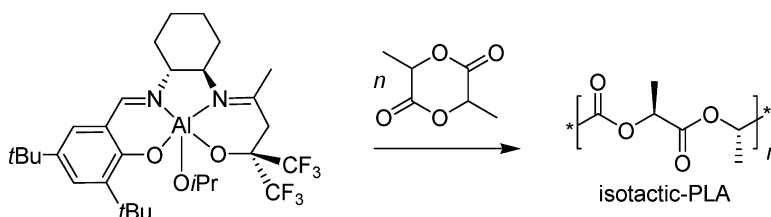


Aluminum and Yttrium Complexes of an Unsymmetrical Mixed Fluorous Alkoxy/Phenoxy-Diimino Ligand: Synthesis, Structure, and Ring-Opening Polymerization Catalysis

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Aluminum and Yttrium Complexes of an Unsymmetrical Mixed Fluorous Alkoxy/Phenoxy-Diimino Ligand: Synthesis, Structure, and Ring-Opening Polymerization Catalysis

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The coordination chemistry of the new unsymmetrical Schiff base ligand $\{(3,5\text{-}i\text{Bu}_2\text{-1-OC}_6\text{H}_4)\text{CH}=\text{N}(\text{trans-1,2-cyclo-C}_6\text{H}_{10})\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}(\text{CF}_3)_2\text{O}\}^{2-}$ ($\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}^{2-}$) onto Al(III) and Y(III) centers has been studied. Pro-ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{H}_2$ (**1**) reacts with AlMe_2Cl , $\text{Al}(\text{OiPr})_3$ and $\text{Y}(\text{N}(\text{SiHMe}_2)_2)_3 \cdot (\text{THF})_2$ to give the corresponding complexes $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{AIX}$ ($\text{X} = \text{Cl}$, **5**; OiPr , **6**) and $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{-Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$ (**7**) in high yields, with concomitant alkane, alcohol, and amine elimination, respectively. Single-crystal X-ray diffraction studies revealed that complexes **5** and **7** are mononuclear in the solid state with, respectively, five-coordinated distorted square-pyramidal and six-coordinated distorted octahedral geometries. Complexes **5**–**7** were also characterized in C_6D_6 solution by ^1H , ^{13}C , and ^{19}F NMR spectroscopy, which indicated the existence of only one isomer at room temperature. Al-OiPr complex **5** is an effective, though sluggish, initiator for the ring-opening polymerization of racemic lactide, giving polymers with a highly isotactic-enriched microstructure ($P_{\text{meso}} = 0.87$), molecular weights that match well the calculated values, and narrow polydispersities ($M_w/M_n = 1.04\text{--}1.18$).

Introduction

Salen-type derivatives (Chart 1) are ubiquitous Schiff base ligands in coordination chemistry and have found also tremendous applications in fine chemicals catalysis.¹ Easy tuning of substituents on the backbone as well as on the phenolate rings in these ligands allows a fine control of sterics and electronics at the metal center, and in turn effective optimization of catalytic processes. Of particular interest are unsymmetrical salen ligands wherein the substituents on the two salicylidene moieties are different, as they can feature original catalytic behavior.^{2,3}

We have recently reported the synthesis of new fluorous diimino-diols of general formula $(\text{CF}_3)_2\text{C}(\text{OH})\text{CR}^1_2\text{C}(\text{R}^2)=\text{N}$ -

$\text{R}^3\text{-N}=\text{C}(\text{R}^2)\text{CR}^1_2\text{C}(\text{OH})(\text{CF}_3)_2$ ($\text{R}^1 = \text{H}, \text{Me}$; $\text{R}^2 = \text{Me}, i\text{Pr}$; $\text{R}^3 = \text{C}_2\text{H}_4$, *trans*-1,2-cyclohexylene) (hereafter abbreviated $\{\text{CF}_3\text{ON}^{\text{R}}\text{NO}^{\text{CF}_3}\}\text{H}_2$, Chart 1)^{4,5} and have shown that these Schiff bases behave as interesting alternatives to salen ligands for oxophilic metals. Discrete complexes of yttrium, lanthanum, and aluminum have been prepared in high yields following simple σ -bond metathesis protocols, taking advantage of the high acidity of the fluorous diprotio pro-ligands.⁶ The presence of strongly electron-withdrawing CF_3 groups in those ligands prevents the high bridging tendency observed with regular alkoxide ligands, which leads to the selective formation of mononuclear complexes,^{7–9} just like phenolate ligands often do.^{1,7} Also, the fluorous alkoxide residue can increase the electrophilicity of the metal center, possibly accounting for the valuable performances observed in polymerization catalysis with some of these new complexes.⁶

