Ligand Transfer Reactions of Mixed-Metal Lanthanide/Magnesium Allyl Complexes with *β*-Diketimines: Synthesis, Structures, and Ring-Opening Polymerization Catalysis

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The reaction of the mixed-metal lanthanide/magnesium allyl complexes [Ln(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)·Mg(η^1-C$_3$H$_5$)$_2$(μ-C$_4$H$_8$O$_2$)$_{1.5}$]$_n$ (Ln = La, **1**; Y, **2**) with the diketimine 2-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imino-2-pentene (BDI-H) in THF at 60 °C leads to the isolation of the magnesium *β*-diketiminato complex Mg{HC(MeCNC$_6$H$_3$Pr$^i_2$-2,6)$_2$}(η^1-C$_3$H$_5$)(THF) (**3**). The same product was obtained in the reaction of BDI-H with the ionic allyl lanthanate compounds [Mg(THF)$_6$][Nd(η^3-C$_3$H$_5$)$_4$]$_2$·2THF (**4**) and [Mg(THF)$_6$][Sm(η^3-C$_3$H$_5$)$_4$]$_2$·2THF (**5**). No lanthanide-containing product could be isolated. The X-ray structure of **3** shows that the complex is a monomeric neutral species with the magnesium center in a distorted tetrahedral arrangement. Complex **3** was found to hydrolyze after repeated crystallization attempts at −26 °C to give the hydroxy complex [Mg{HC(MeCNC$_6$H$_3$Pr$^i_2$-2,6)$_2$}(μ-OH)(THF)]$_2$·4THF (**6**). The X-ray structure of **6** consists of a hydroxide-bridged dimer with the magnesium center in a distorted square pyramid. Lanthanide BDI compounds were, however, obtained by reacting LnCl$_3$(THF)$_x$ (Ln = La, *x* = 4; Ln = Y, *x* = 3) with the lithium salt [Li(BDI)(THF)]$_2$ to give the dimeric complexes [LnCl$_2${HC(MeCNC$_6$H$_3$Pr$^i_2$-2,6)$_2$}]$_2$(THF)·2toluene (Ln = La, **7**; Y, **8**). According to its X-ray structure, **8** possesses distorted octahedral yttrium centers, one terminal chloride, and three bridging chloride ligands. The reaction of **7** or **8** using 4 equiv of allylMgCl did not give the expected mixed-ligand allyl lanthanide complex but led again to the magnesium complex **3** via BDI ligand exchange. Complexes **1**−**5** are highly effective single-component catalysts for the ring-opening polymerization of ϵ-caprolactone. Complex **3** also polymerizes *rac*-lactide efficiently and under mild conditions but with low stereospecificity. ϵ-Caprolactone is polymerized in minutes to high molecular weight materials by an allyl end-group transfer mechanism. The catalysts are active over a wide temperature range.

Introduction

Organolanthanide compounds have found widespread applications in organic synthesis and catalysis, as shown in recent excellent reviews on the synthesis, structural chemistry, and ligand design in "non-cyclopentadienyl" organolanthanides.[1] Allyl lanthanide complexes in particular have been shown to be excellent precatalysts.[2] For instance, Taube et al.[2g] reported the synthesis of the first neutral tris(η^3-allyl)lanthanide complexes [{La(η^3-C$_3$H$_5$)$_3$(η^1-C$_4$H$_8$O$_2$)}$_2$(μ-C$_4$H$_8$O$_2$)] and [Nd(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)]$_n$, which catalyze the 1,4-*trans*-polymeriza-tion of butadiene in toluene with high 1,4-*trans*-stereoselectivity. Other allyl complexes have been used in the polymerization of polar monomers; for example, we showed recently that anionic *ansa*-bis(allyl) lanthanide complexes[3b] and allyl-bridged oligo-nuclear complexes[3a,c] are highly active single-component catalysts for the polymerization of methyl methacrylate, butadiene,[4] and cyclic esters. We have also recently reported that the reaction between LnCl$_3$(THF)$_n$ (Ln = Y, Sm; *n* = 3) and 3 equiv of allylmagnesium chloride affords the new homoleptic tris(η^3-allyl) complexes [Ln(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)]$_n$ (Ln = Y, Sm) in very good yields in an improved one-pot procedure.[5] By contrast, the reaction of iodide complexes LnI$_3$(THF)$_n$ (Ln = La, *n* = 4; Ln = Y, Sm, Nd, *n* = 3.5) with allylMgI under the same reaction conditions yielded unexpectedly either neutral mixed-metal compounds [Ln(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)·Mg(η^1-C$_3$H$_5$)$_2$(μ-C$_4$H$_8$O$_2$)$_{1.5}$]$_n$ (Ln = La, **1**; Y, **2**) or the salts [Mg-(THF)$_6$][Sm$_2$(η^3-C$_3$H$_5$)$_6$(μ-η^3:η^3-C$_3$H$_5$)]$_2$·toluene and [Mg(THF)$_6$]-

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Scheme 1
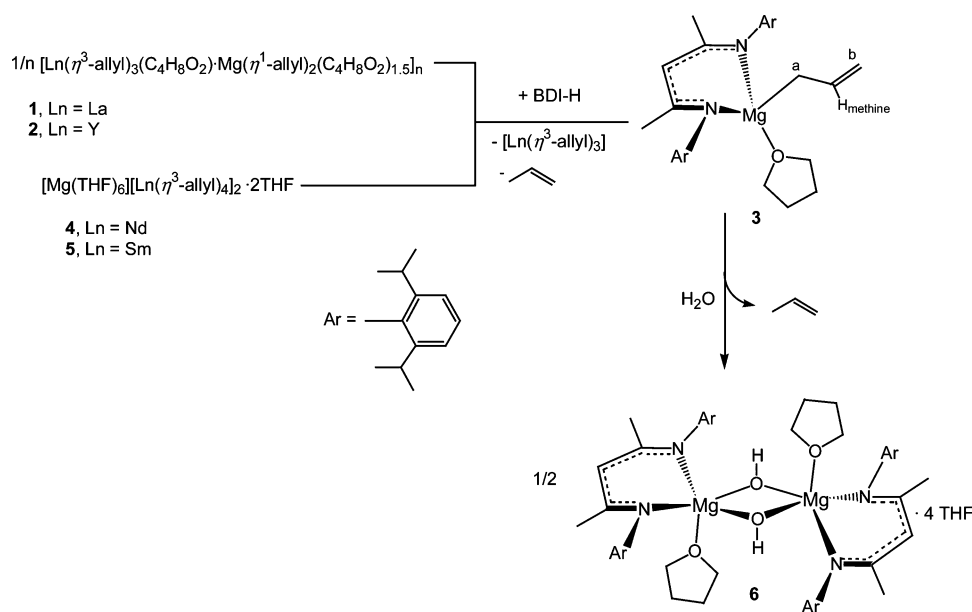
$[Nd(\eta^3\text{-}C_3H_5)_4]_2 \cdot 2THF$ (**4**), depending on the lanthanide metal.[6] Similar attempts to prepare halide-free homoleptic allyl-lanthanide complexes employing 3 equiv of the bulky 1,3-bis-(trimethylsilyl)allyl anion with lanthanide(III) iodides by Hanusa et al. failed, resulting instead in crystalline salts of the general formula $[K(THF)_4][LnI(\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3)_3]$ (Ln = Ce, Er, and Tb).[7]

