]$_2$ (1c). An excess of 1 M aqueous HCl (0.50 mL, 0.50 mmol) was added to a suspension of **L** (0.110 g, 0.137 mmol) in methanol (5 mL). With stirring, a slight excess of $NaBPh_4$ (0.112 g, 0.327 mmol) in MeOH (5 mL) was added, immediately yielding a fluffy white precipitate. Stirring was continued for another 5 min. The precipitate was collected by filtration, washed three times with methanol, and dried *in vacuo* to give the product in 91.2% yield (0.170 g, 0.125 mmol). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 28.1 (s). ^1H NMR (acetone-d_6): δ 8.56 (d, 2H, $^3J_{HH}$ = 7.8 Hz, dbf-$C_{1/9}H$), 8.14 (d, 2H, $^3J_{HP}$ = 9.7 Hz, N*H*), 8.08 (dd, 2H, $^3J_{HP}$ = 14.3 Hz, $^3J_{HH}$ = 7.8 Hz, dbf-$C_{3/7}H$), 7.61 (td, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HP}$ = 1.4 Hz, dbf-$C_{2/8}H$), 7.06 (t, 4H, $^3J_{HH}$ = 7.4 Hz, *p*-PPh_2), 6.84 (td, 8H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 3.8 Hz, *m*-PPh_2), 6.78−6.65 (m, 24H, *o*-BPh_4^- + *o*-PPh_2), 6.47 (t, 16H, $^3J_{HH}$ = 7.2 Hz, *m*-BPh_4^-), 6.33 (t, 8H, $^3J_{HH}$ = 7.2 Hz, *p*-BPh_4^-), 6.22 (s, 4H, *m*-Mes), 1.63 (s, 6H, *p*-Mes), 1.26 (s, 12H, *o*-Mes). ^{13}C NMR (acetone-d_6): 165.0 (1:1:1:1 q, $^1J_{CB}$ = 49.4 Hz, *ipso*-BPh_4^-), 157.6 (d, J_{CP} = 3.4 Hz), 138.2 (s), 137.1 (1:1:1:1 q, $^3J_{CB}$ = 1.4 Hz, *m*-BPh_4^-), 137.0 (br s), 135.0 (s), 134.3 (d, J_{CP} = 11.4 Hz), 132.6 (s), 131.1 (s), 130.9 (s), 130.7 (d, J_{CP} = 1.9 Hz), 130.3 (s), 129.8 (s), 127.8 (s), 127.0 (d, J_{CP} = 11.7 Hz), 126.1 (1:1:1:1 q, $^2J_{CB}$ = 2.8 Hz, *o*-BPh_4^-), 122.3 (1:1:1:1 q, $^4J_{CB}$ = 0.5 Hz, *p*-BPh_4^-), 116.1 (s), 20.8 (s, *p*-Mes (CCH_3)), 19.8 (s, *o*-Mes (CCH_3)). ^{11}B NMR (acetone-d_6): δ −6.5 (br s). Anal. Calcd (%) for $C_{102}H_{90}B_2N_2OP_2 \cdot C_3H_6O$: C, 83.99; H, 6.44; N, 1.87. Found: C, 83.89; H, 6.19; N, 1.94.

