# **ORGANOMETALLICS**

# Anilidopyridyl-Pyrrolide and Anilidopyridyl-Indolide Group 3 Metal Complexes: Highly Active Initiators for the Ring-Opening Polymerization of *rac*-Lactide

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**Supporting Information** 

**ABSTRACT:** Three new group 3 metal complexes, bearing anilidopyridyl-pyrrolide (L<sup>1</sup>) and anilidopyridyl-indolide (L<sup>2</sup>) as dianionic tridentate ligands, with the general formula LMN-(SiHMe<sub>2</sub>)<sub>2</sub> were synthesized (complex 1, M = Y,  $L = L^1$ ; complex 2, M = Sc,  $L = L^1$ ; complex 3, M = Y,  $L = L^2$ ). All complexes were fully characterized and tested as initiators for the ROPs of *rac*-lactide. The yttrium complexes 1 and 3 resulted in highly active catalysts (TOF up to  $10^4 \text{ mol}_{\text{lactide}} \text{ mol}_{\text{y}}^{-1} \text{ h}^{-1}$ ), whereas the scandium complex showed moderate activities. This class of catalysts allowed a good control of the macromolecular architecture of the polymer, namely, the nature of end groups, the molecular weights, and their distribution. Moreover, the obtained PLAs showed  $P_r$  values in the range of 0.57–0.84, depending on the nature of the initiator and solvent. Well-controlled and rapid ROPs of *rac*-lactide were obtained



in the solvent-free polymerizations at 130 °C as well, suggesting that complexes 1–3 are stable at high temperature. Finally, in the presence of 2-propanol, complex 1 promoted the *immortal* ROP of *rac*-lactide, showing a remarkable TOF of  $3.5 \times 10^4 \text{ mol}_{\text{lactide}} \text{ mol}_{\text{Y}}^{-1} \text{ h}^{-1}$ .

# INTRODUCTION

Biodegradable and biocompatible polylactide (PLA), as a thermoplastic resin derived from renewable resources, is attracting considerable attention in both academic and industrial research as a sustainable alternative to traditional commodity polymers, and for special applications in agriculture and medicine.<sup>1</sup> The control of the polylactide chains, in terms of molecular weight, composition, and microstructure, strongly affect the mechanical and physical properties, biodegradability, and the end use of the material.<sup>2</sup>

The ring-opening polymerization (ROP) of lactide promoted by metal coordination catalysts is the elected method to produce polymers of high molecular weight, low polydispersity, and controlled microstructure. To this purpose, the design and synthesis of single-site catalysts for the ROP of *rac*-lactide with high activities and stereoselectivities become a main goal.<sup>3</sup>

In the past decade, a large number of metal coordination catalysts bearing polydentate ligands have been explored. Among various initiators, group 3 metal complexes resulted of particular interest because of their high polymerization rate, good polymerization control, and low toxicity.<sup>3b</sup> Indeed, after the discovery, by Dupont researchers, of homoleptic yttrium alkoxides as highly active initiators for the ROP of lactide,<sup>4</sup> a

variety of coordination environments have been explored. In particular, some promising ligand backbones, such as polydentate phenolate-based ligands, that were previously applied to prepare group 4 metal complexes for ethylene and/or  $\alpha$ -olefin polymerization with high performances,<sup>5</sup> have also been investigated in combination with main group and transition metals as initiators for the ROP of cyclic esters with impressive results.<sup>6</sup> In this context, the proper choice of the ligand framework is crucial, as the reactivity and moreover the stereoselectivity of the rare-earth metal compounds could be significantly modulated by tuning the electronic and steric properties of the coordination environment. Stereoselective catalysts, based on rare-earth metal complexes have also been reported, and they mainly featured bulky bisphenolate-type ligands. For example, scandium complexes bearing a  $1,\omega$ dithiaalkanediyl-bridged bis(phenolate)ligand<sup>7</sup> and yttrium complexes bearing multidentate bis(phenolate)amino ligands displayed excellent heteroselectivity in the ROP of rac-lactide.<sup>8</sup> By contrast, examples of stereoselective catalysts, based on rareearth metal complexes coordinated to ligands other than

Received: December 16, 2011 Published: January 20, 2012 Scheme 1. Synthesis of Group 3 Metal Complexes 1-3



Scheme 2. Synthesis of the Proligand  $H_2L^2$ 



bisphenolate, are rare.<sup>9</sup> In this regard, we recently described rare-earth metal bis(alkyl) complexes bearing phosphido pincer ligands, which showed high catalytic activity in the ROP of  $D_{,L}$ -lactides, although in the absence of stereocontrol.<sup>10</sup>

In recent years, ligands with nitrogen donor atoms have been used for the synthesis of novel rare-earth complexes, as they are expected to stabilize highly electrophilic metals. Examples reported in the literature include rare-earth complexes with bidentate NN ligands, such as amidinates, guanidinates, aminotroponiminates,  $\beta$ -diketiminate, and chelating diamide.<sup>11</sup> On the contrary, the use of a tridentate ["NNN"] ligand is poorly represented, with just few examples of complexes bearing symmetric pyridine-diamide type ligands or diketiminato derivative ligands.<sup>12</sup> We have recently reported the synthesis of anilidopyridyl-pyrrolide dianionic [-NNN-] tridentate ligands that have been already exploited for the preparation of group 4 metal complexes that are very active in the production of highly isotactic polypropylene and poly(1hexene).<sup>13</sup> It is worth to note that such ligands may be suitable as ancillary ligands in the design of "single-site" group 3 metal initiators for the ROP of lactone and lactides.<sup>3e</sup> Indeed, tridentate dianionic ligands may provide the required rigid environment for the steric control during the polymerization of the racemic lactide, leaving the place to a sole labile initiating group.

In the framework of our current interest in the ROP of lactone and lactides,<sup>10,14</sup> we have synthesized novel yttrium and scandium complexes bearing anilidopyridyl-pyrrolide ( $L^1$ ) and anilidopyridyl-indolide ( $L^2$ ) ligands (Scheme 1). In this paper,

we report on their synthesis, characterization, and application in the ROP of *rac*-lactide, resulting in high activity, good control, and heteroselectivity ( $P_r$  up to 0.84).