We have become interested in using lanthanide allyls as convenient starting materials for the synthesis of mixed-ligand complexes and have recently reported the synthesis of bis(allyl) β-diketiminato (BDI) compounds $Ln(\eta^3\text{-}C_3H_5)_2\{HC(MeCNC_6H_3\text{-}Pr^i_2\text{-}2,6)_2\}$ (Ln = La, Y, Sm, Nd) by protolysis of $[Ln(\eta^3\text{-}C_3H_5)_3\text{-}(\mu\text{-}C_4H_8O_2)]_n$ with BDI-H.[5,8] These complexes act as excellent single-component catalysts for the ring-opening polymerization of ϵ-caprolactone and *rac*-lactide over a wide range of conditions.[9] We have now explored the reactivity of the recently reported lanthanide-magnesium allyls $[Ln(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)\cdot Mg(\eta^1\text{-}C_3H_5)_2(\mu\text{-}C_4H_8O_2)_{1.5}]_n$ (Ln = La, **1**; Y, **2**), $[Mg(THF)_6]\text{-}[Nd(\eta^3\text{-}C_3H_5)_4]_2\cdot 2THF$ (**4**), and $[Mg(THF)_6][Sm(\eta^3\text{-}C_3H_5)_4]_2\cdot$ 2THF (**5**) with BDI-H. In view of the current interest in poly(ϵ-caprolactone) and poly(lactide) as biodegradable and biocompatible polymers with potential as environmentally friendly replacement for bioresistant poly(α-olefines),[10,11] specialty medicinal products,[12] drug delivery agents,[13] and artificial tissue matrixes,[14] the new complexes were tested as catalysts for the polymerization of these polar monomers.

Results and Discussion

Synthesis. The reactions of $[Ln(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)\cdot Mg\text{-}(\eta^1\text{-}C_3H_5)_2(\mu\text{-}C_4H_8O_2)_{1.5}]_n$ (Ln = La, **1**; Y, **2**)[6] with the β-diketimine $H_2C(MeCNC_6H_3Pr^i_2\text{-}2,6)_2$ (BDI-H) in THF at 60 °C for 15 h gave high yields of the magnesium allyl complex $Mg\{HC(MeCNC_6H_3Pr^i_2\text{-}2,6)_2\}(\eta^1\text{-}C_3H_5)(THF)$ (**3**) as a colorless microcrystalline solid (Scheme 1). The same product was obtained when BDI-H was reacted with the salts $[Mg(THF)_6]\text{-}[Nd(\eta^3\text{-}C_3H_5)_4]_2\cdot 2THF$ (**4**) and $[Mg(THF)_6][Sm(\eta^3\text{-}C_3H_5)_4]_2\cdot$ 2THF (**5**). The corresponding tris(η^3-allyl)lanthanide compounds are likely byproducts but were not isolated. Magnesium mono-*alkyl* complexes supported by different β-diketiminato ligands have been reported previously.[15,16]

The ^1H spectrum of **3** in benzene-d_6 at room temperature displays one set of signals each for the η^1-allyl group and the β-diketiminato ligand, showing the symmetry in the molecule. A doublet for protons H_a and H_b and a multiplet for the central proton $H_{methine}$ indicate a σ–π fluxionality of the allyl ligand. This pattern remains unchanged down to −60 °C. The BDI ligand shows one signal each for the CH_3 groups and CH. However, the restricted rotation about the N−C_{aryl} bonds gives rise to two separate doublets for the isopropyl methyl groups. Cooling to −30 °C gives rise to four separate doublets for the isopropyl methyl groups and two multiplets for the isopropyl methine groups. The ^{13}C spectra in benzene-d_6 at 20 °C, too, are consistent with a fluxional allyl ligand. The compound retains one molecule of THF in the metal coordination sphere.

The single-crystal X-ray structure of complex **3** is shown in Figure 1. Selected bond lengths and angles are collected in Table 1. The magnesium center exhibits a distorted tetrahedral geometry, in which the N(1) and N(2) atoms occupy two

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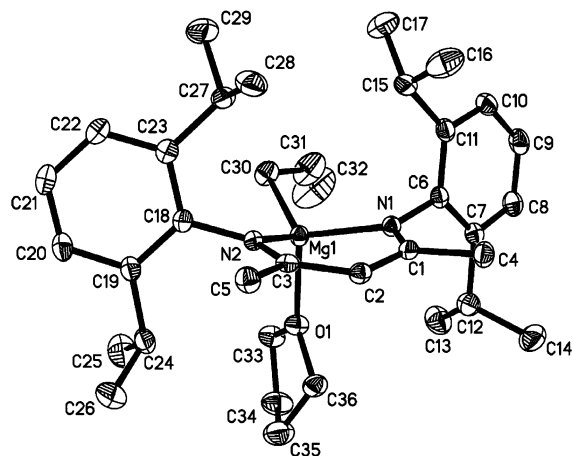
Figure 1. Molecular structure of complex Mg{HC(MeCNC$_6$H$_3$-Pr$^i_2$-2,6)$_2$}(η^1-C$_3$H$_5$)(THF) (**3**), showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.
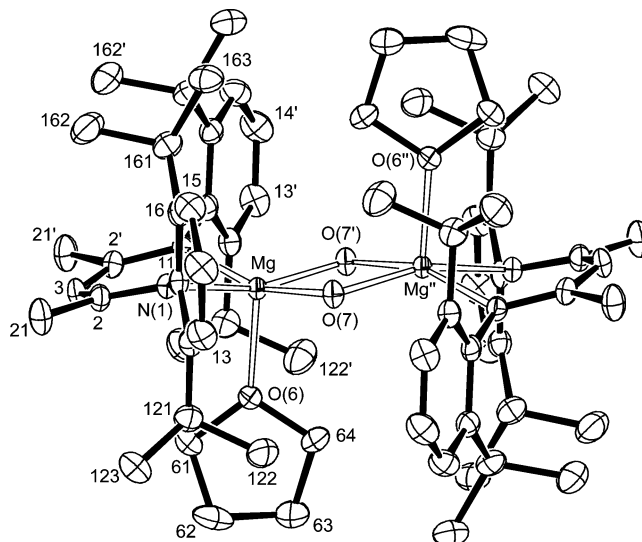
Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 3

