Trimetallic magnesium complexes bearing amine-bis(benzotriazole phenolate) derivatives as bifunctional catalysts for ring-opening polymerization and CO_2/epoxide coupling

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Experimental

General conditions

All manipulations were carried out under a dry nitrogen atmosphere. Solvents and reagents were dried by refluxing for at least 24 h over sodium/benzophenone (hexane, toluene, tetrahydrofuran (THF)), or over phosphorus pentoxide (CH_2Cl_2). Deuterated solvents were dried over 4 Å molecular sieves. Mg^{n}Bu$_2$ (1.0 M in heptane), N,N-dimethylethylenediamine, N-(2-aminoethyl)piperidine, 2-(2H-benzotriazol-2-yl)-4-methylphenol (^{Cl}**BTP**-H) and paraformaldehyde were purchased and used without further purification. Benzyl alcohol, cyclohexene oxide (CHO), ε-caprolactone (ε-CL), n-Bu$_4$NCl, n-Bu$_4$NBr and n-Bu$_4$NI were purified before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Aveance (300 and 400 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a Jasco PU-2080 plus system equipped with a RI-2031 detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 μ 103 Å and the calibration curve used to calculate M_n(GPC) was produced from polystyrene standards. The calibration curve was constructed by ten polystyrene standards, in which their molecular weights range from 1580 to 288000. The GPC results were calculated using the Scientific Information Service Corporation (SISC) chromatography data solution 3.1 edition. UV/Vis absorption spectra were taken on an

Evolution 201 UV-Visible spectrophotometer. Fluorescent measurements were recorded with a Hitachi F-4500.

Synthesis of ^{CINN}BiBTP-H$_2$ ligand

To a mixture of 2-(2H-benzotriazol-2-yl)-4-methylphenol (4.72 g, 21 mmol), N,N-dimethylethylenediamine (1.1 mL, 10 mmol), and paraformaldehyde (0.66 g, 22 mmol) were dissolved in toluene (2 mL). The solution was heated under reflux for 2 days and then cooled to room temperature. The residue was extracted with ethyl acetate (3 x 50 mL) and the organic layers were dried over MgSO$_4$. The final solution was removed from the solvent under vacuum to give pale yellow solids. Yield: 4.49 g (80%). Anal. calc. for C$_{32}$H$_{34}$N$_8$O$_2$: N, 19.91; C, 68.31; H, 6.09. Found: N, 19.65; C, 67.75; H, 6.09%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.92-7.88 (m, 4H, Ar-H), 7.78 (s, 2H, Ar-H), 7.43-7.39 (m, 4H, Ar-H), 7.09 (s, 2H, Ar-H), 3.88 (s, 4H, -NCH_2), 2.72 (t, 2H, -NCH_2), 2.53 (t, 2H, -NCH_2), 2.30 (s, 6H, Ar-CH_3), 2.13 (s, 6H, -NCH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 147.7, 143.4, 132.16, 128.4, 126.9, 126.1, 123.1, 117.9 (*Ph*), 56.5, 54.4, 50.9, 45.4 (-NCH$_2$-), 20.3 (Ar-CH$_3$).

Synthesis of ^{CIPP}BiBTP-H$_2$ ligand

To a mixture of 2-(2H-benzotriazol-2-yl)-4-methylphenol (4.72 g, 21 mmol), N-(2-aminoethyl)piperidine (1.6 mL, 10 mmol), and paraformaldehyde (0.66 g, 22 mmol) were dissolved in toluene (2 mL). The solution was heated under reflux for 2 days and then cooled to room temperature. The residue was extracted with ethyl acetate (3 x 50 mL) and the organic layers were dried over MgSO$_4$. The final solution was removed from the solvent under vacuum to give pale pink solids. Yield: 5.12 g (85%). Anal. calc. for C$_{35}$H$_{38}$N$_8$O$_2$: N, 18.69; C, 69.55; H, 6.40. Found: N, 18.59; C, 69.75; H, 6.35%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.92-7.88 (m, 4H, Ar-H), 7.78 (s, 2H, Ar-H), 7.43-7.39 (m, 4H, Ar-H), 7.09 (s, 2H, Ar-H), 3.88 (s, 4H, -NCH_2), 2.73 (t, 2H, -NCH_2), 2.55 (t, 2H, -NCH_2), 2.30 (s, 6H, Ar-CH_3), 2.26 (br, 4H, -NCH_2), 1.49-1.45 (m,

4H, -NCH$_2$CH_2-), 1.36-1.32 (m, 2H, -NCH$_2$CH$_2$CH_2-). ^{13}C NMR (CDCl$_3$, ppm): δ 147.7, 143.4, 132.16, 128.3, 126.9, 126.1, 123.0, 117.8 (*Ph*), 55.8, 54.6, 54.3, 49.9 (-NCH_2-), 25.4 (-NCH$_2$CH_2-), 24.2 (-NCH$_2$CH$_2$CH_2-), 20.3 (Ar-CH_3).

Synthesis of complex [(^{CINN}BiBTP)$_2$Mg$_3$(OBn)$_2$] (1)

To a solution of ^{CINN}**BiBTP**-H$_2$ (1.12 g, 2.0 mmol) in toluene (40 mL) was slowly added Mg^{n}Bu$_2$ (3.0 mL, 1.0 M in heptane, 3.0 mmol) at 0 ^{o}C. The mixture was stirred for 4 h and then BnOH (0.21 mL, 2.0 mmol) was added and stirred for 16 h at 25 ^{o}C. Volatile materials were removed under vacuum to yield pale yellow solids. The solid was washed with hexane (2 x 40 mL), and the yellow powder was obtained after filtration. Yield: 0.98 g (70%). Anal. calc. for C$_{78}$H$_{78}$Mg$_3$N$_{16}$O$_6$: N, 15.91; C, 66.51; H, 5.58. Found: N, 15.62; C, 66.94; H, 5.74%. Pale yellow crystals were grown from the saturated toluene solution. Complex **1** displays multiple signals of the ligand in NMR spectra (CDCl$_3$); reasonable assignments of these spectral data are impracticable. Attempts to obtain reasonable assignments using the variable temperature NMR technique for complex **1** proved unsuccessful.

