

Comparative Study of the Coordination Chemistry and Lactide Polymerization of Alkoxide and Amide Complexes of Zinc and Magnesium with a β -Diiminato Ligand Bearing Ether Substituents

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A series of β -diiminato complexes of the form (BDI-3)MX where (BDI-3) = [CH(CMeNC₆H₄-2-OMe)₂]; M = Zn, Mg; X = OⁱPr, O^tBu, or N(SiMe₃)₂ has been synthesized. The (BDI-3) ligand is bidentate in (BDI-3)ZnN(SiMe₃)₂ and tetradentate in (BDI-3)MgN(SiMe₃)₂. The alkoxide complexes are shown to be active for lactide polymerization. Polymerization of *rac*-lactide with (BDI-3)ZnOⁱPr gives a moderate preference for heterotactic PLA. Polymerization of *rac*-lactide with [(BDI-3)MgO^tBu]₂ shows a slight preference for heterotactic PLA in CH₂Cl₂ but is highly stereoselective in THF in the production of heterotactic PLA.

Introduction

Polymerization of lactides has been studied extensively in the literature using various single-site metal catalysts.^{1,2} The biocompatible nature of polylactide (PLA) has promoted the use of biocompatible metals because trace amounts of the catalyst may be tenaciously incorporated within the polymer. Biocompatible metals such as zinc and magnesium are of interest, though they exhibit rather different chemical properties. Both are essential nutrients and minerals for plants and humans³ and have similar ionic radii,⁴ but magnesium (2+) is considered as a hard metal, while zinc (2+) is soft.⁵ The similarity in size of the M²⁺ ions⁴ allows a possible comparison of their reactivity when an identical ligand system is employed.^{6–8} Many ligand systems have been employed giving different catalytic activity and selectivity,¹

but for M = Mg and Zn, β -diiminato ligands have received the most attention.^{7–10} First synthesized by Holm,¹¹ bidentate uninegatively charged β -diiminato ligands with a variety of substituents have been attached to various metals.¹²

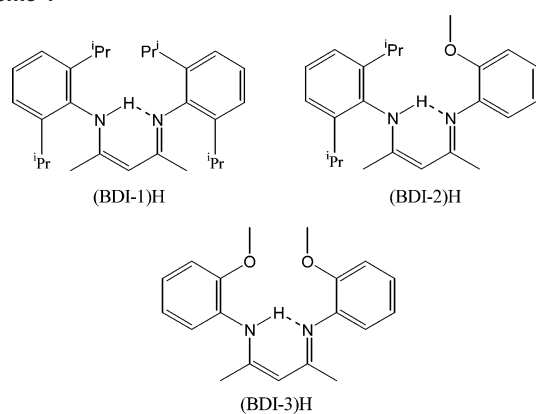
We previously reported that the β -diiminato magnesium complex, (BDI-1)MgO^tBu·THF (Scheme 1), displayed high solvent dependence for the polymerization of *rac*-lactide.⁸ The catalyst produces atactic PLA in CH₂Cl₂ and heterotactic PLA in THF. The extensive coordination of THF to the Mg core was proposed to cause such dramatic stereoselectivity. Although THF can induce heterotactic selectivity, the use of excess THF as a solvent decelerates the polymerization because it competes with lactide for metal coordination. We envisaged that the use of excess THF could be avoided if the β -diiminato ligand possesses ether functionality that takes over the THF's role. By adding ether groups to the β -diimine ligand, the effect of ligand variation from bulky bidentate (BDI-1) to chelating tetradentate (BDI-3) ligand can be investigated (Scheme 1). The potentially tridentate (BDI-2)H ligand¹⁰ retains one of the bulky 2,6-diisopropylphenyl groups of the (BDI-1)H ligand. The magnesium and zinc complexes of the (BDI-2)H ligand have been synthesized

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Scheme 1



by Gibson and co-workers and have been shown to be active initiators for lactide polymerization.¹⁰ The (BDI-3)H ligand has two ether functional groups that allow the ligand to expand its chelating ability from two to three or four.¹³ We hypothesized that the stereoselectivity for heterotactic bias could be reproduced in the chelating (BDI-3) ligand system where the ether groups could bind reversibly to the metal center, creating a similar effect to THF. Herein, the syntheses of the zinc and magnesium complexes of the type (BDI-3)-MX, where X = amide and alkoxide, are reported along with their reactivities toward the ring-opening polymerization of lactides.

Results and Discussion

Syntheses. The (BDI-3)H ligand can be easily synthesized using a published procedure.¹³ The reaction between an equimolar amount of (BDI-3)H with $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ in benzene gave the light yellow compound (BDI-3)ZnN(SiMe₃)₂, **1**, in quantitative yield. The reaction was complete in 10 min at room temperature. For a bulkier ligand such as (BDI-1)H, the reaction requires heating in toluene at 80 °C for 6 days.¹⁴ The faster reaction is probably due to the less sterically demanding OMe groups, and the oxygen may participate in hydrogen bonding which may facilitate proton transfer. Addition of 1 equiv of HO^tPr into a solution of compound **1** in benzene gave the light yellow compound (BDI-3)ZnO^tPr, **2**, in high yield.

