BDI*MgX(L) where X = ⁿBu and O^tBu and L = THF, py and DMAP.

The rates of kinetic exchange of L where BDI* = CH{C(^tBu)N-2,6-ⁱPr₂C₆H₃}₂.[#]

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Abstract.

BDI*MgⁿBu(THF) and *rac*-LA to produce heterotactic PLA have been shown to increase from $P_r = 0.5$ to 0.65 from DCM to neat THF. The increase in concentration of THF from $M_{\text{THF}} = 0$ in toluene to neat THF is shown to occur by THF dissociation as deduced by ¹H NMR studies. In related systems where X = ⁿBu and O^tBu and with ligands L = THF, py and DMAP similar processes occur by which external exchange of L occurs with added free ligand. For X = ⁿBu and L = THF, the activation parameters for the dissociation process are $\Delta H^\ddagger = 7.0 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -11.6 \pm 0.4 \text{ cal mol}^{-1}$ and for X = O^tBu and L = THF are $\Delta H^\ddagger = 11.1 \pm 1.0 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -3.3 \pm 3.9 \text{ cal mol}^{-1}$. The BDI*(R = ^tBu) is notably larger than BDI(R = Me) and this limits the use of THF to coordinate during catalysis. The three coordinate complex BDI*MgⁿBu has been structurally characterized by single crystal X-ray crystallography: where Mg-N = 2.010(4) and 2.026(4) Å and Mg-C = 2.117(5) Å, with N-Mg-N = 94.2(2)° and N-Mg-C = 130.0(2)° and 135.8(2)°. The related complexes BDI*MgⁿBu(L), where L = py and DMAP have similarly structural features.

[#] This paper is dedicated to Professor Catherine Housecroft on the occasion of her 60th birthday

Introduction

The solvent plays a critical role in many reactions^{1,2} of $\text{BDIMg}^n\text{Bu}(\text{THF})$, where $\text{BDI} = \text{CH}\{\text{C}(\text{Me})\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\}_2$ and $\text{BDI}^* = \text{CH}\{\text{C}(^t\text{Bu})\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\}_2$. In non-coordinating solvents such as DCM or benzene the polymerization of *rac*-LA produces $P_r = 0.50$ heterotactic PLA where in neat THF with BDI and BDI* we obtain $P_r \geq 0.95$ and 0.65, respectively. Given in the solid-state that BDI*(R = ^tBu) has significantly more steric influence at the Mg^{2+} center we reasoned that THF might be subject to a dissociative process in its exchange with extra THF present in solution. In the case of BDI(R = Me) we observed that THF exchange could occur by both a dissociative and an associative process. In this work we describe the exchange of THF in a series of complexes $\text{BDI}^*\text{MgX}(\text{L})$ where $\text{X} = ^n\text{Bu}$ and O^tBu , $\text{L} = \text{THF}$, py , DMAP and 2-MeTHF . We do this by the apparent ⁱPr rotation phenomenon of the $\text{N-C}_6\text{H}_3\text{-}^i\text{Pr}_2$ group. In the ground state the two ⁱPr groups are equivalent if we obtain a three-coordinate (**I**) and in a five-coordinate (**II**) complex as shown in Figure 1.^{3,4,5} In the four-coordinated metal the ⁱPr ligands are inequivalent. To do this we employ line broadening with temperature dependence in the ¹H-NMR spectrum.

Figure 1: Three-coordinate **(I)** and a five-coordinate **(II)** complexes of $\text{BDI}^*\text{Mg}^n\text{Bu}$ and $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})_2$.

Results and Discussion

Synthesis

The compound $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$ was reported previously⁶ and is shown in Figure 2. We have shown that in a similar manner we can prepare the compounds $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{L})$ where $\text{L} = 2\text{-MeTHF}$, py and DMAP [$2\text{-MeTHF} = 2\text{-methyltetrahydrofuran}$, $\text{py} = \text{pyridine}$, and $\text{DMAP} = 4\text{-dimethylaminopyridine}$]. The basic reaction involved the addition of the free ligand L to a solution of the compound formed by the addition of one equivalent of BDI^*H to Mg^nBu_2 in hexane followed by crystallization. The new compound $\text{BDI}^*\text{MgO}^t\text{Bu}(\text{THF})$ can be prepared

from the reaction of $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$ with one equivalent of $t\text{BuOH}$ in THF. In the solvents hexane or pentane this compound forms microcrystals.