Synthesis of complex [(^{CIPP}BiBTP)$_2$Mg$_3$(OBn)$_2$] (2)

To a solution of ^{CIPP}**BiBTP**-H$_2$ (1.20 g, 2.0 mmol) in toluene (30 mL) was slowly added Mg^{n}Bu$_2$ (3.0 mL, 1.0 M in heptane, 3.0 mmol) at 0 ^{o}C. The mixture was stirred for 4 h and then BnOH (0.21 mL, 2.0 mmol) was added and stirred for 16 h at 25 ^{o}C. Volatile materials were removed under vacuum to yield pale yellow solids. The resulting solid was washed with hexane (2 x 40 mL), and the yellow powder was obtained after filtration. Yield: 1.22 g (82%). Anal. calc. for C$_{84}$H$_{86}$Mg$_3$N$_{16}$O$_6$: N, 15.05; C, 67.77; H, 5.82. Found: N, 14.96; C, 67.49; H, 5.58%. Pale yellow crystals were grown from the saturated THF solution. Complex **2** displays multiple signals of the ligand in NMR spectra (CDCl$_3$); reasonable assignments of

these spectral data are impracticable.

Polymerization of ε-CL initiated by the magnesium amine-bis(BTP) complexes 1-2

A typical polymerization procedure was exemplified by the synthesis of PCL-200 (the '200' indicates the $[ε-CL]_0/2[1]_0 = 200$ ratio) using **1** as an initiator at 30 °C. Polymerizations were carried out under a dry nitrogen atmosphere. To a mixture of $[(^{CINN}\textbf{BiBTP})_2Mg_3(OBn)_2]$ (**1**) (0.14 g, 0.1 mmol) and ε-CL (4.4 mL, 40 mmol) in THF (10 mL) was stirred at 30 °C for 0.5 h. The conversion yield (99%) of PCL-200 was analyzed by ^1H NMR spectroscopic studies. After the reaction was quenched by the addition of excess water (0.5 mL), the polymer was precipitated into hexane (100 mL). The final polymer was then redissolved in THF (20 mL) and purified upon precipitation again in MeOH (150 mL), collected and dried under vacuum. Yield: 4.10 g (93 %).

Cycloaddition of CO_2 and CHO catalyzed by complexes 1-2 in the presence of quaternary ammonium salts (n-Bu$_4$NX)

A representative procedure for the cycloaddition of cyclohexene oxide with CO_2 (Table 2, entry 7) was exemplified. Catalyst **1** (0.070 g, 0.05 mmol) was dissolved in 5 mL of neat cyclohexene oxide under a dry nitrogen atmosphere. To a mixing solution was added to the 50-mL autoclave with magnetic stirrer and (co-catalyst) n-Bu$_4$NBr (1.605 g, 5 mmol) under CO_2 atmosphere. CO_2 was then charged into the reactor until the pressure of 300 psi was reached, and the stirrer was started. The reaction was performed at 80 °C for 16 h. Then the reactor was placed into ice water and excess CO_2 was released. The CHO conversion (98%) was analyzed by ^1H NMR spectroscopic studies. Spectral characteristics of cyclohexene carbonate: (mutiplets : δ = 3.9 ppm (*trans*-CHC) or 4.63 ppm (*cis*-CHC). The mixture was then quenched by the addition of 1 N HCl solution (1.0 mL), the carbonate was extracted with hexane (3 x 50 mL) and the organic layers were dried over anhydrous $MgSO_4$. The final

solution was removed from the solvent under vacuum to give white oil. Spectrum of *cis*-CHC: ^{1}H NMR (CDCl$_3$, ppm): δ 4.63 (m, 2H, OC*H*CH$_2$CH$_2$), 1.81 (m, 4H, OCHC*H$_2$*CH$_2$), 1.54 (m, 2H, OCHCH$_2$C*H$_2$*), 1.37 (m, 2H, OCHCH$_2$C*H$_2$*). IR ν(C=O), CH$_2$Cl$_2$: 1870 cm^{-1} (w), 1823 cm^{-1} (sh), 1801 cm^{-1} (s), 1793 cm^{-1} (sh).

X-ray crystallographic studies

Suitable crystals of ^{CINN}**BiBTP**-H, complexes **1** and **2** were mounted onto glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas to collect diffraction data at 100K using Bruker APEX2 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.5° per frame). The absorption correction was based on the symmetry-equivalent reflections using SADABS program.[S1] The space group determination was based on a check of the Laue symmetry and systematic absence, and was confirmed by the structure solution. The structures were solved with direct methods using a SHELXTL package.[S1] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H-atoms. Drawing of the molecules was done using Oak Ridge Thermal Ellipdoid Plots (ORTEP).[S2] Crystallographic data of ^{CINN}**BiBTP**-H, complexes **1** and **2** are summarized in Table S1. The selected bond length (Å) and bond angles (°) for complexes **1-2** were listed in Table S2.

