# Triketiminate bis(borohydride) complexes of rare-earth metals $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]Ln(BH_4)_2(THF)_2$ (Ln = Y, Nd): synthesis, structure, and catalytic activity in polymerization of *rac*-lactide, $\varepsilon$ -caprolactone, and isoprene

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A new triketimine  $(2,6-Me_2C_6H_3N=CMe)_2CH(2,6-Me_2C_6H_3N=CBu^{1})$  (1) was synthesized by the reaction of imidoyl chloride  $2,6-Me_2C_6H_3N=CClBu^{t}$  with lithium diketiminate  $(2,6-Me_2C_6H_3N=CMe)_2CHLi$ . In the crystalline state, compound 1 exists in the diimineenamine form; in solution, in the triimine form. The metalation of triketimine 1 with *n*-butyllithium in THF at 0 °C produced lithium triketiminate  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^{t})]Li(THF)_2$  (2). The metathesis reactions of  $Ln(BH_4)_3(THF)_3$  (Ln = Y, Nd) with compound 2 (1:1 molar ratio, THF) gave the neutral triketiminate bis(borohydride) complexes  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^{t})]Ln(BH_4)_2(THF)_2$  (Ln = Y (3), Nd (4)). As opposed to the complexes with neutral triketimine, the monoanionic triketiminate ligand is coordinated to Li and Y or Nd cations in a bidentate fashion. Complexes 3 and 4 catalyze the polymerization of *rac*-lactide and  $\varepsilon$ -caprolactone; in combination with  $[Ph_3C][B(C_6F_5)_4]$  and  $AlBu^{i}_3$  (1 : 1 : 10 molar ratio), these compounds exhibit catalytic activity in the polymerization of isoprene.

**Key words:** rare-earth metals, triketiminate ligand, borohydride ligand, synthesis, structure, catalysis, isoprene, lactide, polymerization.

Due to large ionic radii,<sup>1</sup> high electrophilicity, and Lewis acidity of rare-earth ions, the coordinative and steric saturations of the metal coordination sphere are key factors responsible for stability and reactivity of such compounds. Therefore, in recent years considerable attention has been paid to the synthesis of new ligands, which can be coordinated to rare-earth ions and form stable compounds with these elements.<sup>2-6</sup> Since rare-earth metals are electropositive<sup>7</sup> and the metal-ligand interactions in their organic derivatives are predominantly ionic, ligands capable of forming stable anions are preferred in this field of chemistry. This is the reason why cyclopentadienyl complexes have long been the most popular organic derivatives of rare-earth metals.<sup>8</sup> Polydentate ligand systems containing rigid N- and/or O-coordination sites, which can sterically and coordinatively saturate the rareearth metal ion sphere, thus providing kinetic stability of the metal complex, are of particular interest. Among these

systems are bulky  $\beta$ -diketiminate ligands, which were synthesized for the first time in 1997.<sup>9</sup> This type of coordination environment has great potential for stabilization of organolanthanides, as demonstrated by the fact that the use of  $\beta$ -diketiminate ligands makes it possible to isolate even very unstable diethyl derivatives,<sup>10</sup> which are usually prone to  $\beta$ -hydride elimination. Recently, the synthesis of a series of new related  $\beta$ -triketimines, as well as complexes of a number of metals with these ligands, was reported,<sup>11—16</sup> and these compounds were found to exhibit interesting properties, including catalytic activity in the polymerization of isoprene. However, the coordination of this type of ligands to rare-earth ions is as yet unknown.

Borohydride complexes of lanthanides are of great interest due to their structural diversity and high catalytic activity.<sup>17</sup> In recent years, a renaissance in the chemistry of borohydride derivatives of lanthanides has been inspired by reports on their high catalytic activity in the polymerization of lactones,<sup>18,19</sup> methyl methacrylate,<sup>20</sup> and isoprene.<sup>21</sup>

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In the present work, we synthesized a new triketimine  $(2,6-Me_2C_6H_3N=CMe)_2CH(2,6-Me_2C_6H_3N=CBu^t)$  (1) and investigated possible modes of coordination of its anion  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]^-$  to lithium and rare-earth metal cations. The structures of the complexes  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]Li(THF)_2$  (2) and  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]Ln(BH_4)_2$ -(THF)<sub>2</sub> (Ln = Y (3), Nd (4)) in the crystalline state were determined and the catalytic activity of the borohydride complexes in the polymerization of *rac*-lactide,  $\varepsilon$ -caprolactone, and isoprene was investigated.

### **Results and Discussion**

# Synthesis and structures of triketamine 1 and borohydride complexes 2-4

Triketimine **1** was synthesized by the reaction of imidoyl chloride  $2,6-Me_2C_6H_3N=CClBu^t$  with lithium diketiminate  $(2,6-Me_2C_6H_3N=CMe)_2CHLi$  in toluene and was isolated as a white powder in 80% yield (Scheme 1). Triketimine **1** was characterized by elemental analysis, NMR and IR spectroscopy, and mass spectrometry.

Crystals of triketimine 1 suitable for X-ray diffraction were obtained by slow concentration of a solution of 1 in acetonitrile. The molecular structure of 1 is shown in Fig. 1. Selected bond lengths and bond angles are given in



Fig. 1. Molecular structure of compound 1 with displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms, except for the H(1) atom, are not shown.

Table 1. In the crystalline state, compound **1** exists in the diimine-enamine tautomeric form, in which the hydrogen atom is located on the nitrogen atom of one of the dimethylaniline moieties rather than on the methine



Reagents: i. 1) Toluene, 2) p-toluenesulfonic acid, ii. 1) toluene, 2) nBuLi; iii. CH<sub>2</sub>Cl<sub>2</sub>; iv. PCl<sub>5</sub>; v. toluene.

Angle

N(1) - C(1) - C(2)

N(2) - C(3) - C(2)

N(1) - Nd(1) - N(2)

B(1) - Nd(1) - B(2)

N(1) - Nd(1) - O(1)

N(1) - Nd(1) - O(2)

N(2) - Nd(1) - O(2)

N(2)-Nd(1)-O(1)

O(1) - Nd(1) - O(2)

O(1) - Nd(1) - B(1)

O(2) - Nd(1) - B(2)

N(3) - C(6) - C(2)

H(1) - Nd(1) - H(2)

H(5) - Nd(1) - H(6)

C(1) - N(1) - C(19)

C(3) - N(2) - C(27)

C(1) - C(2) - C(3)

Compound 2

Compound 4

ω/deg

123.84(9)

71.18(8)

163.7(2)

124.5(3)

97.1(2)

166.0(4)

95.2(4)

167.9(2)

96.7(5)

84.6(2)

83.4(4)

125.1(3)

34.8(2)

38.0(2)

116.2(3)

117.6(3)

123.3(2)