# RESULTS AND DISCUSSION

**Synthesis and Characterization.** The proligand  $H_2L^1$  has been synthesized following a previously published synthetic procedure.<sup>13b</sup> For the synthesis of the anilidopyridyl-indolide compound  $H_2L^2$ , a similar synthetic approach was followed, as described in Scheme 2. The Suzuki–Miyaura cross-coupling reaction between 6-bromo-2-pyridine-carboxaldehyde and *N*-Boc-indole-2-boronic acid (Boc = *tert*-butyloxycarbonyl) afforded compound **A**, as a yellow solid, in 86% yield. The condensation reaction between **A** and 2,6-diisopropylaniline by the use of 10 equiv of silica gel 60 as a catalyst gave the indolylpyridylimine precursor **B** as a light yellow solid (yield: 78%), which, by alkylation with 2-*i*PrC<sub>6</sub>H<sub>4</sub>Li, furnished the desired product ( $H_2L^2$ ) as a yellow solid in 88% yield (Scheme 2). All compounds were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies.

Complexes 1-2 were prepared by acid—base transamination reactions between the proligand  $(H_2L^1)$  and 1 equiv of  $Y(N(SiHMe_2)_2)_3(THF)_2$  or  $Sc(N(SiHMe_2)_2)_3(THF)$  in benzene solution at room temperature overnight. The compounds were isolated as light yellow powders in good yields (1, 89%; 2, 78%). Recrystallization of products from cold hexane yielded analytically pure compounds.

Complex 3 was synthesized by reaction of the proligand  $H_2L^2$  with 1 equiv of  $Y(N(SiHMe_2)_2)_3(THF)_2$  at 50 °C for 2 h.

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The compound was obtained as an orange powder in 76% yield (Scheme 1).

All complexes were fully characterized by multinuclear NMR spectroscopy and elemental (C, H, N) analyses (see the Experimental Section).

Single crystals of 1 and 2, obtained from *n*-hexane solutions at 253 K, were characterized by X-ray diffraction, and the molecular structures are shown in Figures 1 and 2. The

![](_page_2_Figure_4.jpeg)

**Figure 1.** ORTEP-3 view of **1.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and a hexane crystallization molecule lying on a crystallographic inversion center are omitted for clarity. Moreover, the statistical alternative positions of two C atoms of a SiMe<sub>2</sub> group are not shown. Selected bond distances (Å) and angles (deg): Y1–N1 2.388(3), Y1–N2 2.438(3), Y1–N3 2.246(3), Y1–N4 2.286(3), Y1–O1 2.412(3), Y1–O2 2.400(3); N1–Y1–N2 67.1(1), N2–Y1–N3 68.6(1), N3–Y1–N4 111.6(1), N4–Y1–N1 112.4(1), O2–Y1–O1 157.9(1), C15–C14–N3–C24 76.0(4).

complexes crystallize in monoclinic (1, space group P21/c) and triclinic (2, space group  $P\overline{1}$ ) systems, respectively. As far as 1, the asymmetric unit contains half a hexane crystallization molecule lying on a crystallographic inversion center.

Complex 1 shows a distorted octahedral geometry around the metal center due to the steric constraints of the [¬NNN¬] tridentate ligand. The four nitrogen atoms lie on a plane containing also the metal (Y is 0.07(2) Å out of the mean plane defined by the N atoms). The coordination is completed by two THF molecules in a trans position, one of them being bent toward the pyrrole ring to avoid steric repulsions with the bulky *i*-Pr group  $[O1-Y1-O2 = 157.9(1)^\circ]$ .

The coordination geometry of the complex 2 at the metal center is best described as distorted square-pyramidal. The metal ion lies 0.578(2) Å out of the plane defined by N1, N2, N3, and N4. A THF molecule occupies the apical position. The anilidopyridyl-pyrrolide fragment is planar in both cases. All the M–N bond distances fall in the range characteristic of similar complexes.<sup>15</sup> The M–N(pyridyl) bond distance is longer than the other ones, according to the different nature of the metal bond.<sup>15,16</sup> Also the M–O bond lengths are in line with those found for similar compounds.<sup>15b</sup>

As far as complex 2, it is interesting to note that one of the silicon atoms of the  $\{N(SiHMe_2)_2\}$  moiety has a shorter distance to the metal center than the other one [Sc1-Si1 3.053(1) Å vs Sc1-Si2 3.380(1) Å], and the corresponding

![](_page_2_Figure_11.jpeg)

**Figure 2.** ORTEP-3 view of **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc1–N4 2.059(3), Sc1–N3 2.075(3), Sc1–O1 2.184(3), Sc1–N1 2.211(3), Sc1–N2 2.243(3); N4–Sc1–N3 112.9(1), N4–Sc1–O1 115.4(1), N3–Sc1–O1 104.4(1), N2–Sc1–O1 111.9(1), N4–Sc1–N1 93.0(1), O1–Sc1–N1 86.0(1), N3–Sc1–N2 72.1(1), N1–Sc1–N2 71.0(1), C15–C14–N3–C24 76.3(2).

angle Sc–N–Si is smaller [Sc1–N4–Si1 108.2(1)° vs Sc1–N4–Si2 127.2(1)°]. These features, not so significant for the similar yttrium complex 1, probably reveal a weak monoagostic  $\beta$ -Si–H interaction, not rarely observed for similar silylamido complexes.<sup>15b,16</sup>

NMR analysis of complexes 1–3, in  $[D_8]$  THF at room temperature, showed in all cases single monomeric species with  $C_1$  symmetry in solution. Particularly diagnostic in the <sup>1</sup>H NMR spectra are two doublets of methyl protons (CH<sub>3</sub>) of -SiHMe<sub>2</sub> groups ranging from -0.13 to 0.004 ppm and six doublets of methyl protons (CH<sub>3</sub>) of isopropyl groups ranging from 2.6 to 3.6 ppm. Single resonances and sharp septets, were observed for the proton of SiH groups. In both the <sup>1</sup>H and the <sup>13</sup>C NMR spectra, coordinated THF molecules were detected, as suggested by the presence of resonances as two multiplets cleanly shifted from free THF solvent ( $\Delta\delta$  (<sup>1</sup>H) = 0.04 ppm;  $\Delta\delta$  (<sup>13</sup>C) = 0.38 ppm)<sup>17</sup> (see the Supporting Information).