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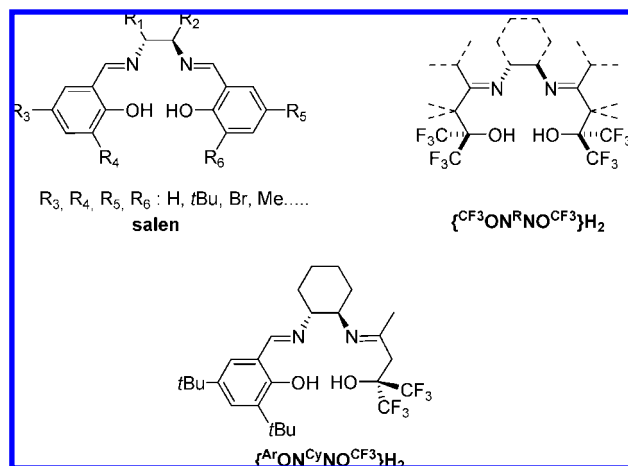
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Chart 1



We report herein the preparation of an original unsymmetrical Schiff base pro-ligand ($\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$, Chart 1), which combines a phenol and a fluorinated alcohol residue. Aluminum and yttrium complexes supported by this mixed tetradentate ligand have been prepared and structurally characterized in solution and in the solid state. Preliminary studies on the catalytic performances of the compounds in the ROP of racemic lactide are also reported.

Results and Discussion

Pro-ligand Synthesis. In principle, the synthesis of dissymmetric salen-like Schiff bases can be addressed in two different ways, according to the nature of the first carbonyl residue introduced on the diamino precursor.² Investigation of these two routes in the present case showed that only one of them is viable to access pro-ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$ (**1**) (Scheme 1). In fact, condensation of 3,5-di-*tert*-butylsalicylaldehyde onto the monohydrochloride salt of 1,2-*trans*-diaminocyclohexane affords readily the corresponding iminophenol-ammonium **2**·HCl in 80% yield.^{2f,g} However, attempts to condense with fluorinated aldol $\text{MeC(O)CH}_2\text{C}(\text{CF}_3)_2\text{OH}$ (**3**) onto **2**·HCl under a variety of conditions (solvent, reaction time, and temperature, preliminary isolation of the free amine base **2**, etc.) never afforded selectively $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$. Rather, mixtures of the symmetrical salen $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{Ar}}\}_2\text{H}_2$ (systematically the major product) and symmetrical fluorinated diimino-diol $\{\text{CF}_3\text{ON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$ ⁴ were obtained, sometimes accompanied with small amounts of the desired mixed compound $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$. Weck et al. recently reported that **2**·HCl is unstable in solution and quantitatively disproportionates at room temperature within 24 h into salen $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{Ar}}\}_2\text{H}_2$ and the disalt of 1,2-diamino-

cyclohexane.^{2g} Obviously, this side reaction proceeds faster than condensation of the fluorinated aldol **3**.

Reversing the reaction sequence provided pro-ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$. Condensation of aldol **3** onto the monohydrochloride salt of 1,2-*trans*-diaminocyclohexane proceeded readily to afford the corresponding fluorinated imino alcohol-ammonium (**4**·HCl), which was isolated in 84% yield. In contrast to **2**·HCl, **4**·HCl proved to be fully stable under Weck's conditions.^{2g} Subsequent condensation of **4**·HCl with the salicylaldehyde under typical conditions for salen synthesis^{2f} afforded analytically pure pro-ligand **1** (as a racemic mixture) in 39% isolated yield after recrystallization. Pro-ligand **1** is a stable compound at room temperature in the solid state and in chloroform solution and was characterized by ¹H, ¹⁹F, and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis and Structure of Al(III) Complexes $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{AIX}$ (X = Cl, OiPr). Reaction of the diprotio pro-ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$ with AlMe_2Cl proceeded cleanly in toluene at room temperature, via methane elimination, to afford the corresponding chloride complex $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{AlCl}$ (**5**), which was isolated in 92% yield (Scheme 2). The analogous alcohol elimination reaction from $\text{Al}(\text{OiPr})_3$ was found to proceed more slowly [as expected from the lower basicity of this Al precursor], and the isopropoxide complex $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2\text{AlOiPr}$ (**6**) was recovered in 91% yield after heating for 3 days at 80 °C in toluene (Scheme 2). It is noteworthy that the latter reaction proceeds apparently more easily than the one from the fluorinated diimino-diol $\{\text{CF}_3\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}\}_2\text{H}_2$, which afforded the corresponding complex $\{\text{CF}_3\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}\}_2\text{AlOiPr}$ in 56% under strictly identical conditions.^{6b}