 $d/\text{\AA}$ 

1.436(2)

1.516(2)

2.434(3)

2.446(3)

2.61(2)

2.74(2)

1.338(4)

1.445(4)

1.341(4)

1.446(4)

1.418(4)

1.419(4)

1.523(4)

1.276(4)

2.651(4)\*

2.661(4)\*

2.37(4) -

2.48(4)

Bond

C(2) - C(3)

C(2) - C(5)

Nd(1) - N(1)

Nd(1) - N(2)

Nd(1) - O(1)

Nd(1) - O(2)

N(1) - C(1)

N(1) - C(19)

N(2) - C(3)

N(2)-C(27)

C(1) - C(2)

C(2) - C(3)

C(2) - C(6)

N(3) - C(6)

Nd(1) - B(1)

Nd(1) - B(2)

Nd(1)-H

Bond	d∕Å	Angle	ω/deg
	Com	pound 1	
N(1) - C(1)	1.303(2)	C(3) - C(2) - C(1)	121.6(2)
N(2) - C(3)	1.349(2)	C(1) - C(2) - C(5)	119.6(2)
N(3) - C(5)	1.284(2)	C(3) - C(2) - C(5)	118.7(2)
C(1) - C(2)	1.454(2)	N(2) - C(3) - C(2)	122.0(2)
C(2) - C(3)	1.393(2)	N(1) - C(1) - C(2)	119.8(2)
C(2) - C(5)	1.509(2)	N(3) - C(5) - C(2)	126.4(2)
N(1) - C(19)	1.414(2)	C(3) - N(2) - H(1)	115.2(9)
N(2)-C(27)	1.432(2)	C(27) - N(2) - H(1)	120.0(9)
N(3) - C(10)	1.418(2)	C(5) - N(3) - C(10)	124.4(2)
N(2)-H(1)	0.92(2)	C(2) - C(5) - C(6)	119.6(2)
	Com	pound 2	
Li(1) - N(2)	1.958(2)	N(2)-Li(1)-N(1)	90.47(9
Li(1) - N(1)	1.973(2)	N(2) - Li(1) - O(2)	117.4(2)
Li(1)-O(2)	1.975(2)	N(1) - Li(1) - O(2)	117.6(2)
Li(1) - O(1)	1.977(2)	N(2) - Li(1) - O(1)	110.7(2)
N(2) - C(3)	1.314(2)	N(1) - Li(1) - O(1)	120.2(2)
N(1) - C(1)	1.324(2)	O(2) - Li(1) - O(1)	101.2(2)
N(3) - C(5)	1.280(2)	C(1) - C(2) - C(5)	119.47(9)
C(1) - C(2)	1.428(2)	C(3) - C(2) - C(5)	117.47(9)

**Table 1.** Selected bond lengths (d) and bond angles ( $\omega$ ) in compounds 1, 2, and 4

\* The distances between the atoms are given.

carbon. The central C(1)C(2)C(3)C(5) moiety is planar (the maximum deviation of the atoms from the plane is 0.008(2) Å). Compound **1** adopts the (E, E, Z) conformation (Scheme 2). The central C(1)C(2)C(3)C(5) moiety is asymmetric because of a considerable difference in the C—C bond lengths. Thus, the C(1)—C(2) and C(2)—C(5) bond lengths (1.454(2) and 1.509(2) Å, respectively) correspond to the single bond length, whereas the C(2)—C(3) bond length (1.393(2) Å) is indicative of its double-bond character.<sup>22</sup> Consequently, the planar structure of the C(1)C(2)C(3)C(5) moiety is attributed to the presence of a double bond between the C(2) and C(3) atoms. The C—N bond lengths in triketimine **1** are also not equivalent. The N(1)—C(1) and N(2)—C(3) bond lengths (1.303(2) and 1.349(2) Å, respectively) are similar to the single bond length, whereas the N(3)–C(5) bond length (1.284(2) Å) is typical of C=N double bonds.<sup>22</sup> Therefore, the geometric parameters of compound 1 in the crystalline state indicate that it exists in the diimineenamine form.

In the <sup>1</sup>H NMR spectrum of triketimine **1**, protons of Bu<sup>t</sup> substituents appear as one singlet at  $\delta$  1.24. The methyl protons of three 2,6-dimethylaniline moieties and imino groups N=CMe are seen as four singlets at  $\delta$  1.98, 2.07, 2.08, and 2.11 with equal integrated intensity each corresponding to six protons. Aromatic protons appear in a weak field as two triplets (<sup>3</sup>J<sub>H,H</sub> = 7.4 Hz) at  $\delta$  6.80 and 6.88, one doublet at  $\delta$  6.94 (<sup>3</sup>J<sub>H,H</sub> = 7.4 Hz), and a multiplet at  $\delta$  7.01. Based on the NMR spectroscopic data (2D <sup>1</sup>H-<sup>13</sup>C HSQC) in deuterobenzene, the singlet at

#### Scheme 2



 $\delta$  5.17 was assigned to the methine proton of the central CHCCC moiety. Therefore, compound 1 exists as triimine. It should be noted that the <sup>13</sup>C NMR spectrum also shows a single set of signals corresponding to the triimine tautomeric form of compound 1. An examination of the <sup>1</sup>H NMR spectra of compound **1** in a wide temperature range (C<sub>7</sub>D<sub>8</sub>, T = -15-50 °C) revealed no evidence of the existence of the second prototropic tautomer in solution. The IR spectrum of 1 recorded as Nujol mulls shows intense absorption bands at 1676 (s), 1662 (s), and 1595  $cm^{-1}$  (s) corresponding to asymmetric vibrations of C=N double bonds of the triketiminate ligand and a broadened absorption band at 3304  $\rm cm^{-1}$  assigned to N-H stretching vibrations of the diimine-enamine form. In the IR spectrum of compound 1 in  $CH_2Cl_2$ , absorption bands characteristic of N-H stretching vibrations are absent.

Therefore, the investigations of the structure of compound 1 by X-ray diffraction, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and IR spectroscopy led to the conclusion that this compound exists in the diimine-enamine form in the crystalline state, while it is transformed into the triimine form in solution.

It is known that alkyl derivatives of rare-earth metals are active catalysts (or their precursors) for a number of transformations of unsaturated substrates.<sup>6</sup> In order to synthesize triketiminate bis(alkyl) complexes of yttrium and lutetium, we performed the reactions of 1 with the tris(alkyl) complexes  $Ln(CH_2SiMe_3)_3(THF)_2$  (Ln = Y, Lu)<sup>23,24</sup> in C<sub>6</sub>D<sub>6</sub> at 25 °C controlled by <sup>1</sup>H NMR spectroscopy. It was found that, despite the presence of a labile proton, compound 1 is inert to  $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu). Besides, triketimine 1 did not react in THF (25 °C, 12 h) with the alkyl derivatives of yttrium  $Y(Me)_6Li_3(TMEDA)_3$  and  $Y(o-CH_2C_6H_4NMe_2)_3$  and with the cationic alkyl complex  $Y(Me)_2(THF)_5^+[BPh_4]^-$ . After the removal of the solvents and recrystallization of the solid residues from a THF-hexane mixture, the starting reagents were isolated in quantitative yield.