Rare-earth silylamido complexes with  $\beta$ -hydrogens often show single or multiple agostic interactions with the metal center.<sup>18</sup> Usually these weak interactions are easily destroyed by the coordination of a strongly coordinating solvent, such as tetrahydrofuran, so we decided to verify the possible presence of the interaction by studying the structure of complex 1 in  $[D_2]$  methylene dichloride and  $[D_8]$  toluene solution.

To promote THF dissociation from the metal center, complex **1** was initially dissolved in methylene dichloride, and subsequently, the added solvent was removed by evaporation in vacuo.

The NMR analysis performed at room temperature showed that the structure of complex 1, in both solvents, was consistent with a single monomeric  $C_1$ -symmetric species consisting of one tridentate anilidopyridyl-pyrrolide ligand and a silylamido moiety,  $-N(SiHMe_2)_2$ , coordinated to the metal center. A complete THF displacement from the metal center was observed.

Table 1. Ring-Opening Polymerization of rac-Lactide Initiated by Complexes  $1-3^a$ 

![](_page_3_Figure_3.jpeg)

rac-lactide polylactide time<sup>b</sup> (min)  $T(^{\circ}C)$  $M_{\rm n}({\rm th})^{c}~(\times~10^{3})$  $M_{\rm n}({\rm GPC})^d (\times 10^3)$ PDI  $P_r^e$  $[I]_0$ solvent conv % run 1 1 THF 20 5 89 25.7 25.4 2.23 0.77 2 1 toluene 20 5 88 25.414.9 2.23 0.57 3 CH<sub>2</sub>Cl<sub>2</sub> 20 2 100 28.8 25.2 1.54 0.64 1 4 2 THF 20 180 21 9.5 1.58 0.72 6.1 5 2 20 960 78 22.5 30.3 1.61 0.73 toluene 6 2 CH<sub>2</sub>Cl<sub>2</sub> 20 180 25 7.2 6.9 1.87 0.73 7 3 THF 20 15 67 19.3 21.9 1.94 0.74 8 3 toluene 20 15 96 27.423.9 2.13 0.73 9 3 CH<sub>2</sub>Cl<sub>2</sub> 20 10 98 28.3 28.6 2.02 0.75 10 1 THF 0 120 83 23.9 37.5 1.70 0.84 11 1 in bulk 130 10 87 25.1 29.7 2.02 0.59 12 2 in bulk 130 10 68 19.6 20.0 1.67 0.53 13 in bulk 130 10 75 21.6 27.0 1.99 0.54 3 14<sup>f</sup> toluene 2.0 10 100 28.8 23.5 1.67 0.69 1

<sup>*a*</sup>Conditions:  $[I_0]$ , 5 mM;  $[rac-LA]/[I_0]$ , 200; 2 mL of solvent. <sup>*b*</sup>Reaction times were not necessarily optimized. <sup>*c*</sup>Calculated  $M_n$  of PLA (g/mol) = 144.14 × ( $[rac-LA]/[I_0]$ ) × conversion (rac-LA)%. <sup>*d*</sup>Experimental  $M_n$  values (corrected using the Mark–Houwink factor of 0.58) were determined by GPC analysis in THF using polystyrene standards. <sup>*e*</sup> $P_r$  value is determined from the methine region of the homonuclear decoupled <sup>1</sup>H NMR spectrum. <sup>*f*</sup>Ten equivalents of pyridine was added in the polymerization medium.

The  ${}^{1}J_{\text{SiH}}$  coupling constant is generally a good probe to evaluate the presence of the metal- $\beta$ -Si-H agostic interactions. For complex 1, the  ${}^{1}J_{\text{SiH}}$  was 176 Hz; this value falls in the range of 160–200 Hz characteristic of the silicon hydrides, <sup>19</sup> suggesting the absence of any agostic Si-H interaction with the yttrium center also in the absence of coordinating solvents.

The same study was extended to complex **2**. In this case, the interaction between the coordinated THF and the more Lewis acidic metal center resulted in being stronger; thus, the solvent dissociation was not achieved, even after evaporation in vacuo for prolonged times.

The <sup>1</sup>H NMR analysis of **2** in  $[D_2]$  methylene dichloride solution showed a <sup>1</sup> $J_{SiH}$  of 164 Hz; this value suggested that the weak Sc- $\beta$ -Si-H agostic interaction detected in the solid state by X-ray analysis is too feeble to survive in solution.

Ring-Opening Polymerization of rac-Lactide. Complexes 1-3 were tested as initiators for the ROP of rac-lactide under a variety of experimental conditions. The main results are listed in Table 1. The yttrium complexes 1 and 3 resulted in being highly active in the ROP of rac-lactide, promoting complete conversion of 200 equiv of monomer within a few minutes at room temperature (TOF up to 6000 mol<sub>lactide</sub>  $mol_{Y}^{-1} h^{-1}$ ).<sup>3b</sup> Their activities were found to be dependent on the polymerization medium, following the order  $CH_2Cl_2 >$ toluene  $\geq$  THF (Table 1). A similar trend of the rate of ROP reactions promoted by group 3 metal complexes has been often observed. sa,b,20 The yttrium complex 1 (runs 1-3) displayed slightly higher activities than those of the yttrium complex 3 (runs 7–9), bearing ligand  $H_2L^2$ . This can be ascribable both to the higher electron-donating character of the indolyl group, which decreases the Lewis acidity of the metal center, and/or to the larger steric hindrance of the indolyl moiety, which can hamper the nucleophilic attack of the monomer to the metal center. Compared with the yttrium complexes, the scandium complex 2 displayed lower activities (runs 4-6). This result is in line with literature data<sup>7a,8b</sup> showing that higher activities are

generally observed for larger rare-earth metal complexes. A polymerization experiment (run 5) carried out with complex 2 in toluene gave about 78% conversion within 16 h (TOF: 10  $\text{mol}_{\text{lactide}}$   $\text{mol}_{\text{sc}}^{-1}$  h<sup>-1</sup>), whereas only low conversions were obtained in more coordinating solvents, such as THF and CH<sub>2</sub>Cl<sub>2</sub>. Reasonably, for this smaller metal, the competition between coordinating solvents and lactide for metal coordination is more significant than that found for yttrium complexes.