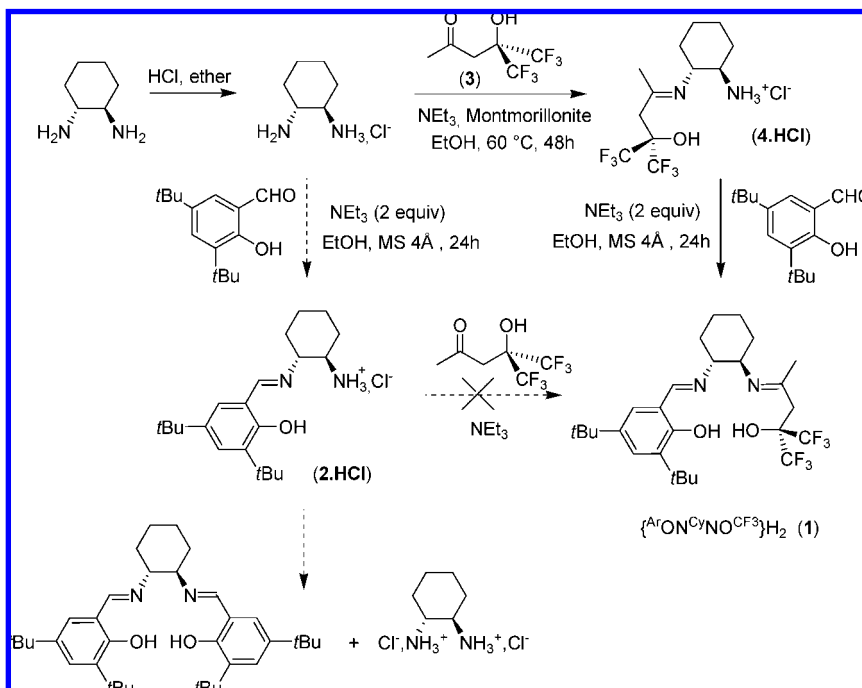
Both compounds were isolated as pale yellow, air-sensitive powders, which are poorly soluble in aliphatic hydrocarbons (pentane, hexane), moderately soluble in aromatic hydrocarbons (benzene, toluene), and very soluble in dichloromethane, chloroform, and THF. Complexes **5** and **6** have been characterized in benzene solution by ¹H, ¹⁹F, and ¹³C NMR spectroscopy. For both complexes, all the NMR spectra at room temperature show a single set of resonances, indicative of a single isomer on the NMR time scale (see the Experimental Section).

Single crystals of **5** suitable for X-ray diffraction studies were grown from a concentrated benzene solution. The solid-state structure of **5** features a monomeric molecule with a five-coordinated aluminum center in a geometry best described as distorted square pyramidal (spp), with the chlorine atom in the axial position (Figure 1, Table 1). The [slight] amount of distortion toward a trigonal bipyramidal (tbp) geometry can be measured using the calculation $\tau = (\beta - \alpha)/60$,¹⁰ which is 0.12. This τ value for **5** is significantly lower than those observed (0.42–0.85) for $\{\text{CF}_3\text{ON}^{\text{R}}\text{NO}^{\text{CF}_3}\}_2\text{AIX}$ (X = Me, Cl, OiPr; R = ethylenyl, 1,2-cyclohexenyl) complexes based on symmetric fluorinated dialkoxy-diimino ligands.^{6b} Obviously, the replacement of a sp^3 -hybridized bis(trifluoromethyl)alkoxy group in the latter complexes by a phenolate moiety conjugated with the imino function in **5** induces a more rigid ligand backbone, and, as a result, the geometry around the metal center changes from tbp to spp. The intermediate rigidity of the mixed phenolate-alkoxide-diimino Schiff base ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2^{2-}$ can be quantified by the torsion angle between the imino-alkoxide(phenolate) mean planes (36.47°). This value is quite larger than

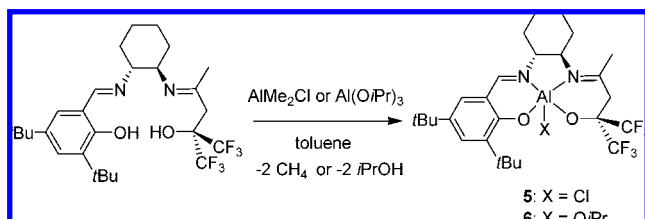
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Scheme 1. Possible Routes Investigated for the Synthesis of Pro-ligand $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}_2$ (1) and Side Processes Observed

Scheme 2



those observed in Al-{salen} complexes, e.g., {diphenylethylene-salen}AlCl (17.86°),¹¹ and obviously smaller than that in $\text{tbp}\{\text{CF}_3\text{ON}^{\text{R}}\text{NO}^{\text{CF}_3}\}\text{AlX}$ complexes, e.g., $\{\text{CF}_3\text{ON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{AlMe}$ (70.44°). Thus, overall, the structural features of **5** are remi-