The lithiation of triimine **1** with *n*-butyllithium readily proceeds at room temperature in THF (Scheme 3). After the recrystallization from tetrahydrofuran, the lithium complex [(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CMe)<sub>2</sub>C(2,6-Me<sub>2</sub>- $C_6H_3N=CBu^t$ ]Li(THF)<sub>2</sub>(2) was isolated as yellow crystals in 76% yield. Complex 2 is extremely sensitive to atmospheric moisture and oxygen, readily soluble in THF, and very poorly soluble in aliphatic hydrocarbons. Compound 2 was characterized by elemental analysis and NMR and IR spectroscopy.

In the <sup>1</sup>H NMR spectrum (25 °C,  $C_6D_6$ ) of complex 2, protons of Bu<sup>t</sup> substituents appear as a singlet at  $\delta$  1.67. Protons of eight methyl groups are seen as four singlets with equal integrated intensity at  $\delta$  1.75, 1.93, 2.18, and 2.33. Two multiplets at  $\delta$  1.15 and 3.12 belong to methylene protons of coordinated THF molecules. Aromatic pro-



tons appear in a weak field as a multiplet (at  $\delta 6.85 - 7.05$ ). The <sup>7</sup>Li NMR spectrum of complex 2 shows a single signal at  $\delta$  1.60.

Transparent yellow crystals of complex 2 suitable for X-ray diffraction were obtained by slow cooling of a concentrated solution of **2** in tetrahydrofuran to  $-20 \,^{\circ}$ C. The structure of complex 2 is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 1. According to the X-ray diffraction data, compound 2 is a monomeric lithium complex, in which the coordination sphere of the Li<sup>+</sup> cation is formed by two nitrogen atoms of the triketiminate ligand and two oxygen atoms of coordinated THF molecules. Therefore, the formal coordination number (CN) of the lithium atom is 4. The nitrogen atom of the  $\{2,6-Me_2C_6H_3N=CBu^t\}$  moiety is not involved in the complexation. In complex 2, the Li–N bond lengths (1.958(2), 1.973(2) Å) are similar to the Li-N bond lengths in the related diketiminate complexes [HC(2,6-



Fig. 2. Molecular structure of compound 2 with displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms and methyl substituents of the *tert*-butyl group at the C(5) atom are not shown.



 $Pr_{2}^{i}C_{6}H_{3}N=CMe_{2}Li(DME)$  and  $[HC(2-Pr_{1}^{i}C_{6}H_{4}-$ N=CMe)<sub>2</sub>]Li(THF)<sub>2</sub> (see Refs 25 and 26). Thus, the analysis of the N(1)-C(1) (1.324(2) Å), C(1)-C(2) (1.428(2) Å), C(2)-C(3) (1.436(2) Å), and C(3)-N(2)(1.314(2) Å) bond lengths in the planar N(1)C(1)C(2)-C(3)N(2) moiety shows that the negative charge is delocalized within the  $\beta$ -diketiminate skeleton {(2,6- $Me_2C_6H_3N=CMe_2C_6$ , whereas the moiety of the triketiminate ligand  $\{2,6-Me_2C_6H_3N=CBu^t\}$  that is not coordinated to the lithium cation contains the isolated C-C single bond (1.516(2) Å) and C=N double bond (1.280(2) Å). The metallocycle Li(1)N(1)C(1)C(2)-C(3)N(2) is non-planar (the average deviation of the atoms from the plane is 0.172(2) Å). The dihedral angle between the N(1)Li(1)N(2) and N(1)C(1)C(2)C(3)N(2)planes is 27.80(8)°.

Earlier, it was demonstrated that neutral triketimines generally act as  $\kappa^3$ -NNN-chelating ligands in the complexation with transition metal ions.<sup>13-15</sup> However, in the recently synthesized cobalt complexes with triketimine (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N=CMe)<sub>2</sub>CH(2,4,6-Me<sub>3</sub>- $C_6H_2N=CMe$ ), the latter is  $\kappa^2$ -NN-coordinated to the metal ion, which is not typical of the neutral ligand.<sup>16</sup> The difference in the coordination mode of neutral triketimines is attributed not only to steric properties of the ligands but also, apparently, to the nature of the complex-forming agent. Thus, triketimine (2,4,6-Me<sub>3</sub>- $C_6H_2N=CMe_2CH(2,4,6-Me_3C_6H_2N=CMe)$ , which acts as a bidentate ligand<sup>16</sup> in the cobalt complexes (0.58 Å, CN = 4),<sup>1</sup> exhibits a  $\kappa^3$ -NNN-coordination mode in the complexes with nickel  $(0.63 \text{ Å}, \text{CN} = 5)^1$  that has a somewhat larger ionic radius.<sup>13</sup> In lithium complex 2 (0.59 Å, CN = 4),<sup>1</sup> unlike compounds with neutral triketimines, the localization of the negative charge on the central carbon atom in the monoanionic ligand [(2,6-Me<sub>2</sub>- $C_6H_3N=CMe_2C(2,6-Me_2C_6H_3N=CBu^t)]^-$ , responsible for the planar structure of the carbanionic C(1)C(2)-C(3)C(5) moiety, virtually excludes the possibility of binding the third nitrogen atom to the lithium cation Li<sup>+</sup> (see Fig. 2).

In order to study the coordination capabilities of the new potentially tridentate triketiminate ligand  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]^-$  in the complexation with lanthanide metal ions  $Ln^{3+}$  with large ionic radii, we performed the reactions of complex **2** with  $Ln(BH_4)_3(THF)_3$  (Ln = Y, Nd) in a 1 : 1 ratio of the reagents in THF (Scheme 4). The reaction with  $Y(BH_4)_3(THF)_3$  was accomplished during 3 h at 65 °C, while the reaction with Nd(BH\_4)\_3(THF)\_3 was performed at 25 °C for 48 h and at 60 °C for 3 h (see Scheme 4). After the extraction of the reaction products with toluene followed by recrystallization from a THF—hexane mixture, the bis(borohydride) complexes  $[(2,6-Me_2C_6H_3-N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]Ln(BH_4)_2(THF)_2$ (Ln = Y (**3**), Nd (**4**) were isolated as colorless (**3**) and green (4) crystals in 71 and 80% yield, respectively. Complexes 3 and 4 are sensitive to atmospheric moisture and oxygen and are readily soluble in aromatic and aliphatic hydrocarbons, as well as in ethereal solvents.