Reference:

S1 G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

S2 Burnett, M. N. & Johnson, C.K.(1996) ORTEPIII, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.
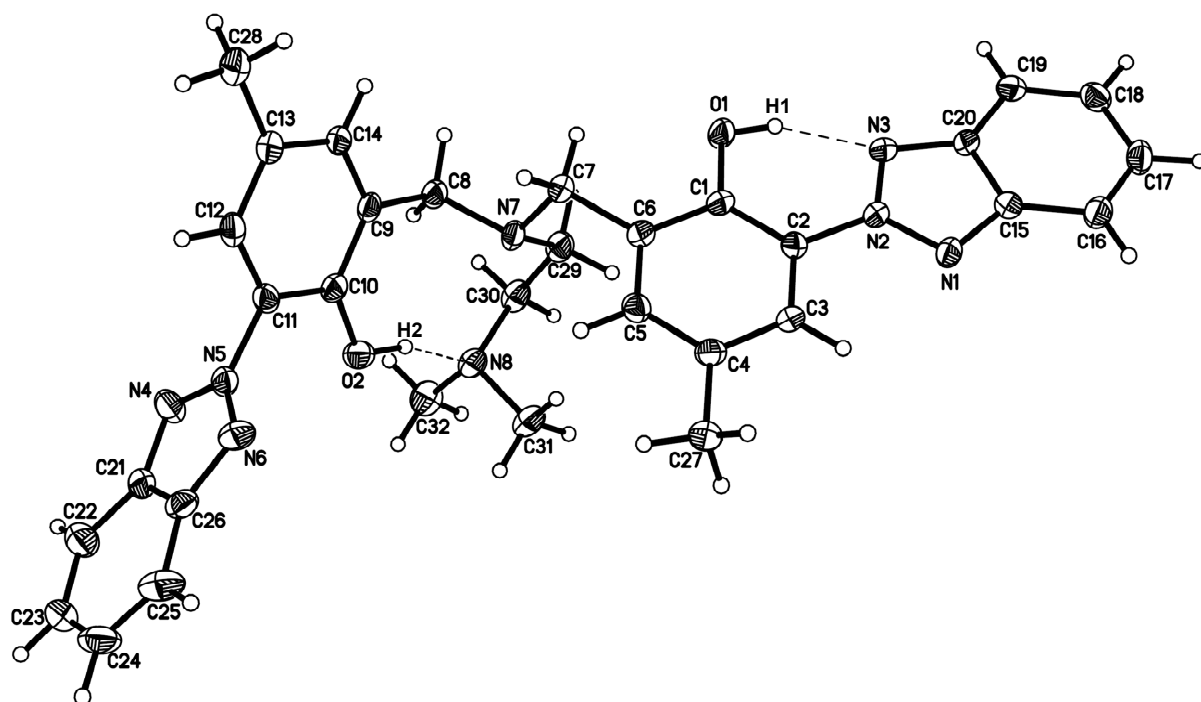
Fig. S1 ORTEP drawing of compound ^{CINN}**BiBTP**-H with probability ellipsoids drawn at level 50%. Selected bond lengths/Å and angles/deg: N(7)-C(7) 