The reaction between 1 equiv of (BDI-3)H with 1 equiv of $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ at room temperature gave an orange compound, (BDI-3)MgN(SiMe₃)₂, **3**. When 2 equiv of (BDI-3)H were used along with heating at 80 °C, bis(β-diiminato) complex, (BDI-3)₂Mg, was obtained in quantitative yield as an orange solid. Addition of 1 equiv of HO^tBu into a solution of compound **3** produced the light yellow complex [(BDI-3)MgO^tBu]₂, **4**, in high yield. Compounds **1**–**4** are highly air- and moisture-sensitive.

Single Crystal and Molecular Structures. (BDI-3)ZnN(SiMe₃)₂, **1**. An ORTEP drawing of the molecular structure of **1** is given in Figure 1 along with selected bond distances

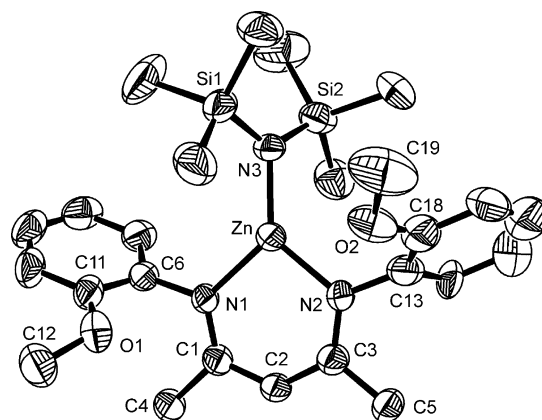


Figure 1. ORTEP drawing of the (BDI-3)ZnN(SiMe₃)₂, **1**, molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (BDI-3)ZnN(SiMe₃)₂, **1**

Zn–N1	1.952(3)	Zn–N2	1.933(3)
Zn–N3	1.881(3)	Zn–O1	4.212(3)
Zn–O2	3.236(3)	N1–Zn–N2	98.9(1)
N1–Zn–N3	129.6(2)	N2–Zn–N3	131.2(2)

(Å) and angles (deg) in Table 1. Compound **1** has a monomeric structure in the solid state where the Zn center is an example of a neutral monometallic three-coordinate zinc complex.^{10,15–20} Compound **1** has a structural similarity to the related (BDI-1)ZnNR₂ complexes where R = SiMe₃¹⁸ and ^tPr.⁸ The zinc atom adopts a distorted trigonal planar geometry with the sum of the angles around the ZnN₃ core of 359.7°. The coordination of the ether functional group to zinc atom is not observed in the solid state (Zn-to-O distances are 4.212(3) and 3.236(3) Å), presumably due to the soft nature of zinc and a steric impediment of the bulky amide. The two ether groups have a syn arrangement. The dihedral angle between the Zn–N1–N2 plane and N3–Si1–Si2 plane is 64.9(4)°. From purely electronic considerations, the Zn–N1–N2 and N3–Si1–Si2 planes are expected to be parallel to maximize the Np_π and Zn p_π interactions. Therefore, such adoption of the amide arrangement must be a result of a compromise imposed by the steric impediment of the bulky amide. The zinc amide nitrogen bond distance in **1** is 1.881(3) Å, which is slightly shorter than in (BDI-1)ZnN(SiMe₃)₂ and (BDI-2)ZnN(SiMe₃)₂,^{13,18} possibly due to less steric hindrance of the (BDI-3) ligand compared to (BDI-1) and (BDI-2) making the amide more accessible to the zinc center. The zinc atom lies only 0.031(1) Å above the plane defined by N1, C2, and N2 making the six-membered ZnNCCCN ring very close to planar.

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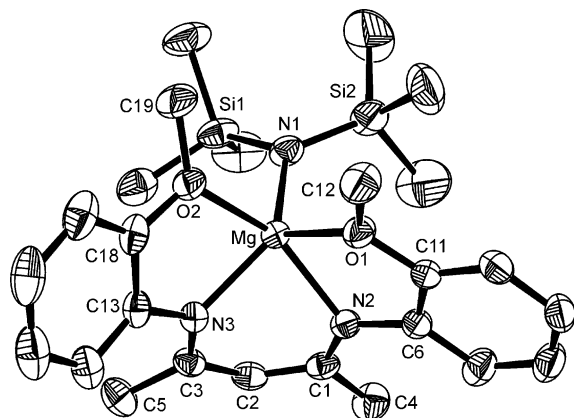


Figure 2. ORTEP drawing of the (BDI-3)MgN(SiMe₃)₂, **3**, molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for (BDI-3)MgN(SiMe₃)₂, **3**