## Scheme 4



Ln = Y (**3**, 71%), Nd (**4**, 80%)

The <sup>1</sup>H NMR spectrum of diamagnetic complex **3** shows a single set of signals of the triketiminate ligand  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]^{-1}$ : a singlet at  $\delta$  1.48 belonging to Bu<sup>t</sup> groups and four singlets at  $\delta$  1.52, 1.85, 2.08, and 2.17 assigned to methyl protons of xylidine and (MeC=N) moieties. Aromatic protons appear as a multiplet at  $\delta$  6.79–7.14. In the <sup>1</sup>H NMR spectrum of complex **3**, BH<sub>4</sub> ligands are seen as four strongly broadened singlets with equal intensity at  $\delta$  1.15, 1.24, 1.36, and 1.57. Two multiplets at  $\delta$  1.29 and 3.62 are assigned to coordinated THF molecules.

In the <sup>11</sup>B NMR spectrum of diamagnetic complex **3**, borohydride ligands give a single singlet at  $\delta$  –25.1. In the IR spectra of complexes **3** and **4**, borohydride ligands exhibit five broad absorption bands in the region characteristic of stretching vibrations of terminal and bridging B–H bonds: 2471, 2372, 2288, 2220, 2164 cm<sup>-1</sup> for **3** and 2434, 2331, 2289, 2250, 2228 cm<sup>-1</sup> for **4**.

Crystals of complex 4 suitable for X-ray diffraction were obtained by slow condensation of hexane into a concentrated solution of 4 in THF. The molecular structure of bis(borohydride) complex 4 is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 1. According to the X-ray diffraction data, compound 4 is a neutral monomeric neodymium bis(borohydride) complex, in which the triketiminate ligand is coordinated to the lanthanide metal ions in a bidentate fashion. The Nd—N distances in complex 4 (2.434(3), 2.446(3) Å) are slightly different from each other and are comparable with the corresponding distances in the related neodymium  $\beta$ -diketiminate complexes  $[HC(2,6-Pr_{2}^{i}C_{6}H_{3}N=CMe)_{2}]$ -NdCl<sub>2</sub>(THF)<sub>2</sub> (2.459(4), 2.444(4) Å)<sup>27</sup> and  $[HC(2,6-Me_{2}-2)^{2}]$  $C_6H_3N=CM\bar{e}_2$ ]NdCl<sub>3</sub>Li(THF)<sub>3</sub> (2.445(5), 2.422(5) Å).<sup>28</sup> The C–N and C–C bond lengths (N(1)-C(1), 1.338(4) Å;N(2)-C(3), 1.341(4) Å; C(1)-C(2), 1.418(4) Å; C(2)-C(3), 1.419(4) Å) in the planar N(1)C(1)C(2)-C(3)N(2) moiety of complex 4 are in the range of 1.338(3) - 1.419(4) Å and are indicative of delocalization of the negative charge over the  $\beta$ -diketiminate group, while the third  $[2,6-Me_2C_6H_3N=CBu^t]$  moiety of the triketiminate ligand, by analogy with complex 2, contains the isolated C–C single bond (1.523(4) Å) and C=N double bond (1.276(4) Å) and is not involved in the interaction with the metal center. As in complex 2, the metallocycle Nd(1)N(1)C(1)C(2)C(3)N(2) is nonplanar (the average deviation of the atoms from the plane is 0.167(2) Å). The dihedral angle between the N(1)Nd(1)N(2) and N(1)C(1)C(2)C(3)N(2) planes is somewhat smaller than the corresponding angle in 2 (27.80(8)°) and is equal to 22.8(2)°. The Nd-B distances in structure 4 are 2.651(4) and 2.661(4) Å, which are substantially longer than those in the borohydride complexes  $[Nd(C_5HPr_{i_4})(BH_4)_2(THF)]$  (2.605(3), Å)<sup>21</sup> and  $[Nd{(Me_3Si)_2NC(NCy)_2}_2$ -2.595(3)  $(BH_4)_2Li(THF)_2]$  (2.454(3), 2.504(4) Å)<sup>29</sup> and are substantially shorter than the corresponding distances in the dinuclear complex [Nd(COT)(BH<sub>4</sub>)(THF)]<sub>2</sub> (2.875(6), 2.941(6) Å).<sup>30</sup> The Nd-B distances in 4 are similar to those in the amidinate complex [6-Me-C<sub>5</sub>H<sub>3</sub>N-2-CH<sub>2</sub>C(NPr<sup>i</sup>)<sub>2</sub>]Nd(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (2.676(3), 2.671(3) Å).<sup>31</sup>

## Polymerization of *rac*-lactide, ε-caprolactone, and isoprene

We studied the catalytic activity of bis(borohydride) complexes **3** and **4** in the polymerization of *rac*-lactide,  $\varepsilon$ -caprolactone, and isoprene.

The polymerization of lactide was performed in toluene at monomer/catalyst ratios of 100/1, 250/1, and 500/1 (Table 2, runs 1-6). The complete conversion of 500 equivalents of the monomer catalyzed by complexes 3 and **4** is achieved in 24 h at 25 °C and produces polymers with an average molecular weight  $M_{\rm w} = 20135 - 59283$ ,  $M_{\rm n} = 13711 - 23713$  and a rather narrow molecular weight distribution  $(M_w/M_n = 1.5-2.5)$ . According to the <sup>1</sup>H NMR data, the resulting polylactides are atactic. A comparison of the experimental number-average molecular weights evaluated by gel-permeation chromatography with the values, which were calculated taking into account the initial monomer/initiator ratio and the conversion values, demonstrates that two polymer chains grow at one metal center, *i.e.*, both borohydride groups of 3 and 4 are involved in the initiation of polymerization. At low monomer/initiator ratios (100-250), apart from a good agreement between the experimental and calculated  $M_n$  values, a relatively narrow molecular weight distribution was observed ( $M_w/M_n = 1.5 - 2.3$ ). However, when the monomer/initiator ratio was increased to 500 equivalents, the experimental  $M_n$  values were substantially smaller than the calculated values, which is indicative of side processes, such as esterification and/or chain transfer to monomer reactions.



Fig. 3. Molecular structure of compound 4 with displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms and methyl substituents of the *tert*-butyl group at the C(6) atom are not shown.