Figure 2: Model of $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens, and disorder omitted for clarity.

We also investigated the nature of the compound formed in the reaction between Mg^nBu_2 and BDI^*H in hexanes. Here we were able to grow crystals and have shown that this forms a 3-coordinate structure which is quite different from the dimeric structure of $[\text{BDIMg}^n\text{Bu}]_2$ ⁷ but more closely related to the structure of BDIMgPh ⁸ which too was a monomer.

Crystal and Molecular structure of $\text{BDI}^*\text{Mg}^n\text{Bu}$

The crystallographic data for all structures can be found in Table 1 and a summary of notable bond distances and angles can be seen in Table 2. $\text{BDI}^*\text{Mg}^n\text{Bu}$ crystallized in the orthorhombic space group Fdd2 where there are two independent molecules found in the asymmetric unit, one of which has a disorder in the ^nBu group. One of these is shown in Figure 3.

Figure 3: Molecular Structure of BDI*Mg''Bu drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.

The N-Mg-N angle is 94.2° and the N-Mg-C angles fall in the range $130\text{--}135^\circ$ and so each N_2MgC unit is trigonal planar. In contrast to the BDI structure the $t\text{Bu}$ groups impart greater stereo regularity and the angle of the aryl ring with respect to N_2MgC plane is around 85° . When comparing the structures seen in Figure 2 and 3, we note that the Mg is $0.67 \text{ \AA}$ out of the N_2C plane and that the distances are notably longer as a result of forming the Mg-O bond distance $2.09 \text{ \AA}$ for the THF structure (Figure 2).

Molecular structures of BDI*MgⁿBu(L), where L= py and DMAP

These two structures are closely related and the py structure is shown in Figure 4 and the DMAP structure is shown in Figure 5. The two compounds show very similar structural parameters as is seen in Table 2. Both structures form a distorted tetrahedron with N₂C base comprised of the BDI* nitrogens and the α -C of ⁿBu carbon. The degree of this distortion can be described by calculating the distance between Mg and the N₂C base with a perfectly trigonal planar arrangement being 0 Å. In this case the Mg atom is 0.62 Å for py and 0.53 Å for DMAP. In a related compound BDI*MgⁿBu(THF), the related compound BDI*MgⁿBu(THF), the Mg atom is 0.67 Å above the related N₂C plane. The Mg-N distances to py is 2.19 Å and to DMAP 2.17 Å. In the related THF structure the Mg-O distances is 2.09 Å, notably smaller than those in this paper. The crystallographic data for all structures can be found in Table 1.

Figure 4: Molecular Structure of BDI*MgⁿBu(py) drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens, and isopropyl groups omitted for clarity.

Figure 5: Molecular Structure of BDI*MgⁿBu(DMAP) drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens, and isopropyl groups omitted for clarity.

Table 1. Crystallographic Data Collection Parameters

Compound	BDI*Mg ⁿ Bu	BDI*Mg ⁿ Bu(py)	BDI*Mg ⁿ Bu(DMAP)
Chemical Formula	C ₃₉ H ₆₂ MgN ₂	C ₄₄ H ₆₇ MgN ₃	C ₄₆ H ₇₂ MgN ₄
Formula Weight	583.21	662.31	705.38
Temperature (K)	150(2)	150(2)	150(2)
Space Group	Orthorhombic, <i>Fdd2</i>	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2₁/n</i>
<i>a</i> (Å)	32.347(7)	18.3074(3)	10.4585(1)
<i>b</i> (Å)	43.499(9)	17.6121(2)	20.3087(2)
<i>c</i> (Å)	21.529(4)	25.4910(3)	20.4533(2)
α (°)			
β (°)			95.593(1)
γ (°)			
<i>V</i> (Å ³)	30293(11)	8219.11(19)	4323.57(7)
<i>Z</i>	32	8	4
<i>D</i> _{calcd} (Mg/m ³)	1.023	1.070	1.084
Crystal Size (mm)	0.42 X 0.35 X 0.27	0.38 X 0.31 X 0.27	0.38 X 0.35 X 0.31
Theta range for data collection	1.229 to 24.982°	1.598 to 27.494°	2.001 to 27.501°
μ (mm ⁻¹) [Mo, K α]	0.073	0.075	0.076
<i>F</i> (000)	10304	2912	1552
Reflections collected	55253	86829	68896
Unique reflections	13053[R(int)=0.065]	9427 [R(int)= 0.044]	9924 [R(int)= 0.032]
Data Completeness to [θ]	99.6% [25.000]	100% [25.242]	99.9% [25.242]
Data/restraints/parameters	13053 / 64 / 801	9427 / 0 / 448	9924 / 0 / 477
<i>R</i> ^{1a} (%) (all data)	7.55 (12.12)	4.30 (6.96)	4.82 (6.22)
<i>wR</i> ^{2b} (%)(all data)	17.45 (20.04)	10.16 (11.28)	12.53 (13.46)
Goodness-of-fit on <i>F</i> ²	1.044	1.021	1.031
Largest diff. peak and hole (e Å ⁻³)	0.613 and -0.271	0.275 and -0.206	1.026 and -0.386

$$^aR1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \times 100$$

$$^b wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (w |F_o|^2)^2]^{1/2} \times 100$$

Table 2: Selected bond distances and angles of BDI*Mg^{II}Bu, BDI*Mg^{II}Bu(Py) and BDI*Mg^{II}Bu(DMAP).

Distances in Å			
	BDI*Mg ^{II} Bu	BDI*Mg ^{II} Bu(py)	BDI*Mg ^{II} Bu(DMAP)
Mg – N(1)	2.010(4)	2.080(1)	2.083(1)
Mg – N(2)	2.026(4)	2.076(1)	2.089(1)
Mg – N(3)	-----	2.194(1)	2.167(1)
Mg – C	2.117(5)	2.132(1)	2.136(2)
Angles in °			
N(1) – Mg – N(2)	94.2(2)	95.14(4)	93.28(4)
N(2) – Mg – C(41)	130.0(2)	122.25(5)	128.17(6)
C(41) – Mg – N(1)	135.8(2)	116.71(5)	119.34(6)
C(41) – Mg – N(3)	-----	116.61(5)	105.19(6)
N(2) – Mg – N(3)	-----	100.84(4)	102.75(5)
N(1) – Mg – N(3)	-----	101.26(4)	105.48(5)

¹H NMR studies

The molecular structure BDI*MgⁿBu(THF) is shown in Figure 2. Here the pseudo tetrahedral central N₂Mg(C)O structure reveals that there are two inequivalent ⁱPr groups: one located toward the THF molecule and the other located toward the ⁿBu group. However, as seen in Figure 1 for the 3-coordinate molecule both ⁱPr groups are equivalent. Similarly for a five-coordinate molecule, the ⁱPr groups are equivalent if the two THF ligands are in axial positions. (See Figure 1(II)).

The ¹H NMR spectra of compound BDI*MgⁿBu(THF) recorded at various temperatures in toluene-d₈ are shown in Figure 6.

Figure 6: The ¹H NMR spectra of compound BDI*MgⁿBu(THF) recorded in toluene-d₈ at different temperatures.

In the region between 3 and 4 ppm we see the α -CH₂ of THF at lower field and the ⁱPr - methine proton at higher field. At 27°C we see that each signal is represented as a multiplet but on lowering the temperature the methine protons split into two resonances below -70°C. The separation of these resonances has a coalescence temperature of ~ -65°C. Also upon lowering the temperature the α -CH₂ group split into two signals with a T_c ~ -75°C. Thus at low temperatures, ~ -90°C, the ¹H NMR spectrum is constant with a rigid structure on the ¹H NMR time scale.

We have now considered what happens when neat THF is added to the solution in toluene d₈. When one equivalent of neat THF is added we observed above 60°C one signal for the α -CH₂ THF signals as the free and coordinated THF are exchanging but below -70°C we see the freezing out of the THF exchange. The T_c is identically the same and the exchange of ⁱPr is also the same as before, T_c ~ -65°C. With increasing concentrations of added THF to where the ratio of [Mg]:THF = 1:0.5, 1:1, 1:2, 1:20, 1:50, 1:100 and the neat THF-d₈ we see the same behavior. In neat THF d₈ as a solvent the chemical shifts of the free ⁱPr ligands are slightly different than those in pure toluene d₈ but the T_c is essentially identical T_c ~ -65°C for ⁱPr group rotation. See Figure 6. The same is also true for the ¹³C NMR spectrum which is shown in Figure S1.

A similar result is determined for the compound BDI*Mg(O'Bu)(THF) where the T_c values for the methine rotation are at ~ -35°C. See Figure 7.

Figure 7: V.T ^1H NMR (500 MHz) spectra of 0.035M (BDI*)MgOBu'(THF) with 0.035M THF (1:1) in toluene- d_8 . Only the α -methylene protons in relation to the oxygen of THF are shown. The coordinated THF signal (left) downfield of the free THF (right).

Thus in calculating the $\Delta H^\ddagger = 7.0 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -11.6 \pm 0.4 \text{ cal mol}^{-1}$ for $X = {}^n\text{Bu}$ and for $X = \text{O}^i\text{Bu}$, $\Delta H^\ddagger = 11.1 \pm 1.0 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -3.3 \pm 3.9 \text{ cal mol}^{-1}$.

While it is not possible to compare the rates of ligand exchange in the series $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{L})$ where $\text{L} = \text{py}$ and DMAP we do note that the rate of ${}^i\text{Pr}$ methine proton resonances increase with $\text{L} = \text{py}$, $T_c \sim -10^\circ\text{C}$ and for $\text{L} = \text{DMAP}$, $T_c \sim 30^\circ\text{C}$. This is entirely consistent with ${}^1\text{H}$ NMR data recorded for $\text{BDIMg}^n\text{Bu}(\text{L})$ as shown in Table 3.

Table 3. The comparison of T_c of the apparent *iso*-propyl rotation between $(\text{BDI})\text{MgBu}^n(\text{L})$ and $\text{BDI}^*\text{MgBu}^n(\text{L})$ where $\text{L} = 2\text{-MeTHF}$, THF , py , and DMAP .

Compound	T_c app. Aryl rotation							
	tol-d8	0.5eq	1eq	2eq	20eq	50eq	100eq	pure L
$\text{BDIMg}^n\text{Bu}(\text{THF})$	-15	-15	-15	-15	-40	-50	-65	-75
$\text{BDIMg}^n\text{Bu}(2\text{-MeTHF})$	-45	-45	-45	-45				
$\text{BDIMg}^n\text{Bu}(\text{py})$	35							-15
$\text{BDIMg}^n\text{Bu}(\text{DMAP})$	75							
$\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$	-60	-60	-60	-60	-60	-60	-60	-60
$\text{BDI}^*\text{Mg}^n\text{Bu}(2\text{-MeTHF})$	complicated							
$\text{BDI}^*\text{Mg}^n\text{Bu}(\text{py})$	-10	-10					-10	
$\text{BDI}^*\text{Mg}^n\text{Bu}(\text{DMAP})$	30	30						

Indeed in going from T_c for THF to T_c for py there is a change of $+50^\circ\text{C}$ and from T_c for THF to DMAP a change of $+90^\circ\text{C}$. The higher values obtained are in the relative strength of the binding of the ligands $\text{L} = \text{DMAP} > \text{py} > \text{THF}$.

Rates of polymerization of LA

In comparing the rates of polymerization at 25°C by $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{L})$ of *rac*-LA in DCM as a solvent we observe that when $\text{L} = \text{THF}$ and 2-MeTHF the rates are very similar. Within 10 min. the rate of PLA that is formed is $\sim 80\%$ but when $\text{L} = \text{py}$ or DMAP the conversion is only $\sim 30\%$. We note that in DCM the binding of L toward to the catalytic center suppress the rate of polymerization.⁵ In DCM the % of heterotactic (*isi*, *sis*) PLA is close to 50%. *i.e.* it is just as expected for a statistical mixture. At 25°C the rate of polymerization, k_p , is $6.12 \text{ M}^{-1}\text{s}^{-1}$ but in neat THF the formation of heterotactic PLA increases to $P_r \sim 0.65$ and is slowed down with $k_p \sim 0.24 \text{ M}^{-1}\text{s}^{-1}$. Both of these rates are slower when compared to $\text{BDIMg}^n\text{Bu}(\text{THF})$ which also gives a $P_r = 0.5$ in DCM but a much higher value in neat THF, $P_r > 0.95$.² Given that in neat THF the rate of THF exchange is greatly influenced by the $[\text{THF}]$ c.f. compare $T_c \sim -15^\circ\text{C}$ for BDI in DCM with $T_c \sim -75^\circ\text{C}$ in neat THF for the ^iPr exchange process, allows us to suggest that THF association is more favorable in the rate determining step for the production of heterotactic PLA. As we have shown here that for $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$ exchange occurs almost exclusively by a dissociative mechanism, the related reaction for $\text{BDIMg}^n\text{Bu}(\text{THF})$ occurs by a dissociative and associative mechanism with the associative mechanism being more dominant in the presence of the neat THF solvent.

Concluding Remarks

The structural parameters for the $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{L})$ where $\text{L} = \text{THF}$, py and DMAP are similar to those of the related BDI compounds but do show an increase in the size of the ligand. For BDI^* the presence of the ^iBu groups suppresses the rate of THF exchange. Indeed, for the complex $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{THF})$ we really only see by NMR spectroscopy that the rate of exchange of added

THF is consistent with a dissociative process. Even in neat THF the rate of THF exchange is essentially identical to that where no THF is present. Based on this observation and the fact that P_r for the heterotactic PLA from *rac*-LA goes from 0.5 to 0.65 in DCM to THF we assume that THF is not present in the rate determining step for ROP of LA. This contrasts with $\text{BDIMg}^n\text{Bu}(\text{THF})$ where P_r goes from 0.5 in DCM to >0.96 in neat THF, where THF can reversibly bind to magnesium.

Experimental Section

General Consideration

Synthesis of magnesium complexes as well as their application in the ring opening polymerization of lactide were carried out in a drybox or under standard Schlenk line techniques. All glassware were dried overnight in the oven at 110 °C before use in the glovebox. Pentane and toluene were distilled from calcium hydride while tetrahydrofuran (THF) was distilled from sodium/benzophenone under a dry nitrogen atmosphere. The solvents were stored over 4 Å molecular sieves that were previously dried at 110° C in the oven under vacuum for a minimum of 8 hours. *L*- and *rac*-Lactide were purchased from Sigma Aldrich, sublimed three times, crystallized one time from dry toluene in the freezer and dried overnight at 40° C under vacuum before use. β -Diiminato ligand (3-[(2,6-diisopropylphenyl)amino]-5-[(2,6-diisopropylphenyl)imino]-2,2,6,6-tetramethyl-hept-3-ene)(BDI*H) and $\text{BDI}^*\text{MgBu}^n(\text{THF})$ were synthesized according to literature procedures.⁶ Di-*n*-butyl magnesium $\{(^n\text{Bu})_2\text{Mg}, 1 \text{ M in heptane}\}$ was purchased from Sigma Aldrich and used as received. Toluene- d_8 , benzene- d_6 , THF- d_8 and CDCl_3 were purchased from Cambridge Isotopes and distilled over calcium hydride under a nitrogen

atmosphere and stored over 4 Å molecular sieves prior to use. Elemental analysis was not undertaken due to their extreme air-sensitivity.

General procedure of lactide ring-opening polymerization

A Schlenk flask, with a magnetic stir bar, was charged with *rac*-lactide (0.50 g, 3.47 mmol) inside the glovebox and dissolved with 9.00 mL solvent (DCM or toluene). Stock solution of magnesium initiators (0.0347 mmol/ mL) was prepared in toluene in another Schlenk flask. The flasks were attached to the Schlenk line and the magnesium initiator (1 mL of initiator for LA: catalyst = 100 : 1) solution was introduced to the lactide solution by syringe at room temperature. Aliquots (~ 0.50 ml) were taken at appropriate time intervals and quenched with one drop of 0.50 M HCl. This were dried under vacuum and then analyzed by ¹H-NMR spectroscopy.

General procedure for the kinetics of lactide ring-opening polymerization

A Schlenk flask was charged with *rac*-lactide (0.50 g, 3.47 mmol) in dichloromethane (DCM). To this solution was added dichloromethane to bring the total volume of the reaction to 20.00 mL. ([*rac*-LA]₀ = 0.17 M) The solution was stirred at room temperature under a nitrogen atmosphere. Then, the equivalence amounts of 0.0350 M catalyst initiator in toluene (0.60 – 1.00 mL) was introduced. At appropriate time intervals, 0.5-1.0 mL aliquots were taken out of the stirred solution and immediately quenched with 1 drop of 0.5 M HCl. The aliquots were then dried under a dynamic vacuum and analyzed by ¹H NMR spectroscopy.

Single Crystal X-Ray Crystallography

Single crystals were isolated as colorless chunks for $\text{BDI}^*\text{Mg}^n\text{Bu}$, and yellow prisms for both $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{py})$ and $\text{BDI}^*\text{Mg}^n\text{Bu}(\text{DMAP})$, and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with $\text{Mo K}\alpha$ radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack.⁹ The structures were solved by the direct methods program in SHELXS-13¹⁰. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-13, as incorporated in the WinGX package.¹¹ For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(\text{H}) = 1.5U_{\text{eq}}$ (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(\text{H}) = 1.2U_{\text{eq}}$ (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.¹² CCDC 1040780 - 1040782 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

$\text{BDI}^*\text{Mg}^n\text{Bu}$: BDI^*H (0.60 g, 1.19 mmol) was dissolved in 10 mL of pentane and 1.0 M $^n\text{Bu}_2\text{Mg}$ solution in heptanes (1.60 mL, 1.6 mmol, 1.34 equiv.) was added to the pentane solution. The resulting solution was refluxed for 8hrs. The resulting mixture was placed in a

freezer at -25° C for an overnight and the pale yellow crystals were obtained with 70% yield. Single X-ray crystals were grown from a concentrated pentane solution at -23° C.

¹H NMR (500 MHz, benzene-d₆, rt.): 6.95-7.10 (m, 6H, ArH), 5.39 (s, 1H, β-CH), 3.27 (m, 4H, CHMe₂), 1.29 (d, 12H, CHMe₂), 1.26 (d, 12H, CHMe₂), 1.19 (s, 18H, (α-CMe₃)₂), 1.22 (m, 2H, β-Buⁿ), 0.95 (m, 2H, γ-Buⁿ), 0.81 (t, 3H, δ-Buⁿ), -0.62 (AA'XX'Y, 2H, α-Buⁿ).

¹³H NMR (125 MHz, C₆D₆, 27°C): 176.01, 145.23, 141.37, 125.39, 123.81, 94.84, 94.84, 44.02, 32.96, 30.73, 30.63, 28.44, 25.25, 25.18, 23.16, 14.30, 6.93.

BDI^{*}MgⁿBu(2-MeTHF): A mixture of BDI^{*}H (1 g, 1.99 mmol) and (ⁿBu)₂Mg (2.60 ml, 1.30 equivalence) in pentane was refluxed for 6 hr and let to cool down for at least 1 hr. Approximately 10 equivalence of 2-MeTHF was added *via* a syringe at room temperature and the reaction mixture was allowed to stir for another 1 hr before removing all the solvent under vacuum affording the title compound as a yellow solid with 90% yield. Single X-ray crystals were grown from a concentrated pentane solution at -23° C. ¹H NMR (400 MHz, Benzene-d₆, 27°C): 6.97 (m, 6H, ArH), 5.35 (s, 1H, β-CH), 3.80 (m, 1H, 2-MeTHF), 3.73 (m, 1H, 2-MeTHF), 3.53 (m, 1H, 2-MeTHF), 3.27 (m, 4H, CHMeMe²), 1.61 (m, 4H, 2-MeTHF), 1.50 (m, 2H, β-Buⁿ), 1.29 (d, 12H, CHMe₂), 1.26 (d, 12H, CHMe₂), 1.17 (s, 18H, (α-CMe₃)₂), 1.13 (d, 3H, 2-MeTHF), 1.11 (m, 2H, γ-Buⁿ), 0.79 (t, 3H, δ-Buⁿ), -0.67 (2H, α-Buⁿ). ¹³C-NMR (125 MHz, Benzene-d₆): 176.16, 145.56, 141.43, 125.23, 123.80, 103.67, 95.07, 75.54, 67.88, 44.07, 33.18, 33.01, 30.99, 28.36, 25.87, 25.49, 23.43, 21.16, 14.33, 7.18.

BDI^{*}MgⁿBu(DMAP): A mixture of BDI^{*}H (1 g, 1.99 mmol) and (ⁿBu)₂Mg (2.60 ml, 1.30 equivalence) in pentane was refluxed for 6 hr and let to cool down for at least 1 hr. DMAP (0.31

g, 2.59 mmol), previously dissolved in pentane in another Schlenk flask, was transferred *via* cannula at room temperature to the main reaction mixture flask and allowed to stir for another 1 hr before removing all the solvent under vacuum affording the title compound as a bright orange solid with 85% yield. Single X-ray crystals were grown from a concentrated pentane solution at -23° C. ¹H NMR (500 MHz, toluene-d₈, rt.): 8.48 (br, 2H, *o*-H DMAP), 7.04 (m, 6H, ArH), 5.95 (d, 2H, *m*-H DMAP), 5.48 (s, 1H, β-CH), 3.57 (br, 2H, CHMeMe'), 3.14 (br, 2H, CHMeMe'), 2.06 (s, 6H, CH₃ DMAP), 1.55 (d, 12H, CHMe₂), 1.52 (d, 12H, CHMe₂), 1.33 (br singlet, 18H, (α-CMe₃)₂), 1.22 (m, 2H, β-Buⁿ), 1.21 (m, 2H, γ-Buⁿ), 0.93 (t, 3H, δ-Buⁿ), -0.378 (AA'XX'Y, 2H, α-Buⁿ). ¹³C-NMR (125 MHz, Benzene-d₆): 176.07, 149.98, 147.35, 124.35, 123.55, 103.66, 95.56, 44.21, 38.15, 33.31, 32.49, 28.36, 26.69, 24.41, 14.54, 6.59.

BDI^{*}MgⁿBu(Py): A mixture of BDI^{*}H (1 g, 1.99 mmol) and (ⁿBu)₂Mg (2.60 ml, 1.30 equivalence) in pentane was refluxed for 6 hr and let to cool down for at least 1 hour. Approximately 3 equivalence of pyridine was added *via* a microsyringe at room temperature and the reaction mixture was allowed to stir for another 1 hour before removing all the solvent under dynamic vacuum affording the title compound as an orange solid with 90% yield. Single X-ray crystals were grown from a concentrated pentane solution at -23° C. ¹H NMR (500 MHz, toluene-d₈, rt.): 8.78 (br, 2H, *o*-H Pyridine), 7.09 (br, 1H, *p*-H Pyridine), 6.99 (m, 6H, ArH), 6.61 (m, 2H, *m*-H Pyridine), 5.45 (s, 1H, β-CH), 3.16 (br, 4H, CHMeMe'), 1.23 (d, 12H, CHMe₂), 1.21 (d, 12H, CHMe₂), 1.20 (br singlet, 18H, (α-CMe₃)₂), 1.08 (m, 2H, β-Buⁿ), 1.07 (m, 2H, γ-Buⁿ), 0.882 (t, 3H, δ-Buⁿ), -0.421 (AA'XX'Y, 2H, α-Buⁿ). ¹³C-NMR (125 MHz, Benzene-d₆): 176.47, 150.16, 146.86, 142.16, 138.64, 124.57, 123.96, 123.56, 95.64, 44.16, 33.14, 32.69, 32.27, 28.28, 26.51, 24.15, 14.45, 6.18.

BDI^{*}MgOⁿBu(THF): A 50ml Schlenk flask with a stir bar was charged with (BDI^{*})MgⁿBu(THF) (1.00 g, 1.53 mmol) along with 25 ml THF inside the glovebox. This flask was attached to the Schlenk line and ^tBuOH (0.18 ml, 1.84 mmol) was added drop wise using a 1 ml syringe. The reaction was allowed to stir for two hours before removing all the volatiles under dynamic vacuum affording the title compound as an off-white solid with 90% yield. ¹H NMR (400 MHz, toluene-d₈, 27°C): 7.04 (m, 6H, ArH), 5.28 (s, 1H, β-CH), 3.93. (m, 4H, O(CH₂CH₂)₂), 3.29 (sept, 4H, CHMeMe'), 1.45 (m, 4H, O(CH₂CH₂)₂), 1.42 (d, 12H, CHMe₂), 1.36 (d, 12H, CHMe₂'), 1.14 (br singlet, 18H, (α-CMe₃)₂), 0.86 (s, 9H, O(CMe₃)). ¹³C-NMR (125 MHz, Toluene-d₈): 177.17, 146.58, 142.05, 123.63, 122.97, 95.71, 69.20, 65.20, 44.21, 35.54, 33.22, 28.16, 26.84, 25.37, 24.60, 1.37.

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BDI*MgX(L), where X = ⁿBu or O^tBu and L = THF, 2-MeTHF, py and DMAP, undergo the reversible reaction shown above by a dissociative process involving the loss of the ligand, L. This process is involved in the rate of polymerization of *rac*-LA to give heterotactic PLA.