Bond Lengths		Bond Angles	
Mg(1)−N(1)	2.052(2)	N(1)−Mg(1)−N(2)	93.76(9)
Mg(1)−N(2)	2.050(2)	C(1)−N(1)−C(6)	119.5(2)
Mg(1)−C(30)	2.139(3)	C(3)−N(2)−C(18)	118.5(2)
Mg(1)−O(1)	2.034(2)	N(1)−Mg(1)−C(30)	120.87(13)
C(30)−C(31)	1.421(5)	N(1)−Mg(1)−O(1)	104.64(9)
C(31)−C(32)	1.187(6)	N(2)−Mg(1)−C(30)	120.22(12)
N(1)−C(1)	1.326(3)	N(2)−Mg(1)−O(1)	105.13(9)
C(1)−C(2)	1.411(4)	Mg(1)−N(1)−C(1)	120.25(17)
C(2)−C(3)	1.408(4)	Mg(1)−N(2)−C(3)	120.20(18)
N(2)−C(3)	1.333(3)	N(1)−C(1)−C(2)	123.9(2)
N(1)−C(1)	1.326(3)	C(1)−C(2)−C(3)	130.1(3)
N(2)−C(18)	1.446(3)	C(2)−C(3)−N(2)	123.8(2)
		Mg(1)−C(30)−C(31)	111.0(3)
		C(30)−C(31)−C(32)	139.3(6)

positions and the η^1-allyl group and the THF molecule the other two positions. The magnesium atom lies 0.598(3) Å out of the C$_3$N$_2$ ligand plane, which compares well with that observed in related four-coordinated (η^1-allyl)magnesium compounds incorporating similar bulky BDI ligands.[15] The two nitrogen−magnesium bonds are similar, Mg−N(1) = 2.052(2) Å and Mg−N(2) = 2.050(2) Å, as are the C−N−C(aryl) angles C(1)−N(1)−C(6) = 119.5(2)° and C(3)−N(2)−C(18) = 118.5(2)°. Finally, the allyl fragment is η^1-bonded in the solid state, with two very different bond lengths, C(30)−C(31) = 1.421(5) Å for the single and C(31)−C(32) = 1.187(6) Å for the double bond. Whereas the carbon C(30) shows essentially sp^3 hybridization, as evidenced in the angle Mg(1)−C(30)−C(31) = 111.0(3)°, the C−C−C angle around carbon C(31) is widened to 139.3(6)°.

Compound **3** is sensitive to hydrolysis, and recrystallization attempts of THF solutions of **3** after several days at −26 °C gave the binuclear hydroxo compound [Mg{HC(MeCNC$_6$H$_3$-Pr$^i_2$-2,6)$_2$}(μ-OH)(THF)]$_2$·4(THF) (**6**) as a colorless microcrystalline solid (Scheme 1). The ^{1}H spectrum in benzene-d_6 at room temperature displays one set of signals for the β-diketiminato ligand, as expected from a molecule containing a mirror plane. There is restricted rotation about the N−C$_{aryl}$ bonds, as observed for **3**. The compound retains one molecule of THF per metal center.

The structure of **6** was determined by single-crystal X-ray diffraction (Figure 2). Selected bond lengths and angles are collected in Table 2. The coordination geometry around the metal center is a distorted square-pyramid, with the THF O atom


Figure 2. Molecular structure of complex [Mg{HC(MeCNC$_6$H$_3$-Pr$^i_2$-2,6)$_2$}(μ-OH)(THF)]$_2$·4(THF) (**6**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 3

Bond Lengths		Bond Angles	
Mg−N(1)	2.1688(18)	C(2)−N(1)−C(11)	116.69(18)
Mg−O(6)	2.093(2)	N(1)−Mg−N(1′)	86.11(10)
Mg−O(7)	1.9878(17)	O(6)−Mg−N(1)	97.70(7)
Mg−Mg″	3.1160(18)	O(7)−Mg−N(1)	95.88(7)
Mg(1)−C(32)	2.702(4)	O(7′)−Mg−N(1)	161.89(7)
O(7)−H(7)	0.77(4)	O(7)−Mg−O(6)	99.86(6)
		O(7)−Mg−O(7′)	76.78(12)
		Mg−O(7)−Mg″	103.22(12)

**Scheme 2**
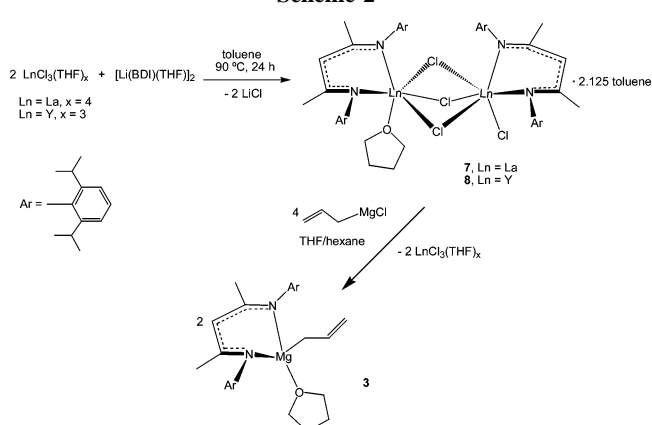
at the apex and N(1), N(1′), O(7), and O(7′) forming the square base. The central Mg$_2$O$_2$ four-membered ring is planar about a center of symmetry, each N$_2$ ligand lies about a mirror plane, and the THF ligand is disordered about that mirror plane. The five-membered β-diketiminato N$_2$C$_3$ moiety forms a plane, the normal of which is tilted by 29.34(8)° from that of the MgN$_2$ plane.

The magnesium atom lies 0.782(3) Å out of the C$_3$N$_2$ ligand plane, which is significantly larger than the displacement observed in complex **3** (0.598(3) Å). The magnesium−nitrogen bonds in **6** are substantially longer than those in **3**, Mg−N(1) = 2.1688(18) Å compared to Mg(1)−N(1) = 2.052(2) Å, reflecting the coordinatively saturated character of **6**. Finally, the two hydroxo groups are μ^2-bonded to the metal centers, with two different bond distances (Δ(Mg−O) = 0.105 Å), to form
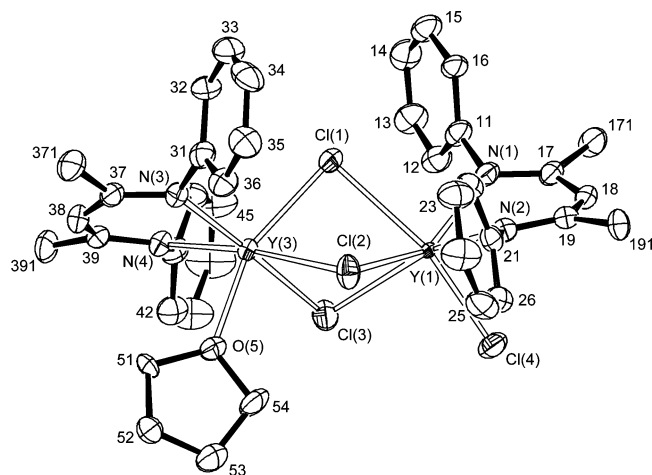
Figure 3. Molecular structure of complex [YCl$_2$\{HC(MeCNC$_6$H$_3$-Pr$^i_2$-2,6)$_2$\}]$_2$(THF)·2toluene (**8**). The isopropyl substituents and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

an Mg$_2$O$_2$ rhombus. There are no hydrogen-bonding interactions to the μ-OH ligands. The complex crystallizes with four molecules of THF in the unit cell.