 Table 2. Polymerization of *rac*-lactide initiated by complexes 3 and 4

Run	Complex	<u>[M]</u> <sub>0</sub> [Ln] <sub>0</sub>	t/h	$M_n^{\text{exp}} \cdot 10^{-3}$	$M_n^{\text{ calc}} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$
1	3	100	6	9.03	7.21	1.6
2	3	250	12	15.40	18.02	1.5
3	3	500	24	13.71	36.04	1.5
4	4	100	6	9.77	7.21	2.0
5	4	250	12	13.41	18.02	2.3
6	4	500	24	23.71	36.04	2.5

*Note.* Conditions: toluene,  $[M] = 1.0 \text{ mol } L^{-1}$ , T = 25 °C. The conversion of the monomer M was determined by <sup>1</sup>H NMR spectroscopy and was equal to 100% in all experiments. The molecular weights  $M_n^{exp}$  of the polymers were determined by gel-permeation chromatography using polystyrene standards.  $M_n^{calc}$  were calculated by the equation 144.14*Y*•0.5[M]/[Ln] (*Y* is the yield).

Table 3. Polymerization of  $\epsilon\text{-caprolactone}$  initiated by complexes 3 and 4

Run	Complex	$\frac{[M]_0}{[Ln]_0}$	t/s	$M_n^{\text{exp}} \cdot 10^{-3}$	$M_{\rm n}^{\rm calc} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$
1	3	100	240	21.38	5.71	2.6
2	3	250	300	33.22	14.27	2.7
3	3	500	480	39.94	28.54	1.8
4	3	1000	1200	27.90	57.07	1.4
5	4	100	10	12.97	5.71	1.7
6	4	250	15	12.71	14.27	1.4
7	4	500	25	21.78	28.54	1.4
8	4	1000	50	37.94	57.07	1.5

*Note.* Conditions: toluene,  $[M] = 1.0 \text{ mol } L^{-1}$ , T = 25 °C. The conversion of the monomer M was determined by <sup>1</sup>H NMR spectroscopy and was equal to 100% in all experiments. The molecular weights  $M_n^{\text{exp}}$  of the polymers were determined by gel-permeation chromatography using polystyrene standards.  $M_n^{\text{calc}}$  were calculated by the equation 114.14*Y*•0.5[M]/[Ln] (*Y* is the yield).

Complexes **3** and **4** exhibited high catalytic activity in the polymerization *of*  $\varepsilon$ -caprolactone. In the polymerization catalyzed by yttrium complex **3**, the complete conversion of 1000 equivalents of the monomer was achieved within 20 min at 25 °C. Neodymium complex **4** is much more active in the polymerization of  $\varepsilon$ -caprolactone compared to yttrium bis(borohydride) **3** and allows the preparation of polymer samples characterized by a narrow molecular weight distribution ( $M_w/M_n = 1.4-1.7$ ) and average molecular weights  $M_w = 18160-58108$ ,  $M_n =$ = 12711-37944 within a few seconds (Table 3, runs 5-8).

It was found that complexes **3** and **4** and the twocomponent systems **3** or **4**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1 : 1) and **3** or **4**/AlBu<sup>i</sup><sub>3</sub> (1 : 10) cannot initiate the polymerization of isoprene in toluene at room temperature. However, the three-component catalytic systems **3** or **4**/AlBu<sup>i</sup><sub>3</sub>/ [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1 : 10 : 1) exhibit moderate activity in the polymerization of isoprene and can provide ~60% conversion of 1000 equivalents of the monomer in 48 h under mild conditions giving polymers composed mainly of *cis*-1,4 units (62.7-66.1% of 1,4-*cis* units) (Table 4, runs 3 and 6). The resulting polymers are characterized by a rather broad molecular weight distribution ( $M_w/M_n$  = = 3.2-3.3) and low molecular weights ( $M_n$  = 6.1-6.3 • 10<sup>3</sup>).

In summary, the lithium triketiminate complex  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]$ Li-(THF)<sub>2</sub> (**2**) was synthesized by the reaction of triketimine **1** with *n*-butyllithium. First rare-earth metal complexes with the anionic triketiminate ligand were prepared and structurally characterized. The bis(borohydride) complexes of rare-earth metals  $[(2,6-Me_2C_6H_3N=CMe)_2C(2,6-Me_2C_6H_3N=CBu^t)]$ Ln(BH<sub>4</sub>)<sub>2</sub>THF<sub>2</sub> (Ln = Y (**3**), Nd (**4**)) were synthesized by the metathesis reactions of Ln(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> (Ln = Y, Nd) with lithium triketiminate **2**. According to the X-ray diffraction data, both in lithium complex **2** (the ionic radius of Li<sup>+</sup> is 0.59 Å, CN = 4)<sup>1</sup> and the complex of neodymium having a much larger ionic radius (1.11 Å, CN = 8),<sup>1</sup> the monoanionic triketiminate ligand is coordinated to the metal ion in

**Table 4.** Polymerization of isoprene initiated by the catalytic systems  $3 - \text{ or } 4 - \text{AlBu}_{3}^{i} - [\text{Ph}_{3}\text{C}][B(\text{C}_{6}\text{F}_{5})_{4}]$  (1 : 10 : 1)

Run	Complex	Borate	AIR <sub>3</sub>	<i>t</i> /h	Y(%)	Positions of units		$M_{\rm n} \cdot 10^{-3}$	$M_{\rm w}/M_{\rm n}$	
						<i>cis</i> -1,4	trans-1,4	3,4		
1	3	_	AlBu <sup>i</sup> 3	24	0	_	_	_	_	_
2	3	TB		24	0	_	_	_	_	_
3	3	ТВ	AlBu <sup>i</sup> 3	48	56	62.7	34.2	3.1	6.1	3.2
4	4	_	AlBu <sup>i</sup> <sub>3</sub>	24	0	_	_	_	_	_
5	4	TB		24	0	_	_	_	_	_
6	4	TB	AlBu <sup>i</sup> 3	48	59	66.1	32.0	1.9	6.3	3.3

Conditions of polymerization: the complex (a solution of 10  $\mu$ mol of complexes 3 or 4 in toluene), [AlR<sub>3</sub>] : [Ln] : [TB] = = 10 : 1 : 1, T = 25 °C, where TB = [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; *t* is the polymerization time; the ratio [IP]/[Ln] = 1000, where IP is isoprene, Ln = Y (3), Nd (4). The molecular weights of the polymers were determined by gel-permeation chromatography using polystyrene standards.

a bidentate fashion only through two nitrogen atoms, while the third nitrogen atom is not involved in the metal-ligand interaction and delocalization of the negative charge. The observed coordination mode differs from  $\kappa^3$ -NNN coordination typical of neutral triketiminate ligands in *d*-transition metal complexes.  $^{13-15}$  The difference in the coordination mode is apparently associated with the electronic state of the ligand rather than with the ionic radius of the metal atom. The localization of the negative charge in the monoanionic ligand on the central carbon atom is responsible for the planar structure of the carbanionic moiety C(1)C(2)C(3)C(5), as opposed to the neutral form, thus excluding the possibility of coordinating the third nitrogen atom to the metal ion. Borohydride complexes 3 and 4 proved to be active catalysts for polymerization of rac-lactide and can be used to prepare atactic polylactides with a narrow molecular weight distribution. Complexes 3 and 4 exhibited high catalytic activity in the polymerization of  $\varepsilon$ -caprolactone giving polylactones with a narrow molecular weight distribution. It was demonstrated that triketiminate bis(borohydride) complexes 3 and 4 included as components in three-component (3 or  $4/[Ph_3C][B(C_6F_5)_4]/AlBu^i_3$ , (1 : 1 : 10)) catalytic systems can be employed to perform polymerization of isoprene with low rate and low stereoselectivity.