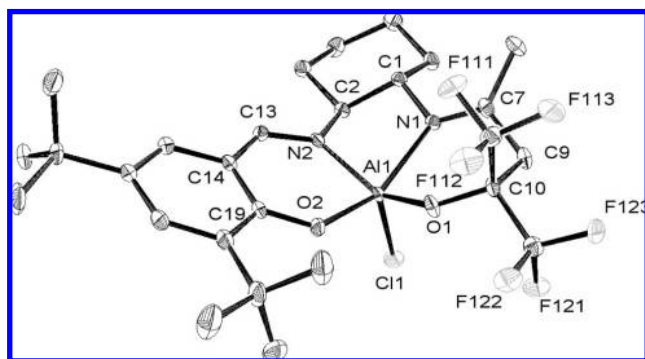


Figure 1. ORTEP view of $\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{AlCl}$ (**5**) depicted with 50% thermal ellipsoids; hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl(1)–Al(1), 2.170(12); O(1)–Al(1)–O(2), 87.94(10); Al(1)–O(1), 1.763(2); O(2)–Al(1)–N(2), 88.92(10); Al(1)–O(2), 1.791(2); O(1)–Al(1)–N(2), 145.92(11); Al(1)–N(2), 1.963(3); O(1)–Al(1)–N(1), 89.85(10); Al(1)–N(1), 2.111(3); O(2)–Al(1)–N(1), 153.32(11); N(2)–Al(1)–N(1), 78.22(10); O(1)–Al(1)–Cl(1), 110.56(9); O(2)–Al(1)–Cl(1), 105.76(9); N(2)–Al(1)–Cl(1), 102.94(8); N(1)–Al(1)–Cl(1), 99.90(8).

Table 1. Summary of Crystal and Refinement Data for Complexes **5** and **7**

	5 · 2benzene	7 · 0.5benzene
empirical formula	C ₃₉ H ₄₈ AlClF ₆ N ₂ O ₂	C ₃₈ H ₆₁ F ₆ N ₃ O ₃ Si ₂ Y
fw	753.22	866.99
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	11.5325(19)	31.345(5)
<i>b</i> , Å	17.087(2)	13.651(2)
<i>c</i> , Å	19.346(3)	23.715(4)
α , deg	90	90
β , deg	96.742(6)	119.909(8)
γ , deg	90	90
volume, Å ³	3785.9(10)	8796(2)
<i>Z</i>	4	8
density, Mg · m ^{−3}	1.321	1.309
abs coeff, mm ^{−1}	0.190	1.443
<i>F</i> (000)	1584	3640
cryst size, mm	0.55 × 0.38 × 0.28	0.50 × 0.36 × 0.10
θ range, deg	2.92 to 27.48	2.98 to 27.48
limiting indices	−14 ≤ <i>h</i> ≤ 14, −22 ≤ <i>k</i> ≤ 18, −22 ≤ <i>l</i> ≤ 25	−40 ≤ <i>h</i> ≤ 40, −17 ≤ <i>k</i> ≤ 17, −30 ≤ <i>l</i> ≤ 30
reflins collected	33 773	62 178
reflins unique [<i>I</i> > 2σ(<i>I</i>)]	8649	10 077
data/restraints/params	8649/0/460	10 077/0/483
goodness-of-fit on <i>F</i> ²	1.045	1.020
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.0730 (0.1705)	0.0402 (0.0894)
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.1080 (0.1882)	0.0751 (0.1028)
largest diff, e · Å ^{−3}	1.588 and −0.575	0.913 and −0.557

niscent of those observed in {salen}AlCl complexes.^{1d,11–13} Metrical data, i.e., Al–O, Al–N, and Al–Cl bond distances and the corresponding bond angles (Figure 1), compare well within these two classes of complexes. The Al(1)–N(2) bond distance (1.963(3) Å) involving the N atom *trans* to the alkoxide group is significantly shorter than the Al(1)–N(1) bond distance (2.111(3) Å) involving the N atom *trans* to the phenolate group.