In an effort to find an alternative strategy to prepare organolanthanide complexes supported by BDI ligands, we focused on the preparation of dichloride species, which might serve as convenient precursors for further transformations. A limited number of mono-, bis-, and tris-diketiminato lanthanide complexes have been described, including more recently octahedral compounds of the type (BDI)LnCl$_2$(THF)$_2$.[17]

The reaction of LnCl$_3$(THF)$_x$ (Ln = La, x = 4; Ln = Y, x = 3) with the lithium salt [Li(BDI)(THF)]$_2$ in toluene at 90 °C for 24 h gave the unexpected asymmetric chloro-bridged dimers [LnCl$_2$\{η^3-(MeC(N-2, 6-^{i}Pr-C$_6$H$_3$)$_2$)CH\}]$_2$(THF)·2toluene (Ln = La, **7**; Y, **8**), with a triple chlorine bridge in the molecule (Scheme 2). Examples of crystallographically characterized multiple halogen bridges between two lanthanide atoms are rare; they include clusters[18] and related BDI complexes of Yb, Sm, and Nd reported recently by Shen et al.[19]

The ^{1}H spectra of **7** and **8** in benzene-d_6 at room temperature display one set of signals for the β-diketiminato ligands. Restricted rotation about the N−C$_{aryl}$ bonds gives rise to two separate doublets for the isopropyl methyl groups.

The single-crystal X-ray structure of the yttrium complex **8** has been determined. There are two independent but very similar molecules in the crystal. The molecular structure of one is shown in Figure 3; selected bond lengths and angles of this molecule are listed in Table 3 and are discussed below. Complex **8** has a binuclear structure in the solid state, with three bridging and one terminal chloride ligand. One of the metal centers coordinates THF; both metals have a distorted octahedral geometry. The backbone of the BDI ligand (NC$_3$N) and the yttrium atom form a stable six-membered ring. The ring adopts a shallow boat conformation, with C(18) and Y(1) deviating from the N(1)C(17)C(19)N(2) plane by 0.099(12) and 0.926(12) Å, and C(38) and Y(3) deviating from the N(3)C(37)C(39)N(4) plane by 0.105(12) and 0.579(12) Å, respectively. The dihedral angle between these planes is 43.2(2)°, which indicates that the two

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 8

Bond Lengths			
Y(1)−N(1)	2.305(7)	Y(3)−N(3)	2.328(6)
Y(1)−N(2)	2.323(6)	Y(3)−N(4)	2.328(6)
Y(1)−Cl(1)	2.782(2)	Y(3)−Cl(1)	2.649(2)
Y(1)−Cl(2)	2.750(2)	Y(3)−Cl(2)	2.681(2)
Y(1)−Cl(3)	2.783(2)	Y(3)−Cl(3)	2.679(2)
Y(1)−Cl(4)	2.551(2)	Y(3)−O(5)	2.326(5)
N(1)−C(17)	1.352(10)	N(3)−C(37)	1.352(9)
C(17)−C(18)	1.414(11)	C(37)−C(38)	1.398(11)
C(18)−C(19)	1.375(11)	C(38)−C(39)	1.402(11)
C(19)−N(2)	1.354(9)	C(39)−N(4)	1.355(9)
Y(1)−Y(3)	3.8133(12)		

Bond Angles			
N(1)−Y(1)−N(2)	82.2(2)	N(3)−Y(3)−N(4)	80.7(2)
C(11)−N(1)−C(17)	116.0(7)	C(31)−N(3)−C(37)	115.0(6)
C(19)−N(2)−C(21)	116.8(6)	C(39)−N(4)−C(41)	116.8(6)
N(1)−Y(1)−Cl(1)	83.65(16)	N(3)−Y(3)−O(5)	92.3(2)
Cl(1)−Y(1)−Cl(3)	74.31(7)	O(5)−Y(3)−Cl(1)	157.48(13)
Cl(1)−Y(1)−Cl(4)	152.51(8)	Cl(1)−Y(3)−Cl(2)	77.00(7)
N(1)−Y(1)−Cl(4)	95.07(16)	N(3)−Y(3)−Cl(3)	177.44(16)
N(2)−Y(1)−Cl(2)	84.34(16)	N(4)−Y(1)−Cl(2)	173.22(16)
Y(1)−Cl(1)−Y(3)	89.15(7)	Y(1)−Cl(3)−Y(3)	88.52(6)
Y(1)−Cl(2)−Y(3)	89.20(6)		

β-diketiminate ligands are not perpendicular, as in the ytterbium complex [(BDI′)YbCl(μ-Cl$_3$)Yb(BDI′)(THF)].[19b] The orientations of the arene rings relative to the NC$_2$N plane are approximately perpendicular (the dihedral angles between the arene rings and the NC$_2$N planes range from 75.9(4)° to 86.7-(4)°).

The Y−N bond distances range from 2.305(7) to 2.328(6) Å and compare well with those found in the isostructural ytterbium complex [(BDI′)YbCl(μ-Cl$_3$)Yb(BDI′)(THF)].[19,20] The Y(1)−Cl(4) and Y(3)−O(5) bond lengths are also comparable to those in the Yb analogue. The three chloride bridges in complex **8** are asymmetric; the average Y(1)−Cl(1,2,3) bond length of 2.771(1) Å is ca. 0.101 Å longer than the Y(3)−Cl(1,2,3) distance. The Y(1)···Y(3) distance of 3.8133(12) Å is a nonbonding distance.

All attempts to produce lanthanide allyl complexes by reacting **7** or **8** with 4 equiv of allylmagnesium chloride in THF/light petroleum mixtures failed. Instead, transfer of the BDI ligand to magnesium took place to give, once again, complex **3**, accompanied by formation of LnCl$_3$(THF)$_x$ and other byproducts. Clearly a ligand exchange equilibrium (eq 1) is established that lies strongly to the right.
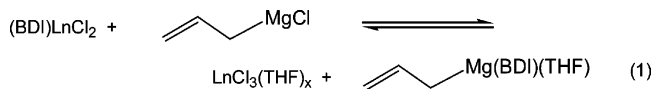
Polymerization Studies. Many complexes of electrophilic metals including magnesium and lanthanide compounds have shown good activity for the polymerization of cyclic esters,[9,21,22] although in some cases anionic lanthanate complexes were found

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Table 4. Polymerization of ε-Caprolactone Catalyzed by the Allyl Complexes 1−5[a]

entry	initiator	T [°C]	t [min]	yield [g]	conv (%)[b]	prod[c]	M_w[d]	M_w/M_n[d]
1	LaMg(allyl)$_5$ **1**	20	0.3	2.06	99	4577	59 000	1.4
2	LaMg(allyl)$_5$ **1**	−20	0.3	1.49	73	3310	28 000	1.1
3	YMg(allyl)$_5$ **2**	20	1.3	1.23	61	630	38 000	1.3
4	YMg(allyl)$_5$ **2**	0	2	0.74	36	246	25 000	1.2
5	YMg(allyl)$_5$ **2**	−20	2	traces				
6	Sm$_2$(allyl)$_7$⁻	20	3	1.66	83	368	14 000	1.3
7	Sm$_2$(allyl)$_7$⁻	0	3	1.12	54	248	20 000	1.2
8	Nd(allyl)$_4$⁻ **4**	20	0.5	2.06	99	2746	25 000	1.4
9	Nd(allyl)$_4$⁻ **4**	0	0.5	1.98	96	2640	18 500	1.2
10	Sm(allyl)$_4$⁻ **5**	20	1.3	1.89	92	969	19 000	1.3
11	Sm(allyl)$_4$⁻ **5**	0	2	1.21	58	403	17 500	1.2
12	Mg{HC(MeCNC$_6$H$_3$Pr$^i_2$-2,6)$_2$}(η^1-C$_3$H$_5$)(THF) (**3**)	20	6	1.89	92	210	19 000	1.4
13	**3**	0	6	0.2	10	22	27 500	1.3