Mg–N1	2.023(1)	Mg–N2	2.094(1)
Mg–N3	2.083(1)	Mg–O1	2.129(1)
Mg–O2	2.144(1)	N1–Mg–N2	114.68(6)
N1–Mg–N3	133.04(6)	N2–Mg–N3	83.98(5)
N2–Mg–O1	74.87(5)	N3–Mg–O2	74.71(5)
O1–Mg–O2	91.42(5)		

(BDI-3)MgN(SiMe₃)₂, 3. An ORTEP drawing of the molecular structure of **3** is given in Figure 2 along with selected bond distances (Å) and angles (deg) in Table 2. Compound **3** has a monomeric structure and the five-coordinate Mg atom adopts a distorted square pyramidal geometry. The Mg atom sits slightly above the square pyramidal base defined by the O1, O2, N2, and N3 atoms. Both ether oxygen atoms coordinate to the Mg atom giving Mg–O bond distances of 2.129(1) and 2.144(1) Å. The coordination of ether groups causes the phenyl rings to be almost parallel to the plane defined by N2, C1, C2, C3, and N3. Compound **3** is a rare example of structurally characterized tetradentate acyclic β-diiminate ligand complexes. The first three examples are [CH(CMeN(CH₂CH₂NEt₂))₂]ScCl₂,²¹ (BDI-3)Li,¹³ and (BDI-3)₂Ca.²²

[(BDI-3)MgO^tBu]₂, 4. An ORTEP drawing of the molecular structure of **4** is given in Figure 3, and selected bond distances (Å) and angles (deg) are listed in Table 3. Compound **4** has a dimeric structure where the four-coordinate Mg core is distorted tetrahedral. The *tert*-butoxides are bridging between the two Mg cores. The Mg-to-Mg distance in **4** is 2.918(2) Å, significantly shorter than in the related compound [(BDI-1)MgO^tPr]₂ (3.01 Å)⁷ possibly due to a less-steric repulsion between the two (BDI-3) ligands. The two ether groups are in a syn arrangement, and they do not coordinate to the Mg atom (Mg-to-O_{ether} distances are 4.221(2) and 4.054(2) Å).

A summary of crystallographic data for compounds **1**, **3**, and **4** is given in Table 4.

Solution Behavior: NMR Studies. The ¹H NMR spectrum of (BDI-3)ZnN(SiMe₃)₂, **1**, indicates that only one

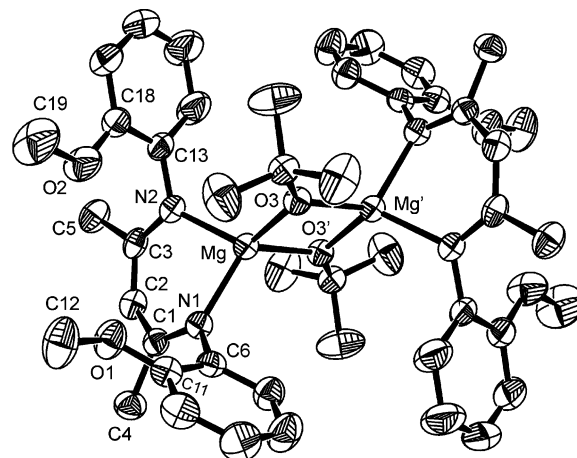


Figure 3. ORTEP drawing of the [(BDI-3)MgO^tBu]₂, **4**, molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [(BDI-3)MgO^tBu]₂, **4**

Mg–N1	2.050(2)	Mg–N2	2.048(2)
Mg–O3	1.944(2)	Mg–O3'	1.965(2)
Mg–O1	4.221(2)	Mg–O2	4.054(2)
Mg–Mg'	2.918(2)	N1–Mg–N2	91.29(8)
N1–Mg–O3	124.90(7)	N1–Mg–O3'	118.17(7)
N2–Mg–O3	121.73(7)	N2–Mg–O3'	120.91(7)
O3–Mg–O3'	83.41(6)	Mg–O3–Mg'	96.58(6)

conformation exists in C₆D₆ in agreement with the crystal structure. From the spectrum, however, one cannot tell if there is a rapid interconversion between syn and anti arrangement of the ether groups. The syn and anti arrangements are expected to have different chemical shifts but otherwise very similar NMR spectra. Cooling compound **1** to –80 °C in toluene-*d*₈ only broadens the peaks slightly. On the basis of the NMR spectrum and the syn conformation in the crystal structure of **1**, we conclude that, in solution, complex **1** exists as a syn conformation, as seen in the crystal structure.