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Scheme 3

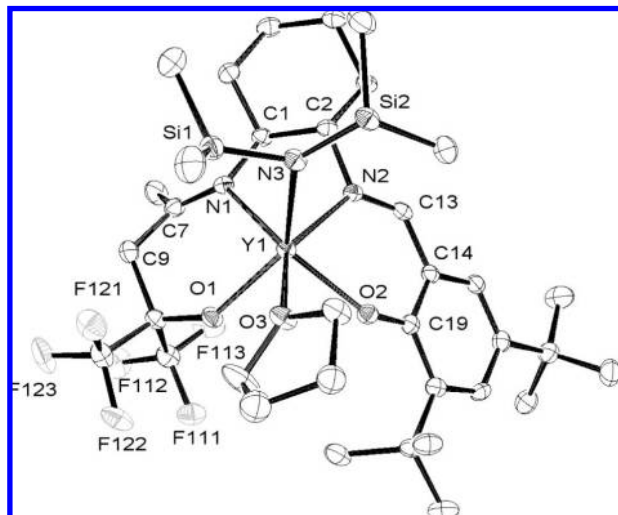
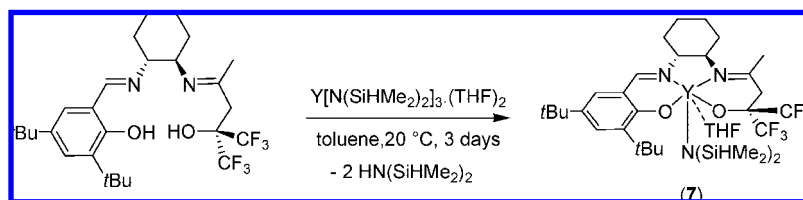


Figure 2. ORTEP view of $\{\text{ArONCyNOCF}_3\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$ (7) depicted with 50% thermal ellipsoids; hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)–O(1), 2.1358(17); Y(1)–O(2), 2.1530(18); Y(1)–N(1), 2.587(2); Y(1)–N(2), 2.423(2); Y(1)–O(3), 2.4240(18); Y(1)–N(3), 2.290(2); Y(1)–Si(1), 3.1460(9); Y(1)···Si(2), 3.628; O(1)–Y(1)–O(2), 95.16(7); O(1)–Y(1)–N(3), 136.69(7); O(2)–Y(1)–N(3), 122.17(7); O(1)–Y(1)–N(2), 122.25(7); O(2)–Y(1)–N(2), 74.33(7); N(3)–Y(1)–N(2), 90.93(7); O(1)–Y(1)–O(3), 82.72(6); O(2)–Y(1)–O(3), 81.55(6); N(3)–Y(1)–O(3), 82.11(7); N(2)–Y(1)–O(3), 146.20(6); O(1)–Y(1)–N(1), 77.62(6); O(2)–Y(1)–N(1), 124.90(7); N(3)–Y(1)–N(1), 95.14(7); N(2)–Y(1)–N(1), 65.32(7); O(3)–Y(1)–N(1), 147.99(6); Si(1)–N(3)–Y(1), 103.40(10); Si(2)–N(3)–Y(1), 130.14(12); Si(1)–N(1)–Si(2), 125.81(2).

This difference most likely reflects the strong electron-withdrawing effect of the bis(trifluoromethyl) moiety.

Synthesis and Structure of $\{\text{ArONCyNOCF}_3\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$. A yttrium complex of the new mixed ligand was also prepared via σ -bond metathesis. The amine elimination reaction between the silylamido precursor $[\text{Y}(\text{N}(\text{SiHMe}_2)_2)_3 \cdot (\text{THF})_2]$ and pro-ligand **1** in toluene at room temperature cleanly afforded the corresponding monosilylamido complex $\{\text{ArONCyNOCF}_3\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$ (**6**), with concomitant release of 2 equiv of bis(dimethylsilyl)amine (Scheme 3). Compound **6** is fairly soluble in aromatic hydrocarbons (toluene, benzene), in which it is stable at least for several days at room temperature. This observation contrasts with the instability noticed for the related complex $\{\text{CF}_3\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$ under similar conditions.^{6a} The ^1H , ^{19}F , and ^{13}C NMR spectra of **6** in C_6D_6 at room temperature all contain a single set of resonances, indicative of a single isomer on the NMR time scale (see the Experimental Section). The ^1H NMR spectrum indicates the presence of one coordinated THF molecule, as also confirmed by ^{13}C NMR spectroscopy. The nonequivalence of the methylsilyl groups (δ 0.42 and 0.45 ppm) and the chemical shifts for the SiH (δ 5.15 ppm), which are shifted downfield compared to the chemical shift in

$[\text{Y}(\text{N}(\text{SiHMe}_2)_2)_3(\text{THF})_2]$ (δ 4.99 ppm), suggest a $\beta(\text{Si}–\text{H})$ agostic interaction with the yttrium center.¹⁴