#### Experimental

All operations during the synthesis and isolation of the products were carried out in evacuated equipment using the standard Schlenk technique. Tetrahydrofuran was dried with potassium hydroxide and distilled over sodium benzophenone ketyl. Hexane and toluene were dried by heating to reflux and distillation over sodium metal. Benzene-d<sub>6</sub> was dried with sodium metal, degassed, and condensed in vacuo. The compounds  $(2,6-Me_2C_6H_3N=CMe)_2CH_2$ ,<sup>11</sup>2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C(Bu<sup>t</sup>)Cl,<sup>32</sup> and  $Ln(BH_4)_3(THF)_3$  (Ln = Y,<sup>33</sup> Nd<sup>34</sup>) were synthesized according to procedures published earlier. Sodium borohydride, *rac*-lactide,  $\Sigma$ -caprolactone, benzene-d<sub>6</sub>, CDCl<sub>3</sub>, and isoprene are commercial reagents (Acros). Isoprene and ε-caprolactone were dried with potassium hydride followed by distillation in vacuo and stored in evacuated containers. rac-Lactide was crystallized from dry THF, dried in vacuo, and stored in a dry nitrogen atmosphere. The IR spectra were recorded on a Bruker-Vertex 70 spectrometer. The samples were prepared under a dry argon atmosphere as Nujol mulls. The <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, and <sup>11</sup>B NMR spectra were measured on a Bruker Avance III spectrometer (400 MHz, 25 °C, benzene-d<sub>6</sub>, CDCl<sub>3</sub>). The chemical shifts are given in ppm relative to known shifts of residual protons of deuterated solvents. The molecular weight characteristics of the polymer samples were determined on a Knauer Smartline chromatograph equipped with Phenogel Phenomenex 5u columns (300×7.8 mm); the average pore diameter was 10<sup>4</sup> and 10<sup>5</sup> Å; a refractometer detector; THF was used as the mobile phase; the flow rate was 2 mL min<sup>-1</sup>,  $T = 40 \,^{\circ}\text{C}$ . The calibration was performed using polystyrene standards with molecular weights varying from 2700 to 2570000.

2,6-Dimethyl-N-[4-(2,6-dimethylphenyl)imino-3-{1-[(2,6dimethylphenyl)imino]ethyl}-5,5-dimethylhex-2-en-2-yl]aniline,  $(2,6-Me_2C_6H_3N=CMe)_2CH(2,6-Me_2C_6H_3N=CBu^t)$ (1). n-Butyllithium (37.00 mL, 42.9 mmol, 1.16 M solution in hexane) was added to a solution of  $(2,6-Me_2C_6H_3N=CMe)_2CH_2$ (12.78 g, 41.7 mmol) in toluene (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and then a solution of  $2,6-Me_2(C_6H_3)N=C(Bu^t)Cl$  (9.55 g, 42.70 mmol) in toluene (20 mL) was added. The resulting reaction mixture was stirred for 48 h, the solution was decanted from the precipitate of LiCl, and the solvents were removed in vacuo. The solid residue was washed with hexane (2×35 mL) and dried in vacuo for 1 h. Triketimine 1 was isolated as a white powder in a yield of 80% (16.49 g). Found (%): C, 83.07; H, 8.69; N, 8.12. C<sub>34</sub>H<sub>43</sub>N<sub>3</sub>. Calculated (%): C, 82.71; H, 8.78; N, 8.51. M.p. 133 °C. MS (EI, 70 eV), m/z ( $I_{rel}$  (%)): 493.71 [M]<sup>+</sup> (10). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>), δ: 1.24 (s, 9 H, C(C<u>H</u><sub>3</sub>)<sub>3</sub>); 1.98, 2.07, 2.08, 2.11 (all s, 24 H,  $CH_3C=N$ ,  $C_6H_3(CH_3)_2$ ); 5.17 (s, 1 H, C<u>H</u>); 6.80 and 6.88 (both d, 3 H,  $C_6H_3(CH_3)_2$ ,  ${}^{3}J_{\text{H,H}} = 7.4 \text{ Hz}$ ; 6.94 (d, 2 H, C<sub>6</sub><u>H</u><sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\text{H,H}} = 7.4 \text{ Hz}$ ); 7.01 (m, 4 H,  $C_{6H_3}(CH_3)_2$ ). <sup>13</sup>C NMR (100 MHz, 25 °C, CDCl<sub>3</sub>), δ: 18.6, 18.9, 20.0, 20.8 (<u>C</u>H<sub>3</sub>C=N, C<sub>6</sub>H<sub>3</sub>(<u>C</u>H<sub>3</sub>)<sub>2</sub>); 28.8 (C(CH<sub>3</sub>)<sub>3</sub>); 44.9 (C(CH<sub>3</sub>)<sub>3</sub>); 67.7 (CH, C(1)C(2)C(3)-C(5)); 121.6, 122.9, 123.3, 125.7, 126.2, 127.8, 128.0, 128.2, 148.8, 170.3 ( $\underline{C}_{6}H_{3}(CH_{3})_{2}$ ,  $CH_{3}\underline{C}=N$ ,  $Bu^{t}\underline{C}=N$ ,). IR (Nujol mulls),  $v/cm^{-1}$ : 3304 (m), 1676 (s), 1662 (s), 1595 (s), 1307 (s), 1287 (s), 1214 (s), 1169 (s), 1096 (s), 1070 (s), 1031 (s), 986 (s), 921 (s), 868 (m), 806 (s), 769 (s), 761 (s), 684 (m), 628 (m), 529 (m), 518 (m), 498 (m).