The five-coordinate complex (BDI-3)MgN(SiMe₃)₂, **3**, also has an expected NMR spectrum for a syn arrangement. The ¹H NMR spectra of **3** do not change upon cooling to –90 °C in toluene-*d*₈, consistent with a five-coordinate complex at low temperature. The addition of THF to **3** does not form (BDI-3)MgN(SiMe₃)₂·THF after any volatile components are removed in vacuo. The surprising behavior was observed in the variable-temperature ¹H NMR spectra after the addition of THF, as shown in Figure 4. The important features are the splitting of signals arising from N(SiMe₃)₂, OMe, and γ-CH₃ from one singlet into two broad singlets upon cooling to –90 °C while the β-CH proton remains unchanged. This implies that THF coordinates to the magnesium atom in a way that removes the mirror plane of symmetry. A possible mechanism involving the coordination of THF is proposed in Scheme 2. At low temperature, a THF molecule displaces one of the ether groups. The N, N, O, and O atoms are no longer in the same plane causing nonequivalent SiMe₃, OMe, and γ-CH₃ groups. The fact that THF molecule can displace an OMe group suggests that the ether groups of (BDI-3) ligand bind to Mg atom reversibly. Thus, the OMe groups

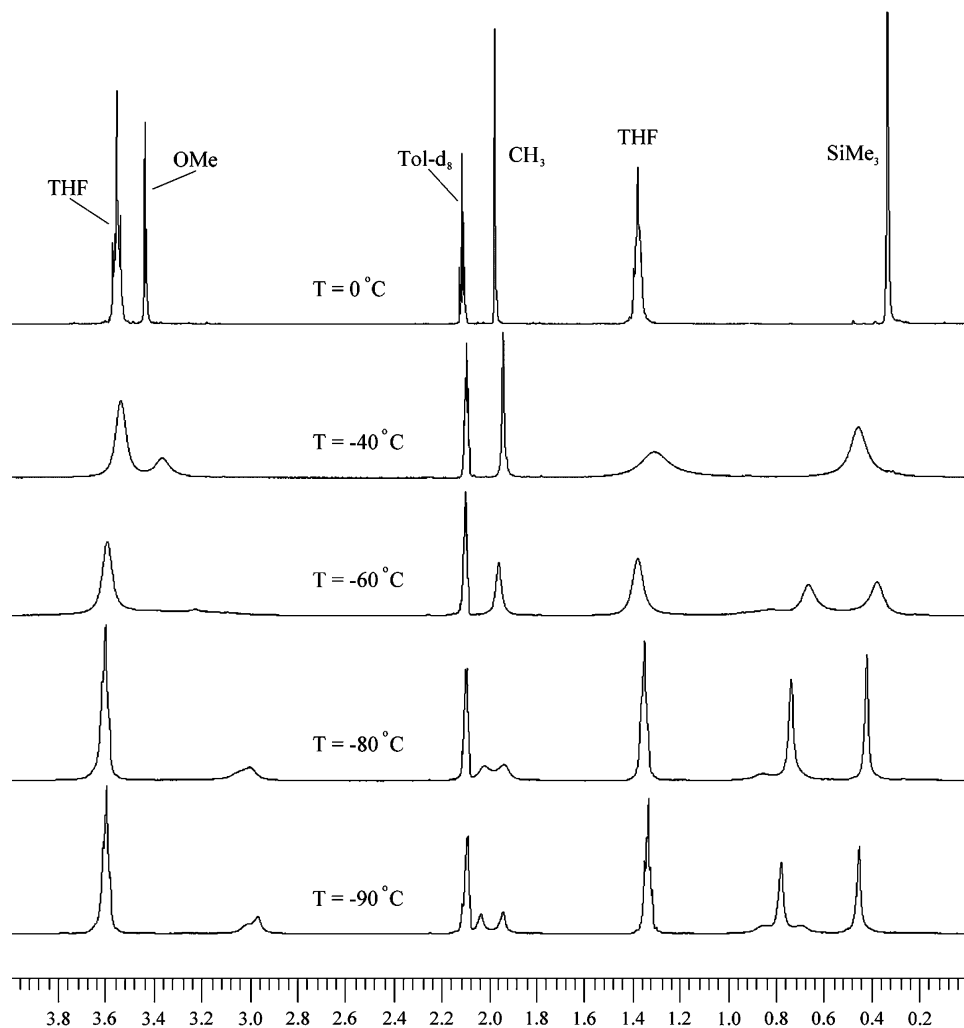
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Table 4. Summary of Crystallographic Data of Compounds **1**, **3**, and **4**

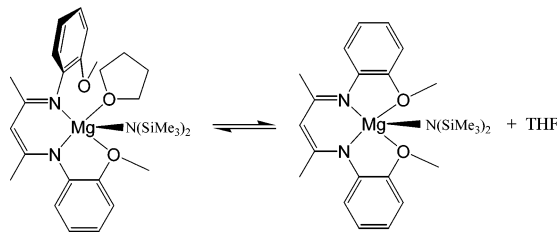
compound	1	3	4
empirical formula	C ₂₅ H ₃₉ N ₃ O ₂ Si ₂ Zn	C ₂₅ H ₃₉ MgN ₃ O ₂ Si ₂	C ₂₃ H ₃₀ MgN ₂ O ₃
fw	535.14	494.08	406.80
cryst syst	triclinic	monoclinic	monoclinic
space group	P1	P2 ₁ /c	P2 ₁ /c
temp (K)	200	200	200
	cell dimensions		
<i>a</i> (Å)	8.139(2)	10.507(2)	11.219(1)
<i>b</i> (Å)	12.057(4)	23.713(2)	19.481(3)
<i>c</i> (Å)	15.201(5)	11.334(1)	11.319(1)
α (°)	95.69(1)		
β (°)	105.07(1)	90.19(1)	109.44(1)
γ (°)	94.69(2)		
Z	2	4	4
<i>V</i> (Å ³)	1424.3(8)	2824.02(4)	2332.8(5)
density _{calc} (g/cm ³)	1.248	1.162	1.158
θ range (°)	2.07–24.99	2.12–27.47	2.09–25.02
reflns collected	22 395	45 638	34 894
independent reflns	4994	6475	4118
R1(<i>F</i>) ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0595	0.0413	0.0513
R1(<i>F</i>) ^a (all data)	0.0788	0.0656	0.0826
wR2(<i>F</i> ²) ^a (all data)	0.1571	0.1207	0.1457
GOF	1.047	1.033	1.020