GPC analysis of the polymer samples obtained by the complexes 1-3 displayed monomodal molecular weight distributions ranging from 1.54 to 2.23. The number-average molecular mass  $(M_n)$  values are in good agreement with the theoretical ones calculated on the assumption that a single PLA chain is produced per metal center. A good control of polymerization by complex 1 was also demonstrated by the linear relationship between number-average molecular masses and the monomer-to-metal ratio (Figure 3 and Table S1 in the Supporting Information). By increasing the monomer-to-initiator molar ratio up to 1200 (run 15 in Table 3), a good agreement between theoretical and experimental molecular weight was still obtained. Most significantly, catalyst 1 was able to convert 1050 equiv of lactide within 6 min at 20 °C, with a remarkable TOF of  $10^4 \text{ mol}_{lactide} \text{ mol}_{r}^{-1} \text{ h}^{-1}$ .

The relatively high PDI values can be due to transesterification processes occurring during the polymerization reactions, a phenomenon that is often observed in the ROP of cyclic esters promoted by group 3 metal initiators. To explore this possibility, low-molecular-weight samples were properly synthesized. The ESI-MS analysis carried out on these products showed that the most intense peaks are consistent with linear both even-membered and odd-membered oligomers, confirming the occurrence of intramolecular transesterification reactions.

For industrial-scale polymerizations, solvent-free conditions offer several advantages over solution polymerization (e.g., no solvent is required and the vulnerability to impurity levels and

![](_page_4_Figure_1.jpeg)

**Figure 3.** Dependence of  $M_n$  on monomer-to-yttrium ratio using complex 1 for *rac*-LA polymerization in THF at 20 °C. ( $\bullet$ ) Experimental data from Table S1 in the Supporting Information  $(M_n(\text{GPC}) \times 0.58)$ . The straight line represents the theoretical trend  $(M_n(\text{th}))$ .

unwanted side reactions is lower).<sup>21</sup> Thus, solvent-free polymerizations at 130 °C were carried out with complexes 1-3 (runs 11-13 in Table 1). Rapid ROP of *rac*-lactide with conversions up to 87% were obtained within 10 min, suggesting that complexes 1-3 are stable at high temperature. The activities follow the same order, 1 > 3 > 2, observed in solution polymerization. Analysis of molecular weights and molecular weight distributions is consistent with well-controlled polymerization, with levels of control similar to those observed in solution. These results suggest that the anilidopyridyl-pyrrolide and anilidopyridyl-indolide dianionic [¬NNN¬] tridentate ligands are able to stabilize the metal center even under drastic reaction conditions.

The stereochemistry of the obtained PLA samples was determined by recording the homonuclear decoupled <sup>1</sup>H NMR spectra (see Figure 4). The peaks were assigned to the appropriate tetrads in accordance with the shifts reported in the

![](_page_4_Figure_5.jpeg)

Figure 4. Methine region of the homonuclear decoupled <sup>1</sup>H NMR spectrum (400 MHz,  $CDCl_3$ , 298 K) of the PLA sample obtained by complex 1 in THF at 0 °C (run 10 in Table 1).

literature<sup>22</sup>, and  $P_{\rm r}$  values were evaluated by integrating the suitable peaks.<sup>23</sup>

As shown in Table 1, the microstructure analysis of the polymer samples obtained by complexes 1-3 showed moderate to good heterotacticity, depending on both the used catalysts and the reaction conditions. In particular, the polymerization medium has a relevant effect on the stereoselectivity of initiator 1. The polymerization in THF was found to be much more selective than those in toluene and in CH<sub>2</sub>Cl<sub>2</sub>. A similar behavior was previously observed for other catalysts.<sup>7b,8b,20,24</sup> A theoretical study examining this effect suggested that the solvent plays a key role in stabilizing the transition state, which dictates the stereochemistry of monomer insertion to give heterotactic PLAs.<sup>25</sup>

To get more insights in this coordination effect, a polymerization run was conducted with catalyst 1, under the same conditions of run 2, but adding 10 equiv of pyridine, a markedly strong donor compound. A positive effect on the degree of control of the catalyst was observed in terms of both molecular mass and stereoselectivity. In fact, a better agreement between theoretical and experimental molecular weight and a narrower molecular weight distribution were observed in the presence of pyridine (cf. run 2 and run 14); at the same time, a significant increase of the  $P_{\rm r}$  value was obtained. These observations support the beneficial effect of the presence of an additional coordinating donor to the metal center.

The  $P_r$  values for the PLAs obtained by the scandium complex revealed close to the best value obtained by the yttrium complex 1, regardless of the solvent. This result probably reflects the influence of the ionic radius of the metal center. Indeed, the environment around the smaller scandium metal center is more hindered, resulting in a better selectivity in each solvent.<sup>7c</sup> In the same way, the yttrium complex 3 produces heterotactic PLAs ( $P_r$  up to 0.75) and the solvent does not play a big effect on the stereoselectivity of the catalyst. Reasonably, the metal center in complex 3, being less acidic and more hindered than yttrium in complex 1, is less prone to solvent coordination.

Not surprisingly, higher heteroselectivity was obtained at lower temperature (run 10) while the stereocontrol was lost at 130  $^{\circ}$ C (runs 11–13).