Single crystals of **7** suitable for X-ray diffraction studies were obtained from a benzene solution at room temperature. The solid-state structure of **7** features a monomeric molecule with a yttrium center in a highly distorted octahedral geometry, six-coordinated by the $\{\text{CF}_3\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}\}^{2-}$ ligand, the silylamido moiety, and a THF molecule (Figure 1, Table 1). In addition, in line with the above NMR observations, the $\text{Y} \cdots \text{Si}$ (3.146 Å) and $\text{Y} \cdots \text{H}(\text{Si})$ (2.669 Å) distances are consistent with a $\beta(\text{Si}–\text{H})$ agostic interaction. This interaction is, however, weak, as attested by the $\text{Si}(1)–\text{N}(1)–\text{Si}(2)$ bond angle of $125.81(2)^\circ$, which is slightly larger than for ideal sp^2 hybridization and falls into the middle range of values reported for Si–N–Si angles (119.93 – 129.58°). As discussed above for aluminum complex **5**, a 0.16 Å difference is noted between the Y(1)–N(1) and Y(1)–N(2) distances. The Y–O(2) and Y–N(2) bond distances associated with the imino-phenolate fragment, as well as the Y–N(silylamido) bond distance, fall in the range of distances observed in related amido-ylttrium- $\{\text{salen}\}$ complexes¹⁵ or amido-ylttrium complexes supported by tetradentate bis(phenolate) ligands.¹⁶ The Y–O (2.136(2) Å) and Y–N (2.587(2) Å) bond distances associated with the fluorous alkoxy-imino fragment compare well with the corresponding ones observed in the fluorous dialkoxy-diimino complex $[\{\text{CF}_3\text{ON}^{\text{Et}}\text{NO}^{\text{CF}_3}\}\text{Y}((R)\text{-}t\text{Bu lactate})]_2$ (Y–O = 2.171(3)–2.175(3) Å; Y–N = 2.530(4)–2.562(4) Å).^{6a}

Preliminary Studies in the Ring-Opening Polymerization of Racemic Lactide. Discrete group 3 metal and aluminum complexes are well-established catalysts-initiators for the ring-opening polymerization (ROP) of lactones and related monomers, such as lactide.^{17–19} Activity, productivity, degree of control/livingness, and stereoselectivity, in the case of chiral monomers, depend crucially on ancillary ligands that define the sterics and electronics around the active metal center. We were therefore interested in evaluating the performances of the new compounds, considering that (i) Al-isopropoxide complex **5** and

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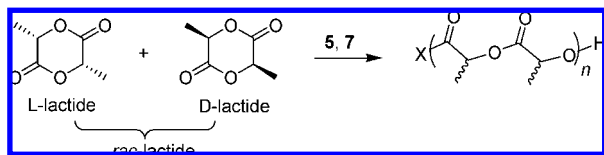
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Table 2. Ring-Opening Polymerization of *rac*-Lactide Promoted by Complexes **5** and **7**^a

entry	compd	[LA]/[M]	temp (°C)	time (d)	conv ^b (%)	<i>M</i> _{n,calc} ^c (g/mol)	<i>M</i> _{n(exp)} ^d (g/mol)	<i>M</i> _w / <i>M</i> _n ^d	<i>mmm</i> ^e (%)
1 ^g	5	50	60	7	0 ^g				
2	5	50	60	7	52	3700	4300	1.04	81
3	5	100	80	3	80	11 500	10 400	1.18	72
4	7	100	20	1	30	4300	4600	2.1	atactic
5 ^h	7 ^h	100	20	1	91	13 100	11 200	1.28	atactic

^a Reactions conducted in toluene slurry at [LA] = 0.8 M, unless otherwise stated. ^b Monomer conversion determined by ¹H NMR. ^c Number average molecular weight calculated from [LA]/[M] × conv(%) × 144. ^d Experimental number average molecular weight (corrected using a factor of 0.58) and polydispersity determined by GPC in THF vs PS standards. ^e Percentage of *mmm* tetrad, as determined from the methine region of the homonuclear decoupled ¹H NMR spectrum. ^f Reaction carried out in THF solution at [LA] = 0.8 M. ^g Reaction carried out by premixing complex **7** with 1 equiv of 2-propanol (vs Y) in toluene for 30 min before addition to the monomer.

Scheme 4



Y-amido complex **7** possess a potentially active nucleophilic group and (ii) Al complexes supported by fluorous diolate-diimino ligands, {CF₃ON^RNO^{CF3}}Al(OiPr), have been shown recently to induce significant isotacticity in the ROP of *rac*-lactide.^{6b}