1.467(3), N(7)-C(8) 1.471(2), C(6)-C(7) 1.511(3), C(8)-C(9) 1.503(3), N(3)···H(1) 1.793(3), N(8)···H(2) 1.678(3), O(1)-H(1)···N(3) 151.3 (2), O(2)-H(2)···N(8) 162.6 (2).
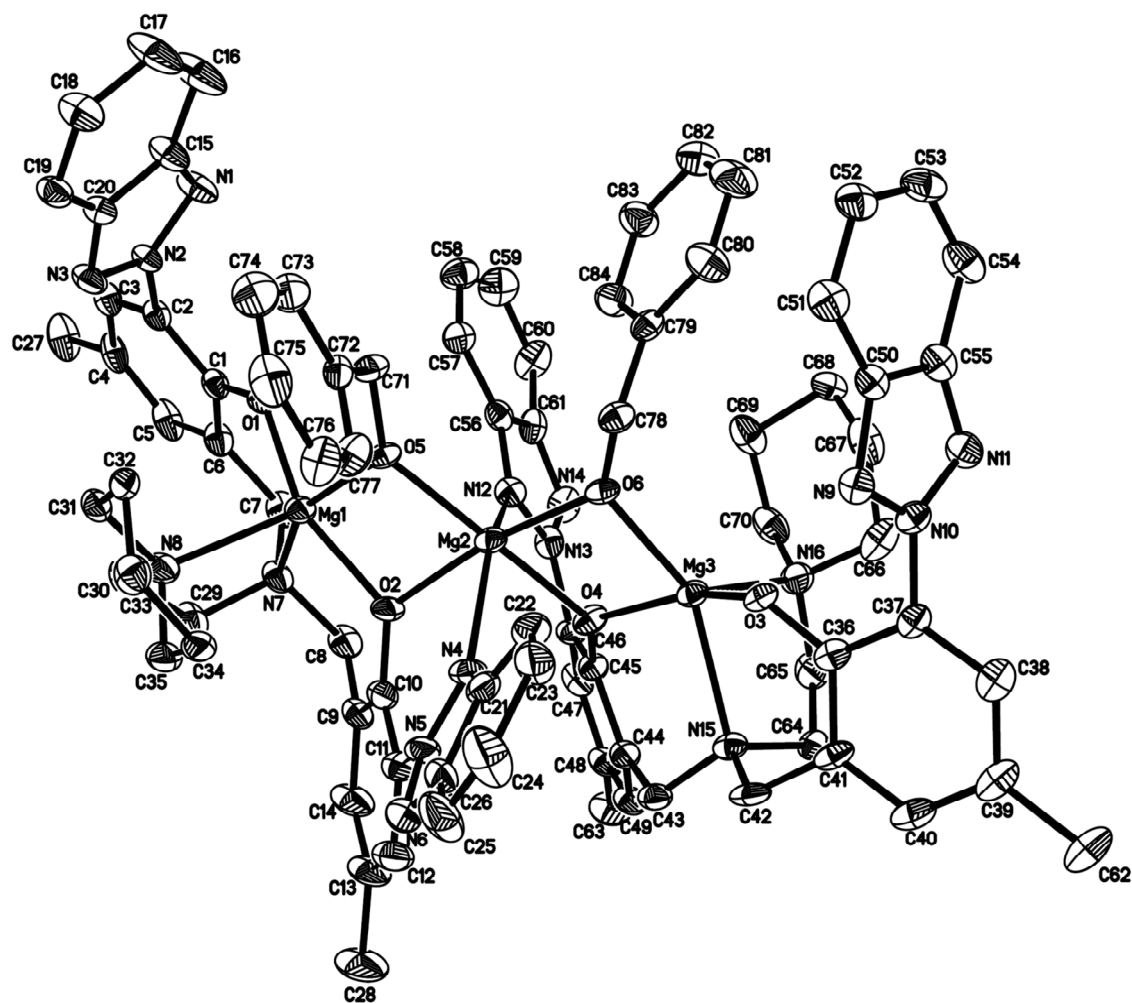
Fig. S2 ORTEP drawing of complex **2** with probability ellipsoids drawn at level 30%.
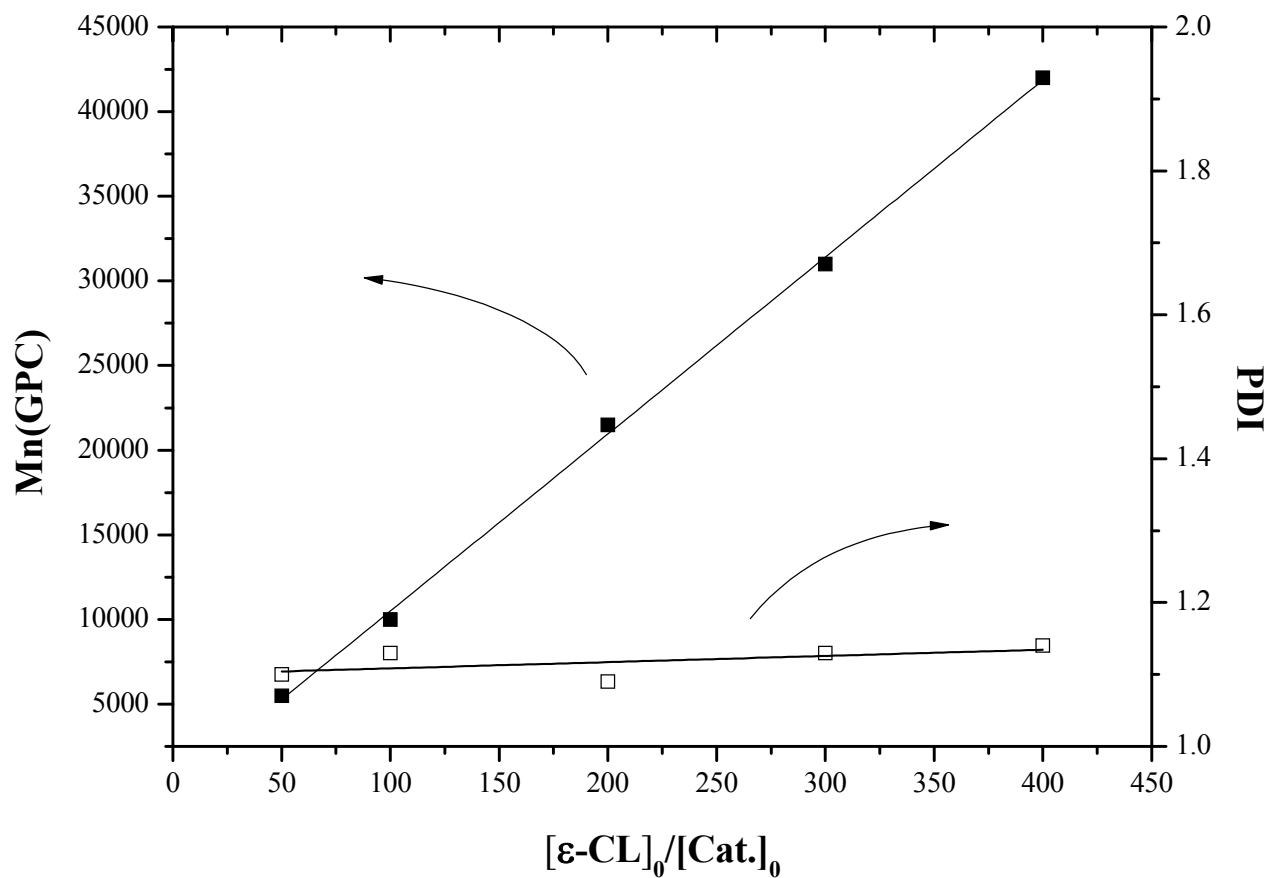
Hydrogen atoms are omitted for clarity.