Detailed microstructural analysis of the PLA produced by complex 1 (run 10) confirmed a chain-end control mechanism (Table 2) whereby the stereochemistry of the last inserted lactide unit controls the binding of the next monomer.<sup>23b</sup>

Table 2. Tetrad Probabilities Based on Bernoullian Statistic (th) for a  $P_r$  of 0.84 and Experimental Values (exptl) As Obtained by NMR Analysis

tetrad	formula	exptl	th
[mmm]	$P_m^2 + P_r P_m / 2$	0.08	0.09
[mmr]	$P_r P_m/2$	0.07	0.07
[ <i>rmm</i> ]	$P_r P_m/2$	0.07	0.07
[rmr]	$P_{r}^{2}/2$	0.35	0.35
[mrm]	$\left(P_r^2 + P_r P_m\right)/2$	0.43	0.42

For a deeper comprehension of the polymerization mechanism, we analyzed the polymer obtained carrying out the ROP of *rac*-lactide at a low monomer-to-initiator molar ratio ( $[LA]_0/[1]_0 = 20:1$ , run 1 in Table S1 (Supporting Information)). <sup>1</sup>H NMR analysis of this sample (Figure S13 in

the Supporting Information) revealed a set of minor resonances at 0–0.3 and 4.53 ppm, which, according to the literature,<sup>26</sup> can be attributed to the methyl groups and the hydrogen atoms, respectively, of the silylamido end group  $(-N(SiHMe_2)_2)$ , generated by the insertion of a monomer unit into the metal– silylamido bond. Other minor resonances at 2.74 ppm (-OH)and 4.35 ppm (-CH-) are attributable to hydroxyl end groups  $(HOCH(CH_3)CO-)$ , generated by hydrolysis of the polymer chain.<sup>27</sup> Therefore, these results suggest that the polymer chain is produced by a coordination–insertion mechanism process in which the silylamido ligand acts as the initiating group.

As is well known in the literature, amido and alkyl initiators are usually inferior initiating groups with respect to metal alkoxides for the ROP of polar monomers. The alkoxide initiating group mimics the propagating groups of the presumed active species, and complexes with these moieties produce polymers of predictable molecular weight and with narrow molecular weight distributions. Alkoxide initiators can be generated in situ by alcoholysis of amido and alkyl complexes.<sup>27</sup> With the aim to optimize the control over the ROP of *rac*-lactide, polymerization experiments by complex 1 in the presence of 2-propanol were carried out. The main results are summarized in Table 3. Remarkably, the yttrium

Table 3. ROP of *rac*-Lactide by Initiator 1 in the Presence of 2-Propanol<sup>a</sup>

run	[ <i>i</i> PrOH]/ [I] <sub>0</sub> (µmol)	time <sup>b</sup> (min)	conv (%)	$M_{\rm n}({ m th})^c$ (× 10 <sup>3</sup> )	$M_{\rm n}({ m GPC})^d$ (× 10 <sup>3</sup> )	PDI	$P_{\rm r}^{\ e}$			
15	0	6	85	147.0	136.1	2.15	0.68			
16	1	2	98	84.8	81.8	2.21	0.66			
17	5	2	98	28.3	28.8	1.19	0.68			
18	10	2	90	14.1	13.5	1.11	0.66			
<sup>a</sup> Conditions: [I <sub>0</sub> ] = 1.7 mM; [rac-LA]/[I <sub>0</sub> ] = 1200; 2 mL of THF;										
room temperature. <sup>b</sup> Reaction times were not necessarily optimized.										
<sup>c</sup> Calculated $M_n$ of PLA (g/mol) = 144.14 × ([rac-LA]/[I <sub>0</sub> + iPrOH])										
$\times$ conversion (rac-LA)%. <sup>d</sup> Experimental $M_{\rm n}$ values (corrected using										
the Mark-Houwink factor of 0.58) were determined by GPC analysis										
in THF using polystyrene standards. <sup>e</sup> P <sub>r</sub> value is determined from the										

methine region of the homonuclear decoupled <sup>1</sup>H NMR spectrum.

alkoxide, generated by treatment of complex 1 with 2-propanol in a 1:1 ratio, can polymerize 1200 equiv within 2 min at 20 °C. The obtained turnover frequency (TOF:  $3.5 \times 10^4 \text{ mol}_{\text{lactide}}$  $mol_{y}^{-1}$  h<sup>-1</sup>) is, to our knowledge, among the best values reported so far for the room-temperature ROP of lactide with metal-based initiatiors.<sup>28</sup> The experimental  $M_n$  value was in good agreement with the theoretical  $M_{\rm n}$  value, while the polydispersity index of the PLA did not change with respect to the polymerization carried out in the absence of alcohol. As expected, changing the initiating group from silylamido to isopropoxide results in no change in the heterotacticity of the obtained PLA. Increasing the amount of 2-propanol resulted in immortal polymerization of rac-lactide,<sup>29</sup> producing polymers with molecular weight values proportional to that equivalent of the 2-propanol added and narrow molecular weight distributions (PDI = 1.19 and 1.11 for 5 and 10 equiv of alcohol, respectively). End group analysis of the obtained PLA samples showed signals at 1.24 and 5.03 ppm attributable, according to the literature,<sup>30</sup> to the methyl and methine protons of the  $-OCH(CH_3)_{2}$  respectively (Figure S14 in the Supporting Information). The signals of the silylamido group (-N- $(SiHMe_2)_2$ ) were not detected. These observations confirmed

that, in these conditions, the isopropoxide ligand is the true initiating group for the ROP process. Moreover, the agreement between the experimental value of  $M_n$  ( $M_n$ (GPC) = 13 500) and that determined by NMR ( $M_n$  = 14 000) indicated that the polymerization proceeds exclusively via insertion of the monomer unit into the Y–OCH(CH<sub>3</sub>)<sub>2</sub> bond.