[a] Polymerization conditions: 90 μmol of initiator, ε-CL/initiator = 200. [b] Percentage conversion of the monomer (weight monomer/weight of polymer recovered × 100). [c] kg polymer (mol initiator)$^{-1}$·h^{-1}. [d] Determined by GPC relative to polystyrene standards.

to be rather less effective than their neutral counterparts.[23] Complexes **1**−**6** were therefore tested for the ring-opening polymerization of ε-caprolactone (CL) and **1**−**5** for the polymerization of *rac*-lactide (*rac*-LA). The compounds act as highly active single-component catalysts for the polymerization of ε-caprolactone (CL) to give high molecular weight polymers (Table 4). A variety of polymerization conditions were explored. The lanthanide/magnesium mixed-metal complexes **1** and **2** initiate very rapid polymerization of CL at room temperature (entries 1 and 3); **1** gives complete conversion of 200 equiv of CL in 20 s, with a productivity of more than 4×10^6 g PCL (mol initiator)$^{-1}$·h^{-1}, to give high molecular weight polymer with good molecular weight control (M_w/M_n = 1.4). Cooling to 0 °C and below narrowed the molecular weight distribution; for example, at 0 °C the yttrium compound **2**, as well as [Mg-(THF)$_6$][Nd(allyl)$_4$]$_2$ (**4**), gave polydispersities of 1.2; [Mg-(THF)$_6$][Sm$_2$(allyl)$_7$]$_2$·toluene, reported earlier[6] and included here for comparison, showed similar results (entries 4, 7, and 9). Further cooling drastically reduced the catalytic activity except for the lanthanum complex **1**, which gave good conversion even at −20 °C and generated polymer with a very narrow polydispersity (M_w/M_n = 1.1, entry 2). Surprisingly, the samarium salts [Mg(THF)$_6$][Sm$_2$(allyl)$_7$]$_2$·toluene and [Mg-(THF)$_6$][Sm(allyl)$_4$]$_2$·(**5**) showed much lower productivity than either neutral lanthanum or anionic neodymium complexes.

The magnesium allyl complex **3** gave near complete conversion of 200 equiv of CL in 6 min (entry 12) and produces medium molecular weight polymer with narrow polydispersity (M_w = 19 000, M_w/M_n = 1.4). The polymerization activity decreases steeply on cooling to 0 °C, although it appears that under these conditions transesterification is minimal and the polymer molecular weight increased substantially (entry 13). Rather surprisingly, the magnesium hydroxo complex **6** was unable to initiate the ring-opening of ε-caprolactone after 6 min, and only traces of polymer were obtained.

The activity of metal allyl precatalysts evidently depends on the nature of the metal center and decreases in the order **1** > **4** ≫ **5** > **2** > **3** under the present polymerization conditions. This sequence is roughly in agreement with the trends in ionic radii

[La^{3+} (1.061 Å) > Nd^{3+} (0.995) > Sm^{3+} (0.964) > Y^{3+} (0.893) > Mg^{2+} (0.66)].

The poly(caprolactone) is produced by a nucleophilic pathway; that is, the process is initiated by the transfer of an allyl ligand to the monomer, with formation of a metal alkoxide-propagating species.[24] End-group analysis by ^{1}H NMR spectroscopy showed that the polymer contained −CH$_2$CH=CH$_2$ termini. Although a number of organolanthanides have been shown to polymerize ε-caprolactone,[21−23] few complexes have been reported[3a,5,25] to polymerize ε-CL at low temperatures and in very short periods of time, as in this case.

Complexes **1**−**5** were examined for the production of polylactide (PLA). The use of well-defined single-site catalyst systems is an attractive possibility for the production of PLAs with specific molecular weights and microstructures. Various discrete metal complexes have been employed in lactide polymerization; these include the metals Al, Zn, Mg, Y, Ln, Sn(II), Sn(IV), and Fe(II), and excellent general reviews of the use of metal coordination complexes in PLA production appeared recently.[9,26] Probably the most successful catalyst developed to date is the Coates' zinc β-diketiminato complex [(BDI)Zn(O^{i}Pr)]$_2$.[27] This shows living polymerization characteristics, is rapid at room temperature, and shows significant stereoselectivity in the production of heterotactic PLA from *rac*-lactide. Hillmyer and Tolman have also recently reported a highly active zinc complex that holds promise for future development,[28] while calcium and aluminum systems of the type LCaX (L = bulky ^{R}Tp, BDI; X = N(SiMe$_3$)$_2$, O-2,6-^{i}Pr$_2$C$_6$H$_3$)

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Table 5. Polymerization of *rac*-Lactide Catalyzed by the Allyl Complexes 1−5[a]

entry	initiator	T [°C]	t [h]	yield [g]	conv (%)[b]	prod[c]	$M_w{}^d$	$M_w/M_n{}^d$
1	LaMg(allyl)₅ **1**	20	2	0.10	10	0.7	29 000	1.1
2	LaMg(allyl)₅ **1**	40	2	0.85	85	6.1	23 000	1.3
3	YMg(allyl)₅ **2**	20	2	traces				
4	YMg(allyl)₅ **2**	40	2	0.25	25	1.8	19 000	1.2
6	Sm₂(allyl)₇⁻	20	2	0.02	2	0.1	21 000	1.2
7	Sm₂(allyl)₇⁻	40	2	0.30	30	2.1	19 000	1.3
8	Nd(allyl)₄⁻ **4**	20	2	0.06	6	0.4	28 000	1.1
9	Nd(allyl)₄⁻ **4**	40	2	0.70	70	5.0	23 500	1.3
10	Sm(allyl)₄⁻ **5**	20	2	0.03	3	0.2	22 000	1.1
11	Sm(allyl)₄⁻ **5**	40	2	0.40	40	2.8	20 500	1.4
12	Mg{HC(MeCNC₆H₃Pr^{i}₂-2,6)₂}(η¹-C₃H₅)(THF) (**3**)	50	2	0.38	38	2.7	19 000	1.3
13	**3**	50	4	0.53	53	1.9	27 500	1.4
14	**3**	50	5	0.78	78	2.2	29 000	1.5

[a] Polymerization conditions: 70 µmol of initiator, *rac*-lactide/initiator = 100. [b] Percentage conversion of the monomer (weight monomer/weight of polymer recovered × 100). [c] kg polymer (mol initiator)$^{-1}$·h^{-1}. [d] Determined by GPC relative to polystyrene standards.

and (*R,R*-salen) and (*S,S*-salen)Al(OR) reported by Chisholm have been described as probably the most reactive and sterose-lective catalysts reported to date for LA polymerization.[29]

Complexes **1**−**5** proved to be very active catalysts for the polymerization of *rac*-lactide (LA) under mild conditions (20−40 °C) (Table 5). A variety of polymerization conditions were explored. At 40 °C the lanthanide/magnesium mixed-metal complexes **1** and **2** initiated very rapid polymerization of LA (entries 2 and 4); **1** gave 85% conversion of 100 equiv of LA in 2 h, with a productivity of more than 6×10^6 g PLA (mol initiator)$^{-1}$·h^{-1}, to give medium molecular weight polymer with good molecular weight control (M_w/M_n = 1.3). On the other hand, with the yttrium complex **2** no polymer was obtained after 2 h at room temperature, whereas the analogous La complex **1** showed good polymerization activity and gave a very narrow molecular weight distribution (entry 1, M_w/M_n = 1.1).