Fig. S3 Polymerization of ε-CL catalyzed by magnesium complex **1** in THF at 30 °C. The relationship between M_n(■)PDI(□) of polymer and the initial molar ratio $[\varepsilon\text{-CL}]_0/[\text{Cat.}]_0$ is shown.
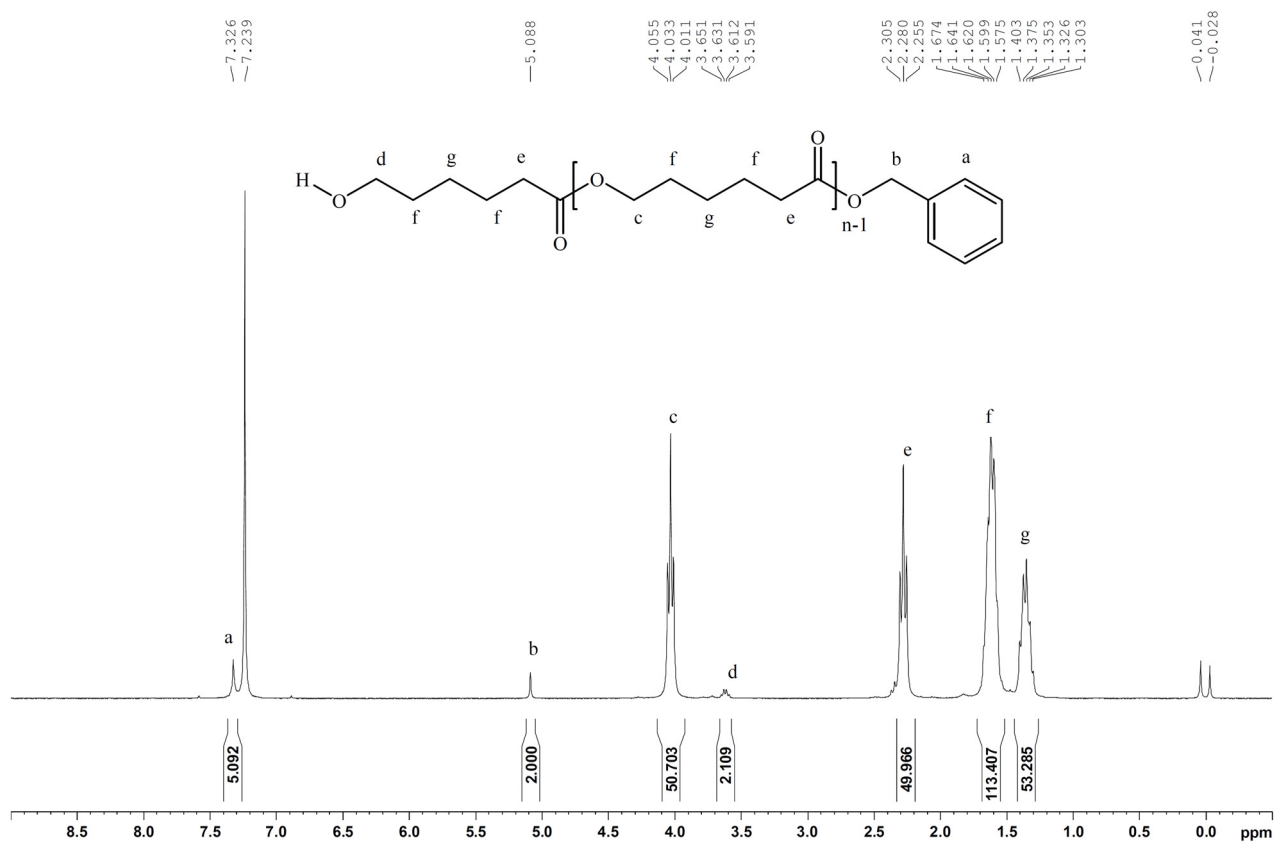
Fig. S4 ^{1}H NMR spectra of PCL (Table 1, entry 3) in CDCl$_3$
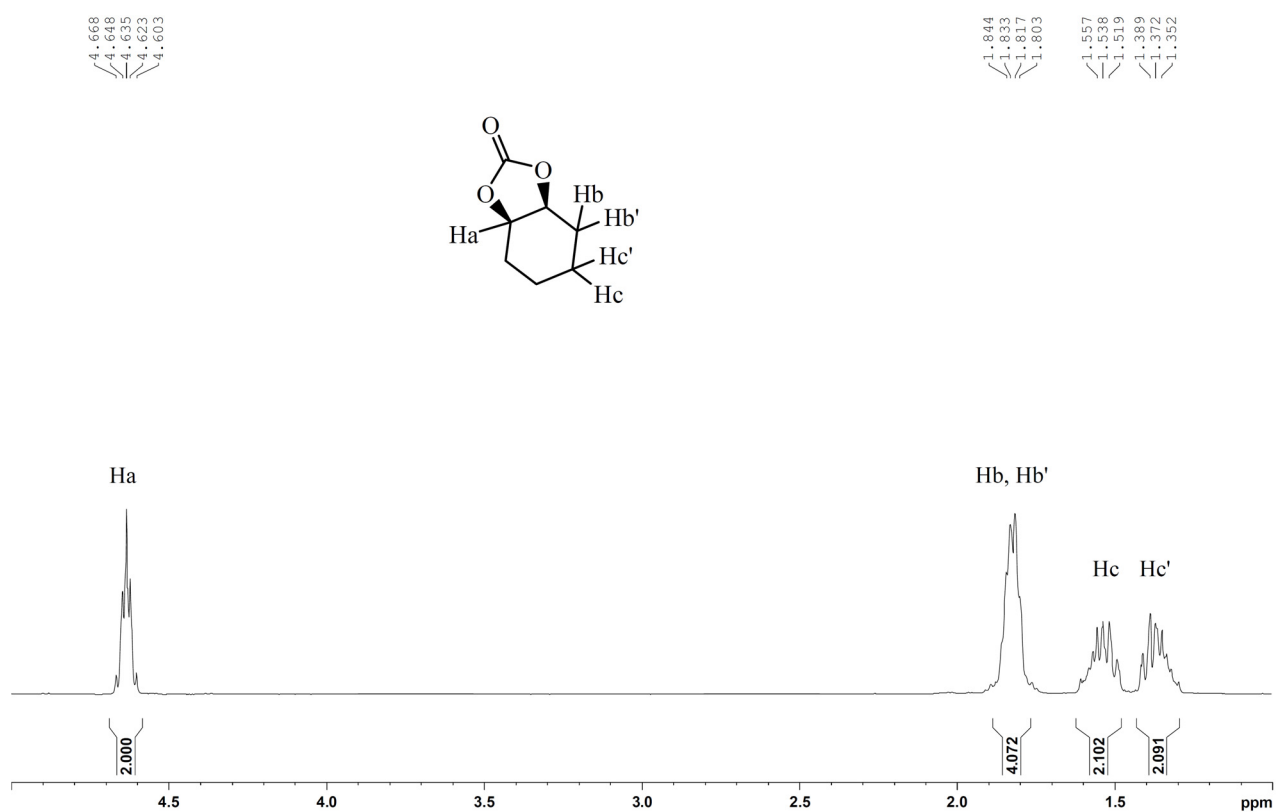
Fig. S5 ^{1}H NMR spectra of *cis*-cyclohexene carbonate (Table 2, entry 7) in CDCl$_3$