#### CONCLUSION

Novel group 3 metal complexes bearing anilidopyridylpyrrolide and anilidopyridyl-indolide dianionic ["NNN"] tridentate ligands were synthesized and fully characterized. All complexes resulted in being active in the ROP of rac-lactide at room temperature, with remarkable activity for the yttrium complexes (TOF up  $10^4 \text{ mol}_{\text{lactide}} \text{ mol}_{\text{Y}}^{-1} \text{ h}^{-1}$ ). A good control of molecular characteristics of the polymer chains, such as end groups, molecular weight, and molecular weight distribution, was obtained in all cases. In the presence of 2-propanol, the immortal ROP of rac-lactide was promoted. Rapid and wellcontrolled ROP of rac-lactide was also obtained in the solventfree polymerizations at 130 °C, showing that this class of ligands is able to stabilize the metal center under drastic reaction conditions, a result that is relevant not only from an academic point of view but also for the potential industrial applicability.

Additionally, the obtained PLAs were heterotactic with  $P_r$  values in the range of 0.57–0.84, depending on the nature of the initiator and solvent. A chain-end control mechanism enhanced by solvent coordination at the active site was recognized to be operating in these systems.

In summary, these novel group 3 metal catalysts bearing the anilidopyridyl-pyrrolide and anilidopyridyl-indolide ligands lead to a promising combination of activity, controlled character, and heteroselectivity in the polymerization of *rac*-lactide.

# EXPERIMENTAL SECTION

**General Considerations.** All manipulations of air- and/or watersensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Glassware and vials were dried in an oven at 135 °C overnight and exposed to a vacuum– nitrogen cycle thrice before use. All solvents were purchased from Carlo Erba. Toluene, THF, and CH<sub>2</sub>Cl<sub>2</sub> were refluxed over sodium/ benzophenone or calcium hydride (CaH<sub>2</sub>) and then distilled under nitrogen before use. 1-Bromo-2-isopropylbenzene was purchased from Alfa Aesar without purification before use. Lanthanide precursors, <sup>18b,31</sup> the anilinepyridinepyrrole compound ( $H_2L^1$ ),<sup>13b</sup> and *N*-(*t*-butoxycarbonyl)-indole-2-boronic acid<sup>32</sup> were prepared by literature procedures. *rac*-Lactide (Aldrich) was purified by crystallization from dry toluene. 2-Propanol was purchased from Sigma-Aldrich and used as received unless otherwise stated.

**Instruments and Measurements.** The NMR spectra were recorded on a Bruker Avance 400 spectrometer (<sup>1</sup>H, 400.00 MHz; <sup>13</sup>C, 100.62 MHz) at 25 °C, unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and degassed and dried over activated 3 Å molecular sieves prior to use. Chemical shifts ( $\delta$ ) are listed as parts per million and coupling constants (*J*) in hertz. <sup>1</sup>H NMR spectra are referenced using the residual solvent peak at  $\delta$  3.58 and 1.73 ppm for THF-*d*<sub>8</sub> and  $\delta$  7.26 ppm for CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra are referenced using the residual solvent peak at  $\delta$  67.57 and 25.48 ppm for THF-*d*<sub>8</sub> and  $\delta$  77.23 ppm for CDCl<sub>3</sub>.

The molecular weights  $(M_n)$  and the molecular weight distribution  $(M_w/M_n)$  of polymer samples were measured by GPC at 30 °C. THF was used as the solvent, the flow rate of the eluant was 1.0 mL/min, and narrow polystyrene standards were used as a reference. The measurements were performed on a Waters 1525 binary system

equipped with a Waters 2414 RI detector using four Styragel columns (range of 1000–1000000 Å). Every value was the average of two independent measurements. It was corrected using the Mark–Houwink factor of 0.58 according to the literature.<sup>33</sup>

X-ray Crystallographic Studies. Single crystals of 1 and 2, suitable for X-ray analysis, were obtained from *n*-hexane solutions at 253 K. Data collection was performed in flowing N2 at 173 K on a Bruker-Nonius  $\kappa$ CCD diffractometer (Mo K $\alpha$  radiation, CCD rotation images, thick slices,  $\varphi$  scans +  $\omega$  scans to fill the asymmetric unit). Cell parameters were determined from 104 reflections in the range of  $3.187^{\circ} \le \theta \le 21.225^{\circ}$ , and 191 reflections in the range of  $3.945^{\circ} \le \theta$  $\leq 20.708^{\circ}$  for 1 and 2, respectively. Semiempirical absorption corrections (multiscan SADABS)<sup>34</sup> were applied. The structure was solved by direct methods (SIR 97 package)<sup>35</sup> and refined by the fullmatrix least-squares method (SHELXL program of SHELX97 package)<sup>36</sup> on  $\tilde{F}^2$  against all independent measured reflections, using anisotropic thermal parameters for all non-hydrogen atoms. H atoms were placed in calculated positions with Ueq equal to those of the carrier atom and refined by the riding method. For 1, a SiMe<sub>2</sub> group was affected by positional disorder, which was rationalized using isotropic thermal parameters for the relative C atoms. All plots were generated by using the program ORTEP-3.37

Crystal data and details of the data collections are reported in Table S1 in the Supporting Information.

CCDC 843706 (1) and 848525 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data request/cif.