^a R1(*F*) = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR2(*F*²) = $\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$; $W = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $P = (F_o^2 + 2F_c^2)/3$ where $x = 0.0691$, $y = 2.5762$ for **1**; $x = 0.0670$, $y = 0.3638$ for **3**; $x = 0.0730$, $y = 1.0001$ for **4**.

**Figure 4.** Variable-temperature ¹H NMR (400 MHz, toluene-*d*₈) of (BDI-3)MgN(SiMe₃)₂, **3**, after the addition of THF.

can dissociate to some extent from the Mg atom, making room for lactide association during the polymerization.

The ^tBu peak in the ¹H NMR spectrum of the dimeric [(BDI-3)MgO^tBu]₂, **4**, is broad at room temperature, sug-

Scheme 2. Proposed Reversible Process When THF Was Added to (BDI-3)MgN(SiMe₃)₂, **3****Table 5.** Polymerization of *rac*-Lactide (100:1 [lactide]/[catalyst]) in CH₂Cl₂ and THF at 20 °C

entry	catalyst	solvent	time (min)	conversion (%)	M_n	M_w/M_n	%het ^a
1	2	CH ₂ Cl ₂	3	95	16 800	1.19	59
2	2	THF	10	91	18 100	1.19	67
3	4	CH ₂ Cl ₂	20	91	96 500	2.23	49
4	4	THF	90	90	40 200	1.70	85

^a % heterotactic junction is defined by $(sis + isi)/(sis + isi + iis + sii + iiii) \times 100\%$.

gesting some dynamic process, but attempts to freeze this process failed as low-temperature spectra were not resolved. On the basis of the crystal structure of **4**, we propose that **4** remains dimeric in solution and the broadening of the 'Bu peak in ¹H NMR spectrum of **4** may arise from a reversible coordination of the ether group to the magnesium (2+) center.

Ring-Opening Polymerization of Lactides. The amide and alkoxide complexes of zinc and magnesium are capable of initiating the ring-opening polymerization (ROP) of *rac*-lactides (100 equiv). For the zinc amide and alkoxide complexes **1** and **2**, the rate of initiation follows the order OⁱPr > N(SiMe₃)₂, reflecting both steric and electronic factors. The N(SiMe₃)₂ group is a more basic ligand than the OⁱPr group, but its lone pair is more sterically protected. A similar trend has been observed in the related bulky (BDI-1)Zn alkoxide and amide complexes.^{7,8} Compound **2** is more reactive than the related [(BDI-1)ZnOⁱPr]₂ as a result of a less-hindered ligand in **2** making the zinc atom more accessible to lactides.¹⁰ The polymerization of *rac*-lactide with **2** in CH₂Cl₂ is shown in Table 5, entry 1. By comparison to the earlier work on (BDI-1) and (BDI-2) ligands, the order of reactivity of β-diiminato zinc complexes containing (BDI-1), (BDI-2), and (BDI-3) can be approximated. The reactivity increases in the order (BDI-1) < (BDI-2) < (BDI-3), reflecting the decrease of steric encumbrance from (BDI-1) to (BDI-3).^{7,8,10} Although the ether groups could bind to the Zn atom decelerating the polymerization, this chelating effect is not predominant in a soft metal such as Zn. The molecular weight of the polymer is 16.8 kDa, which is close to the expected value of 13.7 kDa. The polymer has a narrow polydispersity index (M_w/M_n) of 1.19. The polymer shows a 59% heterotactic junctions (*isi* + *sis*) as a result of a chain-end control. The preference for heterotacticity in **2** is significantly less than that (90%) of the related [(BDI-1)-ZnOⁱPr]₂.⁷ Because the (BDI-3) ligand is less sterically demanding, the catalyst **2** is less discriminating to the incoming lactide compared to [(BDI-1)ZnOⁱPr]₂, causing a less-profound stereoselectivity. Similar loss of heterotactic

bias due to a less-bulky ancillary ligand was also observed in the (BDI-2)Zn system.¹⁰