The allyl lanthanates **4**, **5**, and [Mg(THF)₆][Sm₂(allyl)₇]₂·toluene also proved to be very active catalysts. For instance, the neodymium derivative **4** gave 70% conversion of 100 equiv of LA in 2 h, with a productivity of 5×10^6 g PLA (mol Nd)$^{-1}$·h^{-1}, to give medium molecular weight polymer with good molecular weight control (M_w/M_n = 1.3). Cooling to 20 °C narrowed the molecular weight distribution; both **4** and **5** gave polydispersities of 1.1. As seen in the case of ϵ-caprolactone polymerization, the metal radius affects the catalytic activity, La ≥ Nd > Sm > Y (Table 5, entries 2, 9, 11, and 4). End-group analysis of the polymers by ¹H NMR spectroscopy showed that, as for PCL, the polymerization was initiated by nucleophilic attack of allyl on lactide. The homonuclear decoupled ¹H NMR spectra in the methine region of the PLA[30] (CDCl₃, 298 K, 500 MHz) revealed that, unlike zinc and magnesium BDI complexes, catalysts **1**, **2**, **4**, and **5** were not stereoselective and gave atactic PLA, most probably as the result of the larger ionic radius, which leads to more flexible and sterically less congested active centers. Similar behavior has been recently reported for calcium complexes of the type (BDI)-Ca(N(SiMe₃)₂)·THF in comparison with the corresponding magnesium analogues.[29b]

The magnesium allyl complex **3** also proved to be an active catalyst for the polymerization of *rac*-lactide at mild conditions

(Table 5, entries 12−14) and at 50 °C gives 38% conversion of 100 equiv of *rac*-lactide after 2 h, with a productivity of more than 2.7×10^3 g PLA (mol Mg)$^{-1}$·h^{-1}. The polymer has medium molecular weight and very narrow polydispersity. Extending the reaction to 5 h increased the conversion to 78%, with a small increase in polydispersity, up to M_w/M_n = 1.5. PLA end-group analysis also confirmed that for Mg catalyst, too, the polymerization was initiated by nucleophilic attack of allyl on lactide. The homonuclear decoupled ¹H NMR spectra of the PLA obtained with **3** revealed a low degree of stereo-selectivity, given the fact that the heterotactic tetrads **isi** and **sis** were not greatly enhanced as a result of the preference of the consecutive alternate insertion of the L- and D-lactide units into the growing chain (Figure 4). These results parallel Chisholm's observations on magnesium alkoxides, [(BDI)Mg-(O^{t}Bu)(THF)][31] and [(η³-trispyrazolylborate)MgOR],[32] which polymerize *rac*-lactide to atactic poly(lactide). Rather interest-ingly, in the ¹³C{¹H} spectrum we find some formation of tetrad sequences usually derived from polymerization of *meso*-lactide (see Figure 4), which could arise from back-biting in the polymer chain since polymerization of L-lactide shows only **iii** tetrads.

Conclusions

The reaction of metal-mixed lanthanide allyl complexes [Ln-(η³-C₃H₅)₃(μ-C₄H₈O₂)·Mg(η¹-C₃H₅)₂(μ-C₄H₈O₂)$_{1.5}$]$_n$ (Ln = La, Y) with β-diketimine (BDI-H) affords the magnesium allyl complex (BDI)Mg(allyl)(THF) as the only isolated product. The same compound was obtained from BDI-H and the tetraallyl lanthanate salts [Mg(THF)₆][Ln(η³-C₃H₅)₄]₂·2THF (Ln = Nd, Sm), as well as by treatment of the new mixed-ligand lanthanide chlorides [LnCl₂(BDI)]₂ (Ln = La, Y) with allylmagnesium chloride. The lanthanide and magnesium allyl complexes are active single-component catalysts for the ring-opening polym-erization of ϵ-caprolactone and *rac*-lactide over a wide range of temperatures, without the need of an activator or scavenger. The magnesium BDI complex polymerizes *rac*-lactide at 50 °C. Surprisingly, its hydrolysis product, the hydroxo complex [(BDI)Mg(μ-OH)(THF)]₂, was found to be catalytically inactive. Polymerization is initiated by nucleophilic allyl group transfer to monomer. Not unexpectedly, the polymerization of LA is slower than of CL but offers good control and gives polymers

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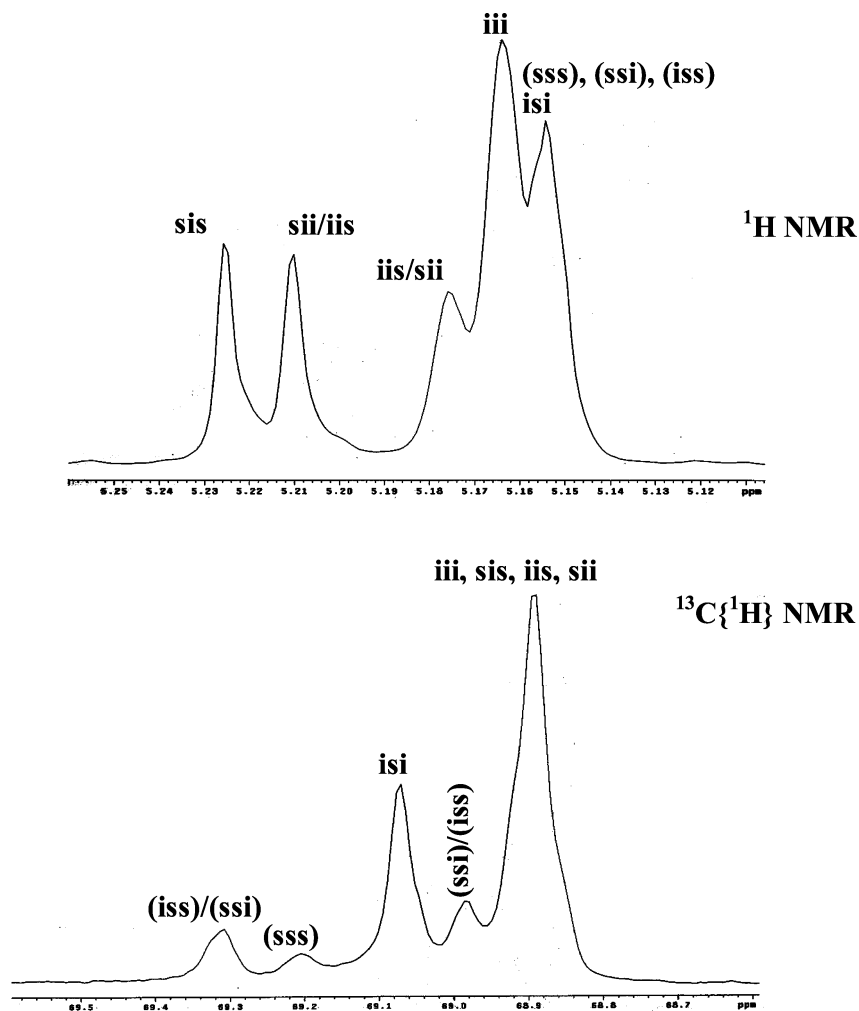
Figure 4. ^{1}H NMR (CDCl₃, 500 MHz) of the homodecoupled C*H* resonance and ^{13}C{^{1}H} NMR (CDCl₃, 125.7 MHz) of the methane carbon signals of poly(*rac*-lactide) initiated by **3**. The tetrad sequence is according to Kricheldorf.[31] The (**sss**), (**iss**), and (**ssi**) tetrads in the ^{1}H NMR homodecoupled and ^{13}C{^{1}H} NMR spectra are proposed to arise from back-biting, as these sequences are normally seen only in poly(*meso*-lactide).

with polydispersities as narrow as $M_w/M_n = 1.1$ under mild conditions.