Synthesis of Proligands. Synthesis of  $H_2L^2$ . *n*-Butyl lithium (1.45 mL, 3.63 mmol, 2.5 M in hexane) was added dropwise to a solution of 1-bromo-2-isopropylbenzene (678 mg, 3.41 mmol) in dry diethyl ether (10 mL) at 0 °C. The colorless solution was warmed to room temperature and stirred for 3 h. The solution was then added dropwise to a dry diethyl ether (5 mL) solution of compound B (434 mg, 1.14 mmol) at -78 °C. The yellow solution was warmed to room temperature and stirred for 30 min. The color turned to red. The reaction was followed by TLC and then quenched with NH<sub>4</sub>Cl(aq) at 0 °C. The organic phase was separated and reserved. The aqueous phase was washed with diethyl ether  $(3 \times 30 \text{ mL})$ . The combined organic phases were extracted with water  $(2 \times 30 \text{ mL})$  and brine  $(1 \times 30 \text{ mL})$ 30 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was distilled off by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using hexane/diethyl ether (20/1) as the eluent. The colorless oil was concentrated under vacuum, affording a yellow solid (yield: 88%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 8.97 (s, 1H, indole-NH), 7.71–7.68 (m, 1H, Ar-H), 7.64 -7.57 (m, 3H, Ar-H), 7.37 (d, J(H,H) = 8 Hz, 1H, Py-H), 7.39–7.28 (m, 3H, Ar-H), 7.21 (m, 1H, Ar-H), 7.11 (d, J(H,H) = 1.2 Hz, 1H, Ar-H), 7.07 (s, 3H, Ar-H), 6.96 (m, 2H, Ar-H), 5.52 (s, 1H, NCH), 4.19 (br, 1H, NH), 3.02 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.89 (sept, 2H,  $CH(CH_3)_2$ ), 1.05 (d, J(H,H) = 7 Hz, 6H,  $CH(CH_3)_2$ ), 0.98 (d, J(H,H) = 7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.96 ppm (m, 9H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 162.48, 149.53, 146.56, 142.96, 142.56, 139.43, 137.30, 136.87, 136.45, 129.31, 127.72, 127.47, 126.17, 125.81, 123.71, 123.63, 123.27, 121.33, 120.26, 119.74, 117.97, 111.54, 100.43, 66.18(NCH), 28.82, 28.00, 24.01, 24.05, 23.97, 24.30 ppm. Elemental analysis calcd (%) for C<sub>35</sub>H<sub>39</sub>N<sub>3</sub>: C, 83.79; H, 7.84; N, 8.38. Found: C, 83.22; H, 7.51; N, 8.29

Synthesis of Complex 1. A solution of  $Y[N(SiHMe_2)]_3(THF)_2$ (315 mg, 0.5 mmol) in benzene (5 mL) was added dropwise into a stirred solution of  $H_2L^1$  (226 mg, 0.5 mmol) in benzene (10 mL). Following by <sup>1</sup>H NMR, the solution was stirred for overnight at ambient temperature. All volatiles were removed under vacuum to yield a yellow solid. The crude product was washed with pentane. The light yellow solid was obtained in 89% yield. <sup>1</sup>H NMR (400 MHz,  $[D_8]$ THF, 25 °C):  $\delta$  = 7.42 (t, 1H, *J*(H,H) = 8.0 Hz, *H*-Py), 7.27 (d, *J*(H,H) = 8.0 Hz, 1H, *H*-Py), 7.12 (dd, 1H, *J*(H,H) = 8.0 Hz, *J*(H,H) = 5.2 Hz, NC<sub>4</sub>H<sub>3</sub>), 7.08–6.79 (m, 7H, Ar-H), 6.69 (dd, 1H, *J*(H,H) = 8 Hz, *J*(H,H) = 1.2 Hz, NC<sub>4</sub>H<sub>3</sub>), 6.31 (d, *J*(H,H) = 7.6 Hz, 1H, *H*-Py), 6.09 (m, 1H, NC<sub>4</sub>H<sub>3</sub>), 5.86 (s, 1H, NCH), 4.56 (m, 2H, SiH), 3.58 (m, 9H,  $\alpha$ -CH<sub>2</sub>, THF and CH(CH<sub>3</sub>)<sub>2</sub>), 3.32 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.80 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.77 (m, 8H,  $\beta$ -CH<sub>2</sub>,THF), 1.40 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.46 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.01 (d, J(H,H) = 2.8 Hz, 6H, HSi(CH<sub>3</sub>)<sub>2</sub>), -0.06 (d, J(H,H) = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), -0.10 ppm (d, J(H,H) = 2.8 Hz, 6H, HSi(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100.62 MHz, [D<sub>8</sub>]THF, 25 °C):  $\delta$  = 169.98, 156.27, 152.90, 147.14, 146.89, 146.31, 146.06, 140.62, 139.43, 132.30, 131.02, 129.19, 127.02, 126.33, 125.67, 125.17, 124.44, 123.45, 116.55, 114.14, 110.91, 109.83, 74.09 (NCH), 68.38 ( $\alpha$ -CH<sub>2</sub>, THF), 28.84, 28.42, 28.16, 26.54, 26.37, 24.71 ( $\beta$ -CH<sub>2</sub>, THF), 23.17(CH-(CH<sub>3</sub>)<sub>2</sub>), 4.34 (HSi(CH<sub>3</sub>)<sub>2</sub>), 4.03 ppm (HSi(CH<sub>3</sub>)<sub>2</sub>). Elemental analysis calcd (%) for C<sub>35</sub>H<sub>49</sub>N<sub>4</sub>Si<sub>2</sub>Y: C, 62.66; H, 7.36; N, 8.35. Found: C, 62.58; H, 7.29; N, 8.27