The magnesium alkoxide complex **4** is also active for ROP of lactides (Table 5, entry 3). The polymerization proceeds to 91% conversion in 20 min. In contrast to the reactivity order observed in the zinc complexes, the less-hindered complex **4** is less reactive than the bulky (BDI-1)Mg complexes.^{7,8} The order of reactivity decreases with increasing number of ether groups: (BDI-1) > (BDI-2) > (BDI-3).^{7,8,10} Clearly, the effect of chelating OMe groups overrides the steric influence. The (BDI-2) and (BDI-3) ligands contain ether groups that can effectively compete with lactide for metal coordination. The chelating effect significantly influences the rate of polymerization in the hard magnesium complex but is negligible for a softer zinc analogue. The molecular weight of the polymer obtained from **4** (Table 5, entry 3) is 96.5 kDa, which is significantly greater than the theoretical value of 13.1 kDa for a living polymerization with $k_{init} \geq k_{prop}$. The polydispersity index of 2.23 is quite high. We tentatively attribute the high M_n and broad PDI of the polymer to a slow initiation possibly as a result of the dimeric structure of **4** and transesterification.⁷ The polymer shows ca. 50% heterotactic junctions (*isi* + *sis*). In contrast to the decrease of heterotactic bias from (BDI-1) to (BDI-3) in the zinc complexes, complex **4** exhibits a higher preference for heterotacticity compared to the (BDI-1)Mg complex, which produces atactic PLA (37.5% heterotactic bias).^{7,8} We have reported that (BDI-1)MgOⁱBu·THF showed no stereocontrol for polymerization of *rac*-lactide in dichloromethane giving atactic poly(*rac*-lactide).⁸ However, when the polymerization was done in THF, the catalyst system exhibited a significant preference for heterotacticity presumably as a result of THF coordination to the magnesium atom making the magnesium core more coordinately hindered. A similar scenario is proposed to take place for **4** where the OMe groups reversibly coordinate to the Mg(II) center causing complex **4** to be coordinately hindered and more discriminating to the incoming lactide. The effect of ether groups becomes important in a hard Mg metal but much less pronounced in a softer Zn metal. As a result, a higher stereoselectivity is observed in **4** although the (BDI-3) ligand is less sterically demanding compared to (BDI-1) ligand. A comparison of the stereoselectivity of the zinc and magnesium complexes is illustrated in Figure 5.

The influence of solvent on the polymerization of *rac*-lactide was also investigated. The polymerization of *rac*-lactide in THF is generally slower than in dichloromethane as a result of a competitive coordination between THF and lactide to the catalysts (Table 5, entries 2 and 4). The molecular weight of the polymer and the stereoselectivity of catalyst **2** only change slightly in THF. The influence of THF is, on the other hand, more profound for complex **4**. The rate of ROP is significantly slower. Nonetheless, the polymerization is more controllable than in CH₂Cl₂ and PLA with lower M_n and narrower PDI is produced. Furthermore, the polymerization of *rac*-lactide using **4** in THF exhibits a significant increase in stereoselectivity over CH₂Cl₂. The extensive coordination of the ether groups and THF to the

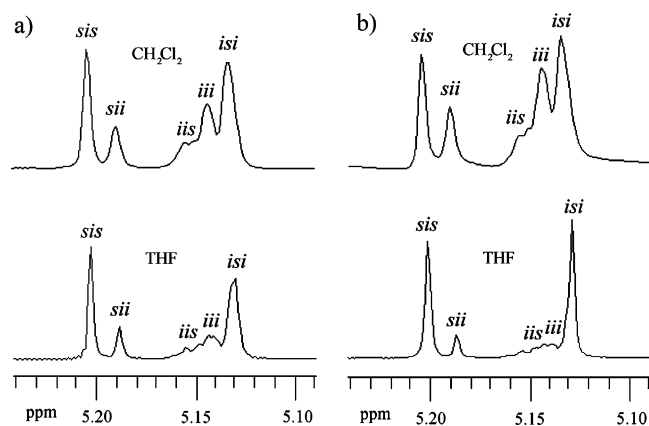


Figure 5. ^1H NMR spectra (CDCl_3 , 400 MHz) of the homodecoupled CH resonance of poly(*rac*-lactide) prepared in CH_2Cl_2 and THF using (a) $(\text{BDI-3})\text{ZnO}'\text{Pr}$, **2**, and (b) $[(\text{BDI-3})\text{MgO}'\text{Bu}]_2$, **4**, as initiators.

magnesium core is proposed to be responsible for the higher stereoselectivity, as was seen for the $(\text{BDI-1})\text{MgO}'\text{Bu}\cdot\text{THF}$ complex.⁸

Conclusions

This work demonstrates the application of the chelating β -diimine (BDI-3) ligand in lactide polymerization. The potential advantage of the (BDI-3) ligand lies in its ability to expand its coordination from two to three and four. The influence of the ether groups is less pronounced with the soft-metal zinc where ether coordination to the metal is less significant. On the other hand, their coordination to the hard-metal magnesium is more aggressive, affecting the solid-state structures and the catalytic activity and stereoselectivity. By comparison to the related bidentate β -diimine ligands, the ether groups in (BDI-3) ligand in conjunction with Mg atom are believed to promote the formation of heterotactic bias in the polymerization of *rac*-lactide. We propose that this is a result of a hemi-labile ether-donor binding in a manner akin to that previously seen in THF solution for $(\text{BDI-1})\text{MgOR}$ initiators.