Complexes **5** and **7** were thus briefly assessed in the ROP of *rac*-lactide (Scheme 4). Representative results are summarized in Table 2. Yttrium complex **7** proved to be active at room temperature. However, the recovered PLAs were atactic and

showed relatively broad molecular weight distributions. We assume that this latter observation reflects, at least in part, the poor initiation efficiency of the amido group [amides are known to be less nucleophilic than other initiating groups such as alkoxides].¹⁸ Consistent with this hypothesis, upon premixing complex **7** with 1 equiv of 2-propanol in toluene for 30 min before addition onto the monomer, in order to generate *in situ* the corresponding isopropoxide complex, a PLA with a narrower molecular weight distribution was formed in higher yield (entry 5). No reaction took place using Al complex **5** in THF solution at 60 °C, but ROP slowly proceeded when toluene was used as the solvent (these reactions proceeded under slurry conditions). This observation can probably be accounted for by the competing role of THF versus lactide for coordination onto the metal center. The activity of **5** slightly increases from 60 to 80 °C but remains low, which is usual for Al complexes and similar to the activities observed with {CF₃ON^{Cy}NO^{CF3}}Al(OiPr).^{6b} Interestingly, the PLAs recovered have quite narrow polydispersities with *M*_n values determined by GPC (and corrected by a Mark–Houwink factor of 0.58, due to the use of PS standards)^{18f,20} that match well those calculated for a living polymerization. Moreover, homonuclear decoupled ¹H NMR experiments revealed that a kinetic resolution takes place; that is, these reactions led to the formation of significantly isotactic-enriched stereoblock PLAs: 81% enrichment for the *mmm* tetrad (*P*_{meso} = 0.87)²¹ was achieved by carrying out the reaction at 60 °C; at higher temperature (80 °C), the level of isotacticity was somewhat decreased (*P*_{meso} = 0.80) (entry 2). These *P*_{meso} values²¹ can be compared with those of 0.91 and 0.93, respectively, achieved at 70 °C with Schiff-base Al complexes, namely, achiral {1,3-propylene-Salpen^{Bu}}^{19c} and chiral racemic (*trans*-1,2-cyclohexylene-Salcen^{Bu})Al(OiPr).^{19d} They are also very similar to those observed with {CF₃ON^{Cy}NO^{CF3}}Al(OiPr), which bears a symmetric fluorous dialkoxy-diimino ligand.^{6b}

The ¹H NMR spectra in CDCl₃ of PLAs obtained with isopropoxide systems (**5**, **7**/iPrOH) show the resonance at δ 1.25 ppm for the methyls of a C(O)OiPr group (the resonance for the OCHMe₂ at δ ca. 5.1 ppm mostly overlaps with those of PLA) and the broadened quartet characteristic of the CH(Me)OH terminal group at δ 4.35 ppm. The observation of these end-groups establishes that, expectedly, the ROP proceeds via a classical “coordination/insertion” mechanism,^{16c,17a,22} i.e., initial acyl-oxygen bond cleavage by the transfer of the nucleophilic isopropoxide group of the metal complex to the monomer with

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the eventual formation of a metal-alkoxide propagating species, which is hydrolyzed at the end of the reaction.²³

In summary, we have developed an effective entry toward an unusual mixed fluorine alkoxy/phenolate Schiff base ligand. This ligand effectively supports oxophilic Al(III) and Y(III) metal centers, yielding discrete mononuclear complexes. Preliminary investigations using racemic ligands show interesting performances of aluminum-isopropoxide complexes in the stereoselective, "living-controlled" ROP of racemic lactide. The many possibilities to tune the substituents on the salicylidene as well as on the fluorine alkoxy-imino moieties,⁴ and to access enantiomerically pure ligands, open large avenues, especially in the field of fine chemicals catalysis.^{1,11}

Experimental Section

General Procedures. All manipulations were performed under argon using standard high-vacuum Schlenk techniques or in a glovebox. Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were distilled from Na/benzophenone; toluene and pentane were distilled from Na/K alloy under nitrogen and degassed by freeze–vacuum–thaw cycles prior to use. Ethanol was distilled over Mg, and chlorinated solvents were distilled from calcium hydride. Benzene-*d*₆ (>99.5% D, Eurisotop) was freshly distilled from K_(met) under argon and degassed prior to use. *trans*-1,2-Diaminocyclohexane (racemic mixture), Montmorillonite K10 (KSF, Acros), AlMe₂Cl, and Al(O*i*Pr)₃ were purchased from Aldrich or Acros and used as received. The monohydrochloride salt of *trans*-1,2-diaminocyclohexane,^{2f,g} 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)pentan-2-one (**3**),⁴ and Y(N(SiHMe₂)₂)₃·(THF)₂^{14a} were synthesized according to the reported procedures. *rac*-Lactide (Aldrich) was recrystallized from dry methanol and toluene and sublimed under vacuum at 50 °C.