Lithium {2,6-dimethyl-N-[4-(2,6-dimethylphenyl)imino-3-{1-[(2,6-dimethylphenyl)imino]ethyl}-5,5-dimethylhex-2-en-2yl]anilide}ditetrahydrofuranate,  $[(2,6-Me_2C_6H_3N=CMe)_2C-$ (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CBu<sup>t</sup>)]Li(THF)<sub>2</sub> (2). *n*-Butyllithium (3.58 mL, 4.15 mmol, 1.16 M solution in hexane) was added to a solution of triketimine 1 (2.04 g, 4.13 mmol) in THF (30 mL) at 0 °C, and the reaction mixture was stirred at 25 °C for 12 h. Yellow crystals of 2 were obtained by slow concentration of a solution of complex 2 in THF at 25 °C. The crystals were washed with cold hexane and dried in vacuo at 25 °C for 30 min. Yellow crystals of complex 2 were isolated in a yield of 2.02 g (76%). Found (%): C, 77.94; H, 9.23; N, 6.70. C<sub>42</sub>H<sub>58</sub>LiN<sub>3</sub>O<sub>2</sub>. Calculated (%): C, 78.35; H, 9.08; N, 6.53. <sup>1</sup>H NMR (400 MHz, 25 °C, benzene-d<sub>6</sub>),  $\delta$ : 1.15 (m, 8 H,  $\beta$ -CH<sub>2</sub>, THF); 1.67 (s, 9 H,  $C(CH_3)_3$ ; 1.75, 1.93, 2.18, 2.33 (all s, 24 H,  $CH_3C=N$ ,  $C_6H_3(CH_3)_2$ ; 3.12 (m, 8 H,  $\alpha$ -CH<sub>2</sub>, THF); 6.85–7.05 (m, 9 H,  $C_{6}H_{3}(CH_{3})_{2}$ ). <sup>13</sup>C NMR (100 MHz, 25 °C, benzene-d<sub>6</sub>), δ: 18.5, 18.7, 20.4, 23.8 (<u>CH</u><sub>3</sub>C=N, C<sub>6</sub>H<sub>3</sub>(<u>CH</u><sub>3</sub>)<sub>2</sub>); 25.4 (β-<u>C</u>H<sub>2</sub>, THF); 32.3 (C(<u>C</u>H<sub>3</sub>)<sub>3</sub>); 44.3 (<u>C</u>(CH<sub>3</sub>)<sub>3</sub>); 67.7 (α-<u>C</u>H<sub>2</sub>, THF); 104.2 (<u>C</u>=CBu<sup>t</sup>, C(1)<u>C</u>(2)C(3)C(5)); 122.1, 122.4, 128.2, 128.4, 129.9, 130.3, 149.8, 152.1, 161.7, 183.6 (CH<sub>3</sub><u>C</u>=N, Bu<sup>t</sup><u>C</u>=N, <u>C</u><sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>). <sup>7</sup>Li NMR (155.5 MHz, 25 °C, benzene-d<sub>6</sub>),  $\delta$ : 1.6. IR (Nujol mulls), v/cm<sup>-1</sup>: 1606 (s), 1592 (s), 1535 (s), 1287 (s), 1251 (s), 1234 (s), 1194 (s), 1135 (s), 1090 (s), 1048 (s), 1014 (s), 941 (s), 915 (s), 890 (s), 828 (s), 780 (s), 761 (s), 741 (s), 721 (s), 670 (s), 639 (m), 597 (m), 572 (s), 518 (s), 496 (s).

Yttrium(III) bis(borohydride) {2,6-dimethyl-N-[4-(2,6-dimethylphenyl)imino-3-{1-[(2,6-dimethylphenyl)imino]ethyl}-5,5-dimethylhex-2-en-2-yl]anilide}ditetrahydrofuranate, [(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CMe<sub>9</sub>)<sub>2</sub>C(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CBu<sup>4</sup>)]Y(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (3). A solution of 2 (0.31 g, 0.48 mmol) in THF (35 mL) was added to a solution of Y(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> (0.17 g, 0.49 mmol) in THF (25 mL), and the reaction mixture was stirred at 65 °C for 3 h. The reaction product was extracted with toluene (50 mL) and separated from the precipitate of LiBH<sub>4</sub>. The toluene was removed in vacuo, and the solid residue was dissolved in THF (3 mL). Colorless crystals of complex 3 were obtained by slow condensation of hexane into a concentrated solution of complex 3 in THF at 25 °C. The crystals were washed with cold hexane and dried in vacuo at 25 °C. Colorless crystals of 3 were isolated in a yield of 0.26 g (0.34 mmol, 71%). Found (%): C, 66.32; H, 9.05; N, 5.74; Y, 11.68. C<sub>42</sub>H<sub>66</sub>B<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Y. Calculated (%): C, 66.77; H, 8.81; N, 5.56; Y, 11.77. <sup>1</sup>H NMR (400 MHz, 25 °C, benzene-d<sub>6</sub>), δ: 1.15 (br.s, 2 H, B<u>H</u><sub>4</sub>); 1.24 (br.s, 2 H, B<u>H</u><sub>4</sub>); 1.29 (m, 8 H, β-C<u>H</u><sub>2</sub>, THF); 1.36 (br.s, 2 H, B<u>H</u><sub>4</sub>); 1.48  $(s, 9 H, C(CH_3)_3); 1.52 (s, 6 H, CH_3C=N, C_6H_3(CH_3)_2); 1.57$ (br.s, 2 H, BH<sub>4</sub>); 1.85, 2.08, 2.17 (all s, 18 H, CH<sub>3</sub>C=N,  $C_6H_3(CH_3)_2$ ; 3.62 (m, 8 H,  $\alpha$ -CH<sub>2</sub>, THF); 6.79–7.14 (m, 9 H,  $C_{6}H_{3}(CH_{3})_{2}$ ). <sup>13</sup>C NMR (100 MHz, 25 °C, benzene-d<sub>6</sub>),  $\delta$ : 18.2, 18.4, 20.1, 21.3 ( $\underline{C}H_3C=N$ ,  $C_6H_3(\underline{C}H_3)_2$ ); 25.5 ( $\beta$ - $\underline{C}H_2$ , THF); 31.5 (C( $\underline{CH}_3$ )<sub>3</sub>); 43.7 ( $\underline{C}(CH_3)_3$ ); 69.5 ( $\alpha$ - $\underline{CH}_2$ , THF); 100.4 (<u>C</u>=CBu<sup>t</sup>, C(1)<u>C</u>(2)C(3)C(6)); 121.6, 123.2, 124.9, 128.6, 129.0, 129.4, 131.6, 143.5, 160.6, 180.1 (CH<sub>3</sub><u>C</u>=N, Bu<sup>t</sup><u>C</u>=N,  $\underline{C}_{6}H_{3}(CH_{3})_{2}$ ). <sup>11</sup>B NMR (128 MHz, 25 °C, benzene-d<sub>6</sub>),  $\delta$ : -25.1. IR (Nujol mulls), v/cm<sup>-1</sup>: 2471 (s), 2372 (s), 2288 (s), 2220 (s), 2164 (s), 1609 (s), 1595 (s), 1513 (s), 1335 (s), 1245 (s), 1192 (s), 1085 (s), 1028 (s), 944 (s), 918 (s), 868 (s), 837(s), 763 (s), 676 (s), 603 (s), 575 (s), 515 (m).