Synthesis of Complex 2. A solution of  $Sc[N(SiHMe_2)]_3(THF)$ (113 mg, 0.22 mmol) in benzene (5 mL) was added dropwise into a stirred solution of  $H_2L^1$  (100 mg, 0.22 mmol) in benzene (10 mL). Following by <sup>1</sup>H NMR, the solution was stirred for overnight at ambient temperature. All volatiles were removed under vacuum to yield a yellow solid. The crude product was washed with pentane. The light yellow solid was obtained in 78% yield. <sup>1</sup>H NMR (400 MHz,  $[D_8]$ THF, 25 °C):  $\delta$  = 7.50 (t, J(H,H) = 8.0 1H, H-Py), 7.27 (d, J(H,H) = 8.0 Hz, 1H, H-Py), 7.08–6.84 (m, 8H, Ar-H and NC<sub>4</sub>H<sub>3</sub>), 6.64 (d, J(H,H) = 3.2 Hz, 1H, NC<sub>4</sub>H<sub>3</sub>), 6.37 (d, J(H,H) = 7.5 Hz, 1H, H-Py), 6.05 (d, J(H,H) = 1.6 Hz, 1H, NC<sub>4</sub>H<sub>3</sub>), 5.76 (s, 1H, NCH), 4.78 (m, 2H, SiH), 3.60 (m, 4H,  $\alpha$ -THF), 3.33 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.18 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.64 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.78 (m, 4H,  $\beta$ -THF), 1.34 (d, J(H,H) = 6.7 Hz, 3H,  $CH(CH_3)_2$ ), 1.16 (d, J(H,H)= 6.7 Hz, 3H,  $CH(CH_3)_2$ ), 1.13 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ , 1.07 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ ), 0.55 (d, J(H,H) = 6.7 Hz, 3H,  $CH(CH_3)_2$ ), 0.03 (d, J(H,H) = 6.7 Hz, 3H,  $CH(CH_{2})_{2}$ , -0.11 (d, I(H,H) = 2.8 Hz, 6H,  $HSi(CH_{2})_{2}$ ), -0.13 ppm  $(d, J(H,H) = 2.7 \text{ Hz}, 6H, \text{HSi}(CH_3)_2)$ . <sup>13</sup>C NMR (100.62 MHz,  $[D_8]$ THF, 25 °C):  $\delta$  = 169.58, 155.97, 152.71, 147.54, 146.42, 145.89, 145.03, 140.55, 140.45, 133.75, 130.51, 127.51, 126.56, 125.90, 125.60, 124.00, 116.02, 113.90, 111.10, 109.36, 74.39 (NCH), 68.38 (α-CH<sub>2</sub>, THF), 29.04, 28.97, 28.46, 26.54, 26.46, 24.87 (β-CH<sub>2</sub>, THF), 22.79 (CH(CH<sub>3</sub>)<sub>2</sub>), 2.86 (HSi(CH<sub>3</sub>)<sub>2</sub>), 2.15 ppm (HSi(CH<sub>3</sub>)<sub>2</sub>). Elemental analysis calcd (%) for C35H49N4Si2Sc: C, 67.05; H, 7.88; N, 8.94. Found: C, 67.11; H, 7.69; N, 8.87

Synthesis of Complex 3. A solution of  $Y[N(SiHMe_2)]_3(THF)_2$ (120 mg, 0.2 mmol) in benzene (5 mL) was added dropwise into a stirred solution of  $H_2L^2$  (100 mg, 0.2 mmol) in benzene (10 mL). The solution was warmed to 50 °C and stirred for 2 hours. All volatiles were removed under vacuum to yield a yellow solid. The crude product was washed with pentane. The orange solid was obtained in 76% yield. <sup>1</sup>H NMR (300 MHz,  $[D_8]$ THF, 25 °C):  $\delta$  = 7.77–7.70 (m, 2H, Ar-H), 7.59 (t, J(H,H) = 7.8, 1H, H-Py), 7.45 (d, J(H,H) = 7.8Hz, 1H, H-Py), 7.10-6.75 (m, 10H, Ar-H), 6.55 (d, J(H,H) = 7.5 Hz, 1H, H-Py), 5.93 (s, 1H, NCH), 4.73 (m, 2H, SiH), 3.61 (m, 9H,  $\alpha$ -THF and CH(CH<sub>3</sub>)<sub>2</sub>), 3.36 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.78 (sept, 1H,  $CH(CH_3)_2$ , 1.78 (m, 8H,  $\beta$ -THF), 1.40 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ ), 1.21 (d, J(H,H) = 6.6 Hz, 3H,  $CH(CH_3)_2$ ), 1.16 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ ), 1.11 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ , 0.50 (d, J(H,H)= 6.6 Hz, 3H,  $CH(CH_3)_2$ ), 0.04 (d, J(H,H) = 2.8 Hz, 6H, HSi(CH<sub>3</sub>)<sub>2</sub>), -0.03 (d, J(H,H) = 6.9 Hz, 3H,  $CH(CH_3)_2$ , -0.10 ppm (d, J(H,H) = 2.8 Hz, 6H,  $HSi(CH_3)_2$ ). <sup>13</sup>C NMR (75.47 MHz  $[D_8]$ THF, 25 °C):  $\delta$  = 170.62, 156.13, 152.97, 147.32, 147.10, 146.56, 145.91, 139.55, 132.30, 131.23, 127.26, 126.47, 125.88, 125.25, 124.67, 123.74, 121.37, 121.03, 119.79, 118.46, 117.69, 116.96, 101.52, 74.26 (NCH), 68.23 (α-CH<sub>2</sub>, THF), 28.90, 28.46, 28.41, 28.36, 26.54, 26.34, 24.43 (β-CH<sub>2</sub>, THF), 23.06 (CH(CH<sub>3</sub>)<sub>2</sub>), 4.63 ( $HSi(CH_3)_2$ ), 3.90 ( $HSi(CH_3)_2$ ). Elemental analysis calcd (%) for C<sub>39</sub>H<sub>51</sub>N<sub>4</sub>Si<sub>2</sub>Y: C, 64.97; H, 7.13; N, 7.77. Found: C, 64.82; H, 7.01; N, 7.69

General Polymerization Procedures. A 12 mL vial in a Braun Labmaster glovebox was charged sequentially with a solution of *rac*lactide in an appropriate ratio in 1.5 mL of dry solvent, and a solution of the required metal initiator in 0.5 mL of dry solvent was added

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rapidly. The mixture was immediately stirred with a magnetic stir bar at the desired temperature for the desired time. After a certain time, an aliquot of the reaction mixture was sampled with a pipet for determining the monomer conversion by <sup>1</sup>H NMR spectroscopy (CDCl<sub>3</sub>, 400 MHz). The reaction mixture was quenched by adding wet *n*-hexane. The polymer was filtered and dried in a vacuum oven at 60 °C for 16 h.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Representative <sup>1</sup>H and <sup>13</sup>C NMR spectra for complexes 1–3, certain intermediates, and some polymers and a table and CIF files giving X-ray crystallographic data for complexes 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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