Experimental Section

General Procedures. All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane) and distilled under nitrogen from sodium (toluene), sodium−potassium alloy (light petroleum, bp 40−60 °C), sodium-benzophenone (THF, diethyl ether), or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. LnCl₃(H₂O)₆ and rare earth metal powders were used as purchased. Anhydrous LnCl₃[34] and the β-diketimine H₂C(MeCNC₆H₃Pr^{i}₂-2,6)₂[35] were prepared according to the literature procedures. ε-Caprolactone was dried by stirring over fresh CaH₂ for 48 h, then distilled under reduced pressure and stored over activated 4 Å molecular sieves. *rac*-Lactide was sublimed twice, recrystallized from THF, and finally sublimed again prior to use. NMR spectra were recorded using Bruker Avance DPX-300 and

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Varian Inova FT-500 spectrometers. ^{1}H NMR spectra (300.1 MHz) were referenced to the residual solvent protons of the deuterated solvent used. ^{13}C NMR spectra (75.5 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. The homodecoupled ^{1}H NMR and ^{13}C NMR spectra of poly(lactide) polymers were recorded using a Varian Inova FT-500 spectrometer. The NMR probe temperature was varied using a thermocouple and calibrated with CH₃OH. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a PLgel 5 Å Mixes-C column, a refractive index detector, and a PD2040 light-scattering detector. The GPC column was eluted with THF at 40 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580−483 000 Da.

Preparation of Mg{HC(MeCNC₆H₃Pr^{i}₂-2,6)₂}(η[1]-C₃H₅)(THF) (3). The synthesis is exemplified by the following procedure. To a solution of [La(η[3]-C₃H₅)₃(μ-C₄H₈O₂)·Mg(η[1]-C₃H₅)₂(μ-C₄H₈O₂)₁.₅]ₙ (**1**) (1.0 g, 1.69 mmol) in THF (100 mL) was added dropwise a solution of BDI-H (0.71 g, 1.69 mmol) in THF at room temperature. The initial yellow solution became pale yellow over time and was stirred at 60 °C for 15 h. After removing of volatiles the pale yellow solid was washed with light petroleum (10 mL). Finally, THF was added (10 mL) and the mixture cooled to −26 °C to afford **3** as a colorless microcrystalline solid, yield 0.65 g (1.17 mmol, 68.9%). Anal. Calcd for C₃₆H₅₄N₂MgO: C, 77.82; H, 9.72; N, 5.04. Found: C, 77.89; H, 9.72, N, 5.09. ^{1}H NMR (benzene-*d₆*, 20 °C):

δ 7.16 (s, 6 H, H$_{o,m,p}$), 6.12 (m, 1 H, $-$CH$_2$CHCH$_2$), 4.76 (s, H, CH$_\beta$), 3.66 (m, 4 H, THF), 3.22 (m, 4 H, CHMe$_2$), 2.67 (d, $^3J_{HH}$ = 11.1 Hz, 4 H, $-$CH_2CHCH$_2$), 1.62 (s, 6 H, Me), 1.27 (m, 4 H, THF), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 24 H, CHMe_2). ^{13}C NMR (benzene-d_6, 20 °C): δ 168.5 ($-$CH$_2$CHCH$_2$), 147.6$-$126.4 (C^{Ph}), 123.9 (C$_\beta$), 94.5 (CH$_\beta$), 69.8 (THF), 56.5 ($-$CH$_2$CHCH$_2$), 29.9 (CHMe$_2$), 28.2 (Me), 25.9 (THF), 25.4$-$24.0 (CHMe$_2$).

Preparation of [Mg{HC(MeCNC$_6$H$_3$Pr^i$_2$-2,6)$_2$}(μ-OH)(THF)]$_2$· 4(THF) (6). A solution of **3** (1.0 g, 1.80 mmol) in THF (100 mL) was left to crystallize for 10 days at $-$26 °C. Colorless crystals of **6** were obtained, yield 1.47 g (1.08 mmol, 60.4%). Anal. Calcd for C$_{82}$H$_{132}$O$_8$Mg$_2$N$_4$: C, 72.86; H, 9.77, N, 4.14 Found: C, 72.89; H, 9.77, N, 4.18. ^{1}H NMR (benzene-d_6, 20 °C): δ 7.11 (s, 12 H, H$_{o,m,p}$), 4.81 (s, 2 H, CH), 3.57 (m, 8 H, THF), 3.13 (m, 8 H, CHMe$_2$), 1.57 (s, 12 H, Me), 1.28 (m, 8 H, THF), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, CHMe_2), 0.87 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, CHMe_2). ^{13}C NMR (benzene-d_6, 20 °C): δ 145.3$-$127.1 (C^{Ph}), 128.9 (C$_\beta$), 96.1 (CH$_\beta$), 70.8 (THF), 29.5 (CHMe$_2$), 28.2 (Me), 26.2 (THF), 23.2$-$18.9 (CHMe$_2$).

Preparation of [LaCl$_2${HC(MeCNC$_6$H$_3$Pr^i$_2$-2,6)$_2$}]$_2$(THF)· 2toluene (7). To a solution of LaCl$_3$(THF)$_4$ (1.0 g, 1.87 mmol) in toluene (100 mL) was added dropwise at room temperature a solution of [Li(THF)(BDI)]$_2$ in toluene (0.93 g, 0.94 mmol). The temperature was increased at 90 °C during 24 h. The initial colorless suspension became pale green over time. After filtration and removal of volatiles, the solid residue was extracted with light petroleum (30 mL), filtrated, and cooled to $-$26 °C to give **7** as a pale green microcrystalline solid, yield 2.11 g (1.39 mmol, 74.5%). Anal. Calcd for C$_{76}$H$_{106}$N$_4$Cl$_4$La$_2$O: C, 61.06; H, 7.09; N, 3.74. Found: C, 61.15; H, 7.12; N, 3.54. ^{1}H NMR (CDCl$_3$, 20 °C): δ 7.29 (s, 6 H, H$_{o,m,p}$), 4.92 (s, H, CH$_\beta$), 3.75 (m, 4 H, THF), 3.10 (sep, $^3J_{HH}$ = 6.8 Hz, 4 H, CHMe$_2$), 1.86 (m, 4H, THF), 1.73 (s, 6 H, CH$_3$), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CHMe_2), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 20 °C): δ 149.7$-$125.6 (C^{Ph}), 124.5 (C$_\beta$), 96.7 (CH), 70.1 (THF), 27.5 (THF), 26.3 (CHMe$_2$), 25.1$-$21.3 (CHMe$_2$).