Reference:

(a) D. J. Darensbourg, S. J. Lewis, J. L. Rodgers and J. C. Yarbrough, *Inorg. Chem.*, 2003, **42**, 581–589. (b) A. Buchard, M. R. Kember, K. G. Sandemanb and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214.

Fig. S6 Plot of M_n and PDI (determined from GPC analysis) vs time for the polymerization of ε-caprolactone using Mg complex **1** as the initiator.
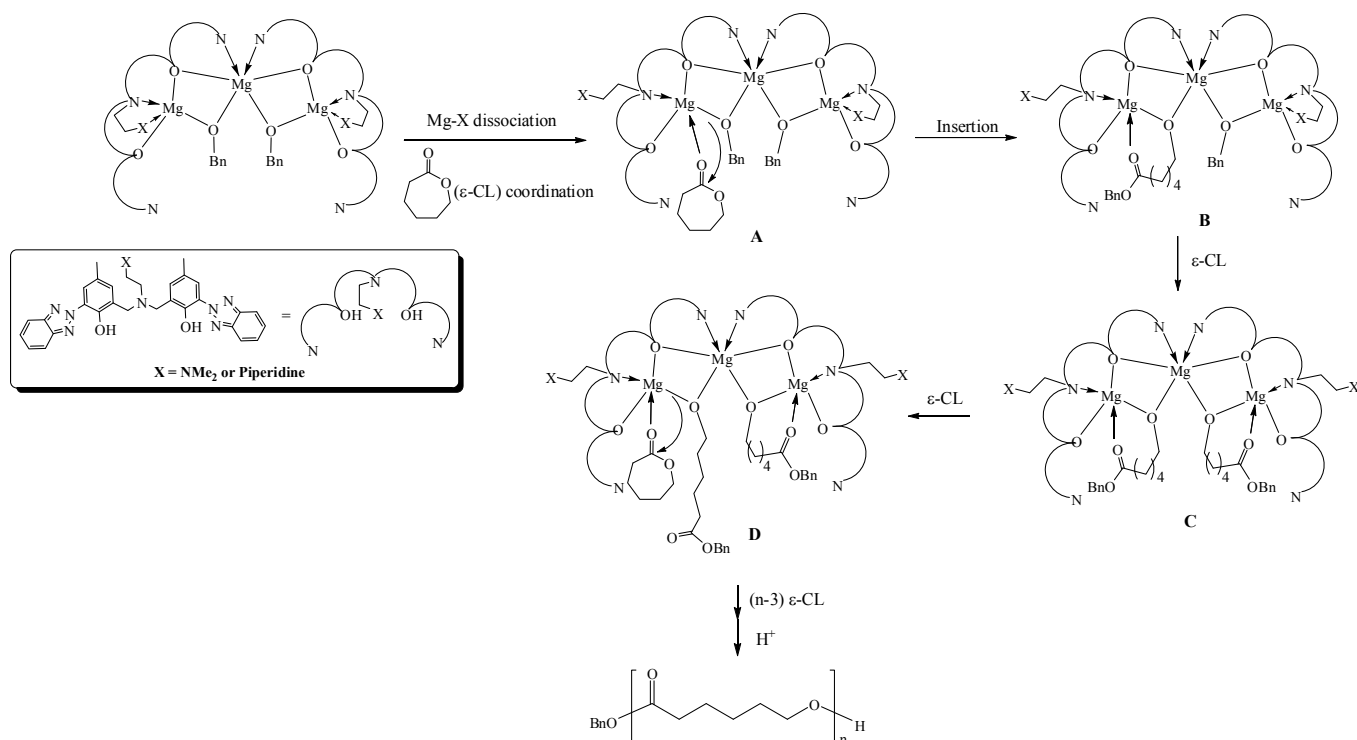
Fig. S7 Proposed mechanism for the ROP of ε-caprolactone initiated by [(BiBTP)₂Mg₃(OBn)₂].
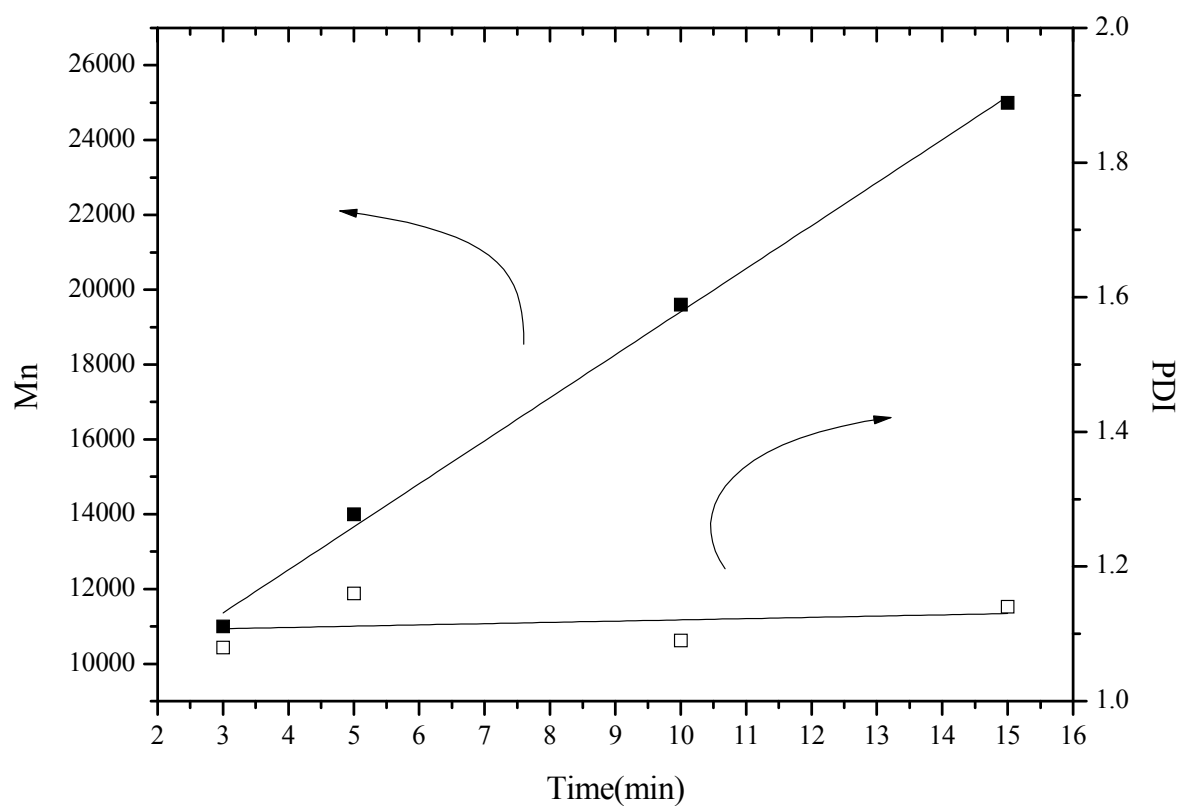
The possible reaction mechanism is proposed as shown in Fig. S7. The ROP of ε-caprolactone (ε-CL) initiated by Mg complex **1** may proceed by the coordination of a molecule of ε-CL on one of the Mg atom along with the dissociation of the nitrogen atom (dimethylamine group) from the metal center, leading to the formation of intermediate **A**. Following the attack by the benzylalkoxy group on the carbonyl group of ε-CL, **B** is formed. By the sequential coordination of ε-CL and insertion of the benzylalkoxy in another magnesium center, intermediate **C** is formed. After initiation of ROP, propagation begins (eg. Intermediate **D**) and continues until all monomers are consumed, yielding polyesters coordinated on the Mg atoms. By terminating the reaction, polyesters with one hydroxyl end group could be obtained.