NMR spectra were recorded on Bruker Avance DPX-200, AM-300, or AM-500 spectrometers at ambient probe temperature (298 K) in Teflon-valve NMR tubes for air-sensitive complexes. ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ and were determined by reference to the residual solvent resonances. Assignment of ¹³C NMR signals was made from 2D ¹H–¹³C HMQC and HMBC NMR experiments. ¹⁹F NMR chemical shifts were determined by external reference to an aqueous solution of NaBF₄. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. ESI-HRMS spectra were obtained on a high-resolution MS/MS Micromass ZABSpecTOF (4 kV) spectrometer. Molecular weights of PLAs were determined by size exclusion chromatography (SEC) at room temperature in THF on a Polymer Laboratories PL-GPC 50 plus apparatus (PLgel 5 μm MIXED-C 300 × 7.5 mm, 1.0 mL/min, RI and dual angle LS (PL-LS 45/90) detectors). The number average molecular masses (*M*_n) and polydispersity index (*M*_w/*M*_n) of the polymers were calculated with reference to a universal calibration versus polystyrene standards. *M*_n values of PLAs were corrected with a Mark–Houwink factor of 0.58, to account for the difference in hydrodynamic volumes between polystyrene and polylactide.^{18f,20} The microstructure of PLAs was determined by homonuclear decoupled ¹H NMR spectroscopy at 20 °C in CDCl₃ with a Bruker AC-500 spectrometer.

Fluorine Imino-Alcohol-Ammonium Salt 4·HCl. To a solution of *rac*-1,2-diaminocyclohexane hydrochloride (1.00 g, 6.66 mmol) in dry ethanol (60 mL) were added Montmorillonite (400 mg) and a solution of fluorinated aldol **3** (1.79, 8.0 mmol) in dry

ethanol (5 mL). The reaction mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the mixture was filtered and the solution concentrated under vacuum. The solid residue was washed with diethyl ether (10 mL) and dried under vacuum to give **4·HCl** as a pale brown powder (1.80 g, 84%). ¹H NMR (DMSO-*d*₆, 300 MHz, 20 °C): δ 8.03 (br s, 3H, NH₃⁺), 3.52 (m, 1H, CHNH₃⁺), 3.08 (m, 1H, CHN=C), 2.90 (d, 1H, *J* = 15 Hz, CHHC(CF₃)₂), 2.83 (d, 1H, *J* = 15 Hz, CHHC(CF₃)₂), 2.06 (s, 3H, CH₃), 1.27–1.67 (m, 8H, CH₂ Cy). ¹⁹F{¹H} NMR (DMSO-*d*₆, 188 MHz, 20 °C): δ –77.61 (q, ⁴*J*_{F–F} = 9 Hz, 3F), –76.40 (q, ⁴*J*_{F–F} = 9 Hz, 3F). ¹³C{¹H} NMR (DMSO-*d*₆, 125 MHz, 20 °C): δ 171.94 (*N* = C), 60.78 (CHNH₃⁺), 54.74 (CHN=C), 35.42 (CH₂C(CF₃)₂), 30.54, 30.76, 23.62, 23.75 (CH₂ Cy), 20.78 (CH₃). ESI-HRMS: *m/z* calcd for C₁₂H₁₉N₂O₆F₆ 321.14; found 321.14. Anal. Calcd for C₁₂H₁₉ClF₆N₂O: C, 40.40; H, 5.37; N, 7.85. Found: C, 40.5; H, 5.4; N, 7.7.

{ArONCyNO^{CF3}}H₂ (1**).** To a solution of **4·HCl** (1.00 g, 2.80 mmol) in dry ethanol (60 mL) were added 4 Å molecular sieves (ca. 1.0 g) and then a solution of 3,5-*tert*-butyl-2-hydroxybenzaldehyde (657 mg, 2.80 mmol) and NEt₃ (787 μL, 5.60 mmol) in dry ethanol (20 mL). The reaction mixture was stirred at room temperature for 24 h. The mixture was filtered and the solution concentrated under vacuum. The solid residue was dissolved in diethyl ether (10 mL), the solution was filtered, and the filtrate was concentrated under vacuum to give a solid residue, which was further recrystallized in hexane at –50 °C to give **1** as a pale yellow solid (585 mg, 39%). ¹H NMR (CDCl₃, 200 MHz, 20 °C): δ 8.28 (s, 1H, N=CH), 7.42 (d, 1H, *J* = 2 Hz, *H* aro), 7.13 (d, 1H, *J* = 2 Hz, *H* aro), 3.63 (m, 1H, CHN=C(CH₃)), 3.22 (m, 1H, CHN=CH), 2.57 (s, 2H, CH₂C(CF₃)₂), 1.95 (s, 3H, CH₃), 1.54–1.89 (m, 8H, CH₂ Cy), 1.47 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu). ¹⁹F{¹H} NMR (CDCl₃, 188 MHz, 20 °C): δ –78.42 (q, ⁴*J*_{F–F} = 6.5 Hz, 3F), –79.43 (q, ⁴*J*_{F–