Experimental Section

General Considerations. The manipulation of air-sensitive compounds involved the use of anhydrous solvents and dry and oxygen-free nitrogen with standard Schlenk line and drybox techniques. *rac*-Lactide was purchased from Aldrich and was sublimed three times prior to use. Tetrahydrofuran, dichloromethane, hexanes, and toluene were distilled under nitrogen from sodium/benzophenone, calcium hydride, potassium metal, and sodium metal, respectively. The (BDI-3)H ligand,¹³ $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$,²³ and $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ ²⁴ were prepared according to literature procedures. Anhydrous $^t\text{BuOH}$ and $^i\text{PrOH}$ were purchased from Aldrich and used as received.

Measurements. ^1H (400.1 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100.6 MHz) spectra were recorded in C_6D_6 and toluene- d_8 on Bruker DPX-400 NMR spectrometers and were referenced to the residual protio impurity peak (C_6D_6 , δ 7.15; toluene- d_8 , 2.09 for ^1H and, C_6D_6 , δ

128.0; toluene- d_8 , 20.4 for $^{13}\text{C}\{^1\text{H}\}$). Elemental analyses were done by Atlantic Microlab, Inc. Gel permeation chromatography (GPC) measurements were carried out using a Waters 1525 binary HPLC pump and Waters 410 differential refractometer equipped with styragel HR 2 and 4 columns (100 and 10 000 Å). The GPC was eluted with THF at 35 °C running at 1 mL/min and was calibrated using polystyrene standards.

$(\text{BDI-3})\text{ZnN}(\text{SiMe}_3)_2$, **1.** A solution of (BDI-3)H (0.500 g, 1.61 mmol) in 10 mL of benzene was added dropwise to a solution of $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (0.622 g, 1.61 mmol) in 5 mL of benzene at room temperature. The reaction was stirred for 10 min, and any volatile components were removed under a dynamic vacuum giving a light yellow solid in quantitative yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated hexanes solution in a freezer. CCDC 217760. Anal. Calcd for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{O}_2\text{Si}_2\text{Zn}$: C, 56.14; H, 7.29; N, 7.86. Found: C, 56.15; H, 7.15; N, 7.55. ^1H NMR (C_6D_6): 6.96–7.01 (m, 4H, ArH), 6.85 (t, 2H, $J = 7.6$ Hz, ArH), 6.59 (d, 2H, $J = 8.4$ Hz, ArH), 4.88 (s, 1H, β -CH), 3.34 (s, 6H, OMe), 1.76 (s, 6H, α -Me), 0.04 (s, 18H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 168.81 (C=N); 153.17, 138.04, 126.74, 126.11, 120.82, 111.36 (Ar–C); 96.32 (β -C), 54.80 (OCH₃), 23.35 (α -CH₃), 4.78 (Si(CH₃)₃).

$(\text{BDI-3})\text{ZnO}'\text{Pr}$, **2.** HO'Pr (72 μL , 0.94 mmol) was added dropwise to a solution of $(\text{BDI-3})\text{ZnN}(\text{SiMe}_3)_2$ (0.500 g, 0.934 mmol) in 15 mL of benzene and stirred for 30 min. The reaction mixture was dried in vacuo giving a light yellow solid (0.361 g, 89%). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3\text{Zn}$: C, 60.93; H, 6.46; N, 6.46. Found: C, 60.46; H, 6.45; N, 6.38. ^1H NMR (C_6D_6): 6.99 (m, 4H, ArH), 6.79 (t, 2H, $J = 7.5$ Hz, ArH), 6.63 (d, 2H, $J = 8.6$ Hz, ArH), 4.85 (s, 1H, β -CH), 3.97 (br, 1H, CHMe₂), 3.34 (s, 6H, OMe), 1.74 (s, 6H, α -Me), 1.16 (br, 6H, CHMe₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 168.50 (C=N); 153.45, 140.45, 126.77, 124.72, 121.76, 112.31 (Ar–C); 95.15 (β -C), 65.90 (OCHMe₂), 55.12 (OMe), 27.92 (OCHMe₂), 23.48 (α -CH₃).