Preparation of [YCl$_2${HC(MeCNC$_6$H$_3$Pr^i$_2$-2,6)$_2$}]$_2$(THF)· 2toluene (8). Following the procedure described for **7**, a solution of YCl$_3$(THF)$_3$ (1 g, 2.43 mmol) in toluene (100 mL) was treated with [Li(THF)(BDI)]$_2$ in toluene (1.20 g, 1.21 mmol). The initial colorless suspension became green over time. Workup gave **8** as a green microcrystalline solid, yield 2.61 g (1.85 mmol, 76.1%). Anal. Calcd for C$_{76}$H$_{106}$N$_4$Cl$_4$Y$_2$O: C, 64.69; H, 7.51; N, 3.97. Found: C, 64.74; H, 7.60; N, 4.01. ^{1}H NMR (CDCl$_3$, 20 °C): δ 7.13 (s, 6 H, H$_{o,m,p}$), 4.87 (s, H, CH$_\beta$), 3.75 (m, 4 H, THF), 3.09 (sep, $^3J_{HH}$ = 6.8 Hz, 4 H, CHMe$_2$), 1.86 (m, 4 H, THF), 1.72 (s, 6 H, CH$_3$), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CHMe_2), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CHMe_2). ^{13}C NMR (CDCl$_3$, 20 °C): δ 148.6$-$125.9 (C^{Ph}), 123.8 (C$_\beta$), 94.6 (CH), 70.1 (THF), 27.5 (THF), 26.2 CHMe$_2$, 25.1$-$21.3 (CHMe$_2$).

X-ray Crystallography. Crystals coated with dry Nujol or perfluoropolyether were mounted on a glass fiber and fixed in a cold nitrogen steam (T = 180(2) K). Intensity data were collected on a Nonius Kappa CCD diffractometer equipped with a Mo Kα radiation (λ = 0.71073 Å) source and graphite monochromator. Data were processed using the DENZO/SCALE PACK programs[36] and absorption corrections applied in SORTAV.[37] The structures were determined by direct methods in the SHELXS programs[38] and refined by full-matrix least-squares methods on F^2 in SHELXL.[39] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their U_{iso} values set to ride on the U_{eq} values of the parent

carbon atoms. Scattering factors for neutral atoms were taken from the literature.[40] Computer programs used in this analysis have been noted above and were run on a DEC-AlphaStation 200 4/100, in the Biological Chemistry Department, John Innes Centre.

Crystal Data for 3: C$_{36}$H$_{54}$MgN$_2$O, fw 555.12; crystal size 0.32 × 0.12 × 0.10 mm^3; triclinic, space group P$\bar{1}$ (no. 2), a = 9.0247-(3) Å, b = 12.1940(4) Å, c = 15.9219(5) Å; α = 86.9435(15)°, β = 78.1780(15)°, γ = 89.2258(11)°; V = 1 712.55(10) Å^3; Z = 2; ρ_{cal} = 1.077 g/cm^3; μ(Mo Kα) = 0.080 mm^{-1}; F(000) = 608; 3.60° $\leq \theta \leq$ 26.01°; $-$10 $\leq h \leq$ 11; $-$14 $\leq k \leq$ 15; $-$19 $\leq I \leq$ 19; 16 395 reflections collected, of which 6650 were independent (R_{int} = 0.0601) and 4155 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.0734, wR_2 (all data) = 0.1644, w = [$\sigma^2(F_o^2)$ + (0.0393)^2 + 1.80P]$^{-1}$ with P = (F_o^2 + 2F_c^2)/3; no. of data/restraints/ parameters 6650/0/514; goodness of fit (F^2) = 1.051. In the final difference map, the highest peaks (to ca. 0.35 e Å^{-3}) were close to the allyl ligand.

Crystal Data for 6: C$_{66}$H$_{100}$O$_4$Mg$_2$N$_4$·4(C$_4$H$_8$O), fw 1350.5; crystal size 0.23 × 0.21 × 0.05 mm^3; monoclinic, space group C2/m (no. 12), a = 18.1687(5) Å, b = 18.5070(6) Å, c = 14.0704(4) Å; β = 121.970(2)°; V = 4 013.5(2) Å^3; Z = 2; ρ_{cal} = 1.118 g/cm^3; μ(Mo Kα) = 0.084 mm^{-1}; F(000) = 1480; 3.6° $\leq \theta \leq$ 25.0°; $-$21 $\leq h \leq$ 21; $-$21 $\leq k \leq$ 22; $-$16 $\leq I \leq$ 16; 15 070 reflections collected, of which 3644 were independent (R_{int} = 0.062) and 2681 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.064, wR_2 (all data) = 0.161, w = [$\sigma^2(F_o^2)$ + (0.0696P)^2 + 4.41P]$^{-1}$ with P = (F_o^2 + 2F_c^2)/3; no. of data/restraints/parameters 3644/0/270; goodness of fit (F^2) = 1.048. In the final difference map, the highest peaks (to ca. 0.38 e Å^{-3}) were close to the disordered THF molecule.

Crystal Data for 8: C$_{62}$H$_{90}$N$_4$Cl$_4$Y$_2$O ca. 2.125(C$_7$H$_8$), fw 1422.8; crystal size 0.37 × 0.35 × 0.35 mm^3; monoclinic, space group P2$_1$/c (no. 14), a = 23.842(5) Å, b = 26.615(5) Å, c = 26.493(5) Å; β = 109.95(3)°; V = 15 803(5) Å^3; Z = 8; ρ_{cal} = 1.196 g/cm^3; μ(Mo Kα) = 1.639 mm^{-1}; F(000) = 6002; 3.5° $\leq \theta \leq$ 22.5°; $-$25 $\leq h \leq$ 25; $-$28 $\leq k \leq$ 28; $-$28 $\leq I \leq$ 28; 174 240 reflections collected, of which 20 591 were independent (R_{int} = 0.064) and 12 966 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] = 0.067, wR_2 (all data) = 0.191, w = [$\sigma^2(F_o^2)$ + (0.0670P)^2 + 34.73P]$^{-1}$ with P = (F_o^2 + 2F_c^2)/3; no. of data/restraints/ parameters 20 591/0/1578; goodness of fit (F^2) = 1.067. In the final difference map, the highest peaks (to ca. 1.54 e Å^{-3}) were close to a Y atom.

Polymerization Procedures. Polymerizations of ϵ-caprolactone (CL) were carried out on a Schlenk line in a flame-dried round-bottom flask equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent, and the temperature equilibration was ensured by stirring the solution for 15 min on a temperature bath. ϵ-CL was injected, and polymerization times were measured from that point. Polymerizations were terminated by addition of acetic acid (5 vol %) in methanol. Polymers were precipitated in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

Polymerizations of *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of *rac*-lactide and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in the appropriate amount of solvent, and the temperature equilibration was ensured in both Schlenk flasks by stirring the solution for 15 min in a bath. The appropriate amount of initiator was added via syringe, and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of acetic acid (5 vol %) in methanol. Polymers were

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precipitated in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

Supporting Information Available: Full listing of crystallographic details for compounds **3**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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