Table S1 Crystallographic data of ligand ^{CINN}**BiBTP**-H and complexes **1-2**

	^{CINN}**BiBTP**-H	**1**·C_7H_8	**2**·$0.5C_4H_8O$
formula	$C_{32}H_{34}N_8O_2$	$C_{89}H_{78}Mg_3N_{16}O_6$	$C_{86}H_{90}Mg_3N_{16}O_{6.5}$
Formula weight	562.67	1540.60	1524.68
Temp (K)	100(2) K	100(2) K	100(2) K
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2(1)/c$
a (Å)	10.2090(3)	14.4831(3)	12.8610(2)
b (Å)	15.6603(5)	17.4925(3)	22.5964(5)
c (Å)	19.1412(6)	17.6584(3)	29.0187(6)
α (deg)	77.598(2)	93.0500(10)	90
β (deg)	80.191(2)	109.1210(10)	106.3330(10)
γ (deg)	73.079(2)	105.8990(10)	90
$V(\text{Å}^3)$	2840.30(15)	4014.55(13)	8092.9(3)
Z	4	2	4
$D_{calc}(\text{Mg/m}^3)$	1.316	1.274	1.251
μ (Mo Kα)(mm^{-1})	0.086	0.103	0.102
$F(000)$	1192	1616	3224
Reflections collected	49543	70663	73363
No. of parameters	765	1044	1031
Indep. reflns (R_{int})	14069 (0.0425)	19916 (0.0623)	20031 (0.1256)
$R1[I > 2\sigma(I)]$	0.0517	0.0579	0.0988
w$R2$ [$I > 2\sigma(I)$]	0.1133	0.1316	0.2480
Goodness-of-fit on F^2	1.046	1.037	1.002

Table S2 Selected bond length (Å) and bond angles (°) for complexes 1 and 2

Complex 1			
Mg(1)-O(1)	1.9138(16)	Mg(1)-N(7)	2.2600(18)
Mg(1)-O(2)	1.9894(16)	Mg(1)-N(8)	2.1557(19)
Mg(1)-O(5)	1.9659(15)		
Mg(2)-O(2)	2.0344(15)	Mg(2)-O(6)	1.9804(15)
Mg(2)-O(4)	2.0060(17)	Mg(2)-N(4)	2.3189(18)
Mg(2)-O(5)	1.9621(16)	Mg(2)-N(12)	2.4361(19)
Mg(3)-O(3)	1.9347(15)		
Mg(3)-O(4)	1.9967(15)	Mg(3)-N(15)	2.249(2)
Mg(3)-O(6)	1.9696(17)	Mg(3)-N(16)	2.1638(19)
O(1)-Mg(1)-O(2)	152.58(7)	O(2)-Mg(1)-N(7)	87.18(7)
O(1)-Mg(1)-O(5)	95.94(7)	O(2)-Mg(1)-N(8)	107.66(7)
O(2)-Mg(1)-O(5)	80.63(6)	O(5)-Mg(1)-N(7)	162.14(7)
O(1)-Mg(1)-N(7)	88.86(7)	O(5)-Mg(1)-N(8)	113.89(7)
O(1)-Mg(1)-N(8)	98.63(7)	N(7)-Mg(1)-N(8)	82.18(7)
O(2)-Mg(2)-O(4)	96.37(6)	O(2)-Mg(2)-N(12)	76.98(6)
O(2)-Mg(2)-O(5)	79.62(6)	O(4)-Mg(2)-N(4)	85.62(7)
O(2)-Mg(2)-O(6)	170.83(7)	O(4)-Mg(2)-N(12)	75.48(6)
O(4)-Mg(2)-O(5)	166.16(7)	O(5)-Mg(2)-N(4)	106.12(7)
O(4)-Mg(2)-O(6)	77.47(6)	O(5)-Mg(2)-N(12)	90.70(7)
O(5)-Mg(2)-O(6)	107.94(7)	O(6)-Mg(2)-N(4)	95.61(6)
O(2)-Mg(2)-N(4)	76.99(6)	O(6)-Mg(2)-N(12)	107.57(6)
N(4)-Mg(2)-N(12)	145.69(7)		
O(3)-Mg(3)-O(4)	159.76(7)	O(4)-Mg(3)-O(6)	77.94(6)
O(3)-Mg(3)-O(6)	99.39(7)	O(4)-Mg(3)-N(15)	83.86(7)
O(3)-Mg(3)-N(15)	90.63(7)	O(4)-Mg(3)-N(16)	100.55(7)
O(3)-Mg(3)-N(16)	98.07(7)	O(6)-Mg(3)-N(15)	152.59(7)
N(15)-Mg(3)-N(16)	83.02(7)	O(6)-Mg(3)-N(16)	120.21(7)