Synthesis of [4,6-(MesN=PPh_2)$_2$dibenzofuranMgBu][$B(C_6F_5)_4$] (2a). Under argon, a 50 mL round-bottom flask was charged with 0.1791 g (0.1207 mmol) of **1a** to which 12 mL of benzene was added. Di(*n*-butyl)magnesium (0.112 mL of 1.0 M solution in heptane, 0.11 mmol) was slowly injected, and evolution of a colorless gas was noted. The solution was stirred for 50 min; then benzene was removed *in vacuo*. This afforded the desired product as a pale yellow solid in 73% yield (0.1286 g, 0.08226 mmol). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 23.0 (s). ^1H NMR (benzene-d_6): δ 7.80 (d, $^3J_{HH}$ = 6.0 Hz, 2H, dbf-$C_{1/9}H$), 7.28 (dd, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 9.2 Hz, 8H, *o*-PPh_2), 7.09−6.97 (br ov m, 6H, dbf-$C_{2/8}H$ + *p*-PPh_2), 6.97−6.80 (br ov m, 10H, dbf-$C_{3/7}H$ + *m*-PPh_2), 6.36 (s, 4H, *m*-Mes), 2.04 (s, 6H, *p*-Mes), 1.50 (s, 12H, *o*-Mes), 1.38−1.32 (ov m, 4H, $MgCH_2CH_2CH_2CH_3$), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $MgCH_2CH_2CH_2CH_3$), −0.13 (t, $^3J_{HH}$ = 9.2 Hz, 2H, $MgCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 156.8 (s, dbf-quaternary), 137.3 (s, *p*-Mes (CCH_3)), 135.6 (d, $^2J_{CP}$ = 6.8 Hz, dbf-quaternary), 134.1 (d, $^2J_{CP}$ = 9.1 Hz, *o*-PPh_2), 133.9 (s), 133.7 (d, $^1J_{CP}$ = 45.5 Hz, dbf-$C_{4/6}$), 133.1 (d, $^2J_{CP}$ = 9.8 Hz, dbf-$C_{3/7}$), 130.0 (s, *m*-Mes), 129.6 (s), 129.4 (s), 128.1 (s), 126.4 (s), 125.3 (d, J_{CP} = 8.3 Hz), 112.7 (d, $^1J_{CP}$ = 106 Hz, *ipso*-PPh_2), 32.0, 30.2 (s, $MgCH_2CH_2CH_2CH_3$), 20.6 (s, *p*-Mes (CCH_3)), 20.1 (s, *o*-Mes (CCH_3)), 14.1 (s,

$MgCH_2CH_2CH_2CH_3$), 12.0 (s, $MgCH_2CH_2CH_2CH_3$). B-$(C_6F_5)_4^-$ resonances not reported. ^{19}F NMR (benzene-d_6): δ −130.7 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-C_6F_5), −161.7 (t, $^3J_{FF}$ = 22 Hz, 4F, *p*-C_6F_5), −165.5 (m, 8F, *m*-C_6F_5). ^{11}B NMR (benzene-d_6): δ −15.8 (br s). Anal. Calcd (%) for $C_{82}H_{57}BF_{20}MgN_2OP_2$: C, 62.99; H, 3.68; N, 1.79. Found: C, 62.17; H, 3.86; N, 1.84.

Synthesis of [4,6-(MesN=PPh$_2$)$_2$dibenzofuranMgBu][BPh$_4$] (2b). Under argon, a 100 mL round-bottom flask was charged with 0.7422 g (0.6608 mmol) of **1b** to which 40 mL of benzene was added. A solution of Di(*n*-butyl)magnesium (0.67 mL of 1.0 M solution in heptane, 0.67 mmol) in 4 mL of benzene was slowly injected. Evolution of a gas was noted, followed by a color change from yellow to pale pink as the reaction mixture was stirred for 30 min at ambient temperature. The solvent was removed *in vacuo*, yielding the desired material as a white solid (0.7242 g, 0.6017 mmol, 91.07%). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 23.2 (s). ^1H NMR (benzene-d_6): δ 8.09−8.01 (br m, 8H, *o*-BPh_4^-) 7.64 (d, $^3J_{HH}$ = 6.0 Hz, 2H, dbf-$C_{1/9}H$), 7.26 (dd, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 9.1 Hz, 8H, *o*-PPh_2), 7.19 (ov t, $^3J_{HH}$ = 7.4 Hz, 4H, *p*-BPh_4^-), 7.09−6.97 (br ov m, 14H, dbf-$C_{2/8}H$ + *p*-PPh_2 + *m*-BPh_4^-), 6.97−6.84 (br ov m, 10H, dbf-$C_{3/7}H$ + *m*-PPh_2), 6.35 (s, 4H, *m*-Mes), 2.03 (s, 6H, *p*-Mes), 1.52 (s, 12H, *o*-Mes), 1.38−1.32 (ov m, 4H, $MgCH_2CH_2CH_2CH_3$), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $MgCH_2CH_2CH_2CH_3$), −0.13 (t, $^3J_{HH}$ = 9.2 Hz, 2H, $MgCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 165.4 (1:1:1:1 q, $^1J_{CB}$ = 48.3 Hz, *ipso*-BPh_4^-), 156.6 (s, dbf-quaternary), 137.5 (s, *m*-BPh_4^-), 137.2 (s), 135.7 (d, $^2J_{CP}$ = 6.8 Hz, dbf-quaternary), 133.9 (ov, *o*-PPh_2), 133.8 (s), 133.1 (d, $^2J_{CP}$ = 9.1 Hz, dbf-$C_{3/7}$), 129.9 (s, *m*-Mes), 129.7 (s), 129.5 (s), 128.1 (s), 126.5 (s), 126.2 (s, *o*-BPh_4^-), 125.4 (d, J_{CP} = 8.3 Hz), 122.2 (s, *p*-BPh_4^-), 112.2 (d, $^1J_{CP}$ = 107 Hz, *ipso*-Ph), 32.0, 30.2 (s, $MgCH_2CH_2CH_2CH_3$), 20.6 (s, *p*-Mes (CCH_3)), 20.3 (s, *o*-Mes (CCH_3)), 14.0 (s, $MgCH_2CH_2CH_2CH_3$), 11.9 (s, $MgCH_2CH_2CH_2CH_3$). Dbf-$C_{4/6}$ not observed. ^{11}B NMR (benzene-d_6): δ −5.6 (br s). Anal. Calcd (%) for $C_{82}H_{77}BMgN_2OP_2$: C, 81.81; H, 6.46; N, 2.33. Found: C, 80.85; H, 6.33; N, 2.72.