Neodymium(III) bis(borohydride) {2,6-dimethyl-N-[4-(2,6-dimethylphenyl)imino-3-{1-[(2,6-dimethylphenyl)imino]ethyl}-5,5-dimethylhex-2-en-2-yl]anilide}ditetrahydrofuranate, [(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CMe)<sub>2</sub>C(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CBu<sup>t</sup>)]Nd(BH<sub>4</sub>)<sub>2</sub>-(THF)<sub>2</sub> (4). A solution of 2 (0.55 g, 0.85 mmol) in THF (35 mL) was added to a solution of Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> (0.35 g, 0.86 mmol) in THF (25 mL), and the reaction mixture was stirred at 25 °C for 48 h and at 60 °C for 3 h. The reaction product was extracted with toluene (50 mL) and separated from the precipitate of LiBH<sub>4</sub>. The toluene was removed *in vacuo*, and the solid residue was dissolved in THF (3 mL). Green crystals of complex **4** were obtained by slow condensation of hexane into a concentrated solution of complex **4** in THF at 25 °C. The crystals were washed with cold hexane and dried *in vacuo* at 25 °C for 30 min. Green crystals of complex **4** were isolated in a yield of 0.554 g (0.68 mmol, 80%). Found (%): C, 61.89; H, 8.54; N, 5.43; Nd, 17.50. C<sub>42</sub>H<sub>66</sub>B<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Nd. Calculated (%): C, 62.21; H, 8.20; N, 5.18; Nd, 17.79. IR (Nujol mulls), v/cm<sup>-1</sup>: 2434 (s), 2331 (s), 2289 (s), 2250 (s), 2228 (s), 1606 (s), 1589 (s), 1513 (s), 1327 (s), 1231 (s), 1178 (s), 1096 (s), 1023 (s), 946 (s), 918 (s), 876 (s), 834(s), 766 (s), 665 (s), 606 (s), 577 (s), 498 (m).

**Polymerization of isoprene (general procedure).** One equivalent of borate  $[Ph_3C][B(C_6F_5)_4]$ ) (10 µmol) and AlBu<sup>i</sup><sub>3</sub> (0.1 mmol, 10 equiv.) were successively added to a solution of complex **3** or **4** (10 µmol) in toluene (1 mL). Then isoprene (10 µmol, 1 mL, 1000 equiv.) was added with stirring to the resulting solution. The reaction mixture was stirred for 48 h and then ethanol (10 mL) was added. The polymer that precipitated was washed with ethanol (5×10 mL) and dried *in vacuo* at 60 °C to constant weight. The molecular weight characteristics of the polymers were determined by gel-permeation chromatography. The number-average molecular weights ( $M_n$ ) and the polydispersity indices ( $M_n/M_w$ ) were calculated using polystyrene standards. The content of *cis*-1,4, *trans*-1,4, and 3,4 units in the polymer samples was determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Polymerization of** *rac*-lactide (general procedure). Complex **3** (7.6 mg, 0.010 mmol) and *rac*-lactide (0.360 g, 2.50 mmol)

Parameter	1	2	4
Formula	C <sub>34</sub> H <sub>43</sub> N <sub>3</sub>	C <sub>42</sub> H <sub>58</sub> LiN <sub>3</sub> O <sub>2</sub>	$C_{42}H_{66}B_2N_3NdO_2$
Molecular weight	493.71	643.85	810.83
Space group	$P2_1/n$	P21	$P2_1/c$
a/Å	12.3957(12)	10.1224(2)	20.1153(5)
b/Å	16.5709(15)	17.1888(2)	16.9059(5)
c/Å	14.7696(11)	11.8855(2)	12.2731(2)
α/deg	90	90	90
β/deg	103.942(3)	113.731(2)	91.918(2)
γ/deg	90	90	90
V/Å <sup>3</sup>	2944.4(4)	1893.12(6)	4171.34(17)
Z	4	2	4
$d_{\rm calc}/{\rm g}{\rm cm}^{-3}$	1.114	1.129	1.291
$\mu/mm^{-1}$	0.065	0.068	1.281
$\theta$ -Scan range/deg	1.88 - 27.00	3.02-30.51	2.84 - 26.00
Number of measured reflections	19188	40921	62572
Number of reflections with $I > 2\sigma(I)$	6414	11542	8184
R <sub>int</sub>	0.0229	0.0221	0.0537
Number of refined parameters	349	444	518
GOOF $(F^2)$	1.034	1.035	1.036
$R_1 (I \ge 2\sigma(I))$	0.0448	0.0359	0.0363
$wR_2$ (based on all reflections)	0.1269	0.0945	0.0771
Residual electron density $(max/min)/e \text{ Å}^{-3}$	0.289/-0.186	0.273/-0.156	1.374/-1.833

Table 5. Crystallographic data and the X-ray data collection and structure refinement statistics for compounds 1, 2, and 4

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were dissolved in toluene (2.5 mL). The mixture was stirred at 25 °C for 12 h and then ethanol (5 mL) was added. The solvents were removed, and the residue was dried *in vacuo* to constant weight. The degree of conversion of the monomer and the microstructure of the polymer were determined by NMR spectroscopy. The yield was determined by the weight method.

**Polymerization of \varepsilon-caprolactone (general procedure).** Complex 3 (7.6 mg, 0.010 mmol) and  $\varepsilon$ -caprolactone (0.285 g, 2.50 mmol) were dissolved in toluene (2.5 mL). The mixture was stirred at 25 °C for 5 min and then ethanol (5 mL) was added. The solvents were removed, and the residue was dried *in vacuo* to constant weight. The degree of conversion of the monomer was determined by NMR spectroscopy. The yield was determined by the weight method.

X-ray diffraction study of compounds 1, 2, and 4 was performed on Bruker Smart Apex (1) and Agilent Xcalibur E (2, 4)diffractometers ( $\omega$ -scanning technique, Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100 K). The structures were solved by direct methods and refined by the full-matrix least-squares method based on  $F_{hkl}^2$  with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atom H(1) in 1 and the hydrogen atoms of the bis(borohydride) groups, H(1)-H(8), in 4 were located in difference electron density maps and refined isotropically. The other hydrogen atoms in compounds 1, 2, and 4 were positioned geometrically and refined isotropically with fixed thermal parameters  $U(H)_{iso} = 1.2 U(C)_{eq} (U(H)_{iso} =$ =  $1.5 U(C)_{eq}$  for methyl groups). The X-ray data integration was performed, absorption corrections were applied, and the structures were refined using the APEX2,35 SADABS,36 SHELX,37 and CrysAlis PRO program packages.<sup>38</sup> The crystallographic data and the X-ray data collection and structure refinement statistics are given in Table 5. The structures were deposited with the Cambridge Crystallographic Data Centre (CCDC 1558092 (1), 1558093 (2), and 1558094 (4)) and are available at ccdc.cam.ac.uk/getstructures.

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