Complex 2

Mg(1)-O(1)	1.916(3)	Mg(1)-N(7)	2.305(4)
Mg(1)-O(2)	1.980(4)	Mg(1)-N(8)	2.240(5)
Mg(1)-O(5)	2.002(3)		
Mg(2)-O(2)	2.016(4)	Mg(2)-O(6)	1.995(4)
Mg(2)-O(4)	2.013(3)	Mg(2)-N(4)	2.390(4)
Mg(2)-O(5)	1.989(3)	Mg(2)-N(12)	2.409(4)
Mg(3)-O(3)	1.932(3)		
Mg(3)-O(4)	1.985(4)	Mg(3)-N(15)	2.293(4)
Mg(3)-O(6)	1.998(3)	Mg(3)-N(16)	2.230(5)
O(1)-Mg(1)-O(2)	153.85(17)	O(2)-Mg(1)-N(7)	84.29(16)
O(1)-Mg(1)-O(5)	96.30(14)	O(2)-Mg(1)-N(8)	106.73(16)
O(2)-Mg(1)-O(5)	77.78(14)	O(5)-Mg(1)-N(7)	151.38(17)
O(1)-Mg(1)-N(7)	90.02(15)	O(5)-Mg(1)-N(8)	127.22(16)
O(1)-Mg(1)-N(8)	97.17(17)	N(7)-Mg(1)-N(8)	79.20(16)
O(2)-Mg(2)-O(4)	96.51(15)	O(2)-Mg(2)-N(12)	81.87(14)
O(2)-Mg(2)-O(5)	77.24(14)	O(4)-Mg(2)-N(4)	81.41(14)
O(2)-Mg(2)-O(6)	169.31(15)	O(4)-Mg(2)-N(12)	75.89(14)
O(4)-Mg(2)-O(5)	167.49(14)	O(5)-Mg(2)-N(4)	107.08(15)
O(4)-Mg(2)-O(6)	77.92(14)	O(5)-Mg(2)-N(12)	92.37(14)
O(5)-Mg(2)-O(6)	109.92(14)	O(6)-Mg(2)-N(4)	94.31(15)
O(2)-Mg(2)-N(4)	75.72(16)	O(6)-Mg(2)-N(12)	105.26(14)
N(4)-Mg(2)-N(12)	145.89(15)		
O(3)-Mg(3)-O(4)	155.14(16)	O(4)-Mg(3)-O(6)	78.50(13)
O(3)-Mg(3)-O(6)	97.35(14)	O(4)-Mg(3)-N(15)	84.75(14)
O(3)-Mg(3)-N(15)	88.72(14)	O(4)-Mg(3)-N(16)	96.15(17)
O(3)-Mg(3)-N(16)	106.37(18)	O(6)-Mg(3)-N(15)	152.45(16)
N(15)-Mg(3)-N(16)	80.33(15)	O(6)-Mg(3)-N(16)	122.84(15)

Table S3 Ring-opening polymerization of ε-caprolactone (ε-CL) catalyzed by complexes **1-2**[a]

Entry	Cat.	$[\varepsilon\text{-CL}]_0/[\text{Cat.}]_0/$ $[\text{BnOH}]_0$	t (min)	Conv. (%)[c]	M_n (calcd.)[d]	M_n (obsd.)[e]	M_n (NMR)[f]	PDI[g]
S1	**2**	50/1/0	180	99	2800	4000(2200)	2500	1.13
S2	**2**	100/1/0	180	99	5600	8200(4600)	4700	1.05
S3	**2**	400/1/0	180	95	21600	37300(20800)	23900	1.16
S4	**1**	100(100):1:0[h]	30(30)	99	11500	20900(11700)	11600	1.25
S5	**1**	400/1/0	3	27	6260	11000(6160)	6200	1.08
S6	**1**	400/1/0	5	35	8090	14000(7840)	8000	1.16
S7	**1**	400/1/0	10	50	11500	19600(11000)	11200	1.09
S8	**1**	400/1/0	15	61	14000	25000(14000)	14500	1.14

[a] $[\text{Cat.}]_0 = 0.01$ M, 10 mL THF, 30 °C. [b] Obtained from ^{1}H NMR determination. [c] Calculated from the molecular weight of ε-CL times $[\varepsilon\text{-CL}]_0/2[\text{Cat.}]_0$ times conversion yield plus the molecular weight of BnOH. [d] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56.[17] [e] Obtained from ^{1}H NMR analysis. [f] Obtained from GPC analysis. [g] Not determination. [h] Pre-polymerization of ε-CL with initiator for 30min followed by the addition of ε-CL and stirred for another 30 min.