General Procedures for the Polymerization of ε-Caprolactone. Both **2a** and **2b** were found to be active in the polymerization of ε-caprolactone. Representative procedures for examination of polymerization activity by NMR spectroscopy and preparation of polymer samples for GPC analysis are described herein. GPC analyses were performed using a Viscotek Triple Detector GPC system outfitted with a model 270 Dual Detector Platform (four-capillary viscometer and light-scattering detector). Polymer samples were run in THF at a concentration of 1 mg/mL.

***In Situ* NMR Analysis of ε-Caprolactone Polymerization.** A representative procedure for the polymerization of ε-caprolactone by **2b** is described herein. All NMR-scale polymerization procedures using **2a** and **2b** made use of similar methods. Polymerization reactions at low temperature (−40 to 0 °C) were performed by allowing the solution containing initiator to equilibrate within the precooled instrument for 20 min prior to monomer injection. Low-temperature reactions were run in toluene-d_8 rather than benzene-d_6.

An NMR tube was charged with 0.0010 g (0.00083 mmol) of **2b** to which 2.2 mL of benzene-d_6 was added. The tube was capped with a rubber NMR tube septum, which was then wrapped in parafilm and shaken vigorously. Dry, distilled ε-caprolactone (48 μL, 0.43 mmol, 5.2×10^2 equiv) was measured under an inert atmosphere into a 100.0 μL gastight microsyringe, which was sealed by inserting the needle into a rubber septum until immediately before addition to the reaction mixture. Prior to monomer injection, all appropriate instrumental parameters were set and NMR spectra of the initiator were collected. The sample was then removed from the instrument, injected with the monomer, shaken, and reinserted into the NMR spectrometer. Collection of NMR data began within 60 s of injection of the monomer. Conversion percentages were determined by integration of the most downfield methylene resonance (−COOCH_2−) of the polymer (^1H NMR (benzene-d_6): δ 3.98 (t, $^3J_{HH}$ = 6.1 Hz, 2H)) relative to those of the residual monomer (^1H NMR (benzene-d_6): δ 3.59 (t, $^3J_{HH}$ = 6.1 Hz, 2H)), as these resonances were most clearly resolved from all other monomer, polymer, initiator, and residual solvent resonances.

Preparation of Isolated Poly(ε-caprolactone) Samples. A representative procedure for the polymerization of ε-caprolactone by **2b** is described herein. All preparations of polymer and oligomer samples for GPC, NMR, or MALDI-ToF analysis used a similar methodology.

Under an inert atmosphere, a 50 mL round-bottom flask was charged with 0.0310 g (0.0258 mmol) of **2b**, to which 10 mL of benzene was added. The solution was stirred rapidly, and 1.20 mL (1.24 g, 10.8 mmol, 418 equiv) of ε-caprolactone was injected, resulting in the immediate formation of a thick gel. After 30 min, the reaction mixture was transferred to a 60 mL syringe and added to 100 mL of rapidly stirring methanol under aerobic conditions. This resulted in the immediate precipitation of polymer, which formed a single solid mass that could easily be mechanically separated. The polymer was dried *in vacuo*, yielding 0.700 g of material (∼57%).

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Supporting Information Available: Supporting experimental and X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.