$(\text{BDI-3})\text{MgN}(\text{SiMe}_3)_3$, **3.** A solution of (BDI-3)H (0.500 g, 1.61 mmol) in 10 mL of benzene was added dropwise to a solution of $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ (0.556 g, 1.61 mmol) in 5 mL of benzene. The solution was stirred at room temperature for 10 min and dried in vacuo giving an orange solid (0.602 g, 92%). Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated hexanes solution in a freezer. CCDC 217758. Anal. Calcd for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{O}_2\text{Si}_2\text{Mg}$: C, 60.81; H, 7.90; N, 8.51. Found: C, 60.55; H, 7.65; N, 8.47. ^1H NMR (C_6D_6): 6.99 (d, 2H, $J = 8.0$ Hz, ArH), 6.87 (t, 2H, $J = 8.0$ Hz, ArH), 6.75 (t, 2H, $J = 7.8$ Hz, ArH), 6.54 (d, 2H, $J = 8.1$ Hz, ArH), 5.08 (s, 1H, β -CH), 3.42 (s, 6H, OMe), 2.06 (s, 6H, α -Me), 0.21 (SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 164.68 (C=N); 151.49, 140.36, 123.88, 121.41, 120.64, 109.38 (Ar–C); 100.28 (β -C), 54.48 (OCH₃), 23.10 (α -CH₃), 4.38 (Si(CH₃)₃).

$(\text{BDI-3})_2\text{Mg}$. A solution of (BDI-3)H (0.500 g, 1.61 mmol) and $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ (0.278 g, 0.805 mmol) in 15 mL of benzene was refluxed for 20 min. The solution was dried in vacuo giving an orange solid in quantitative yield. Anal. Calcd for $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_4\text{Mg}$: C, 71.01; H, 6.53; N, 8.72. Found: C, 70.79; H, 6.48; N, 8.66. ^1H NMR (C_6D_6): 6.96 (d, 2H, $J = 7.6$ Hz, ArH), 6.70–6.79 (m, 4H, ArH), 6.33 (d, 2H, $J = 7.8$ Hz, ArH), 4.73 (s, 1H, β -CH), 3.29 (s, 6H, OMe), 1.89 (s, 6H, α -Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 164.89 (C=N); 151.69, 140.57, 124.08, 121.62, 120.85, 109.59 (Ar–C); 100.48 (β -C), 54.69 (OMe), 23.30 (α -CH₃).

$(\text{BDI-3})\text{MgO}'\text{Bu}]_2$, **4.** HO'Bu (97 μL , 1.0 mmol) was added dropwise to a solution of $(\text{BDI-3})\text{MgN}(\text{SiMe}_3)_2$ (0.500 g, 1.01 mmol) in 15 mL of benzene and stirred for 30 min. The reaction mixture was dried in vacuo giving a yellow solid (0.349 g, 85%).

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Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated THF solution in a freezer. CCDC 217759. Anal. Calcd for $C_{23}H_{30}N_2O_3Mg$: C, 67.95; H, 7.38; N, 6.89. Found: C, 67.34; H, 7.26; N, 6.84. 1H NMR (C_6D_6): 6.90–7.10 (m, 6H, ArH), 6.70 (d, 2H, $J = 7.9$ Hz, ArH), 4.99 (s, 1H, β -CH), 3.36 (s, 6H, OMe), 1.83 (s, 6H, α -Me), 1.05 (br, 9H, t Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): 169.08 (C=N); 153.38, 140.92, 126.48, 124.34, 121.78, 111.81 (Ar-C); 95.89 (β -C), 67.24 (OCMe₃), 55.16 (OCH₃), 33.30 (OCMe₃), 23.61 (α -CH₃).

General Polymerization Procedure. *rac*-Lactide (0.500 g, 3.47 mmol) was dissolved in 6.00 mL of CH_2Cl_2 or THF. A solution of the corresponding catalyst precursor (3.47×10^{-5} mol) in 1.50 mL of CH_2Cl_2 or THF was then added to the lactide solution (100:1 [lactide]/[catalyst]). The reaction was stirred at room temperature for the desired time, after which small aliquots were taken to monitor the conversion. When the conversion was greater than 90%, the polymerization was quenched with excess methanol. The polymer precipitate was then filtered and dried under vacuum to constant weight.

X-Ray Crystallography. Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer at low temperature using an Oxford Cryosystems Cryostream Cooler. Crystals were coated with oil prior to being placed in the nitrogen gas stream. The data collection strategy was set up to measure a hemisphere of reciprocal space for compounds **1**, a quadrant for **3**, and **4** with a redundancy factor of 2.3, 3.9, and 3.6, which means that 90% of the reflections were measured at least 2.3, 3.9, and 3.6 times, respectively. A combination of ϕ and ω scans with a frame width of 1.0° was used. Data integration was done with Denzo.²⁵ Scaling and merging of the data were done with Scalepack.²⁵ The

structures were solved by either the Patterson method or direct methods in SHELXS-86.²⁶ Full-matrix least-squares refinements based on F^2 were performed SHELXL-93.²⁷ The methyl-group hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5 \times U_{eq}$ (bonded C atom). For each methyl group, the torsion angle which defines its orientation about the C–C bond was refined. The other hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2 \times U_{eq}$ (bonded C atom). Neutral-atom scattering factors were used and include terms for anomalous dispersion.²⁸

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Supporting Information Available: Crystallographic data for compounds **1**, **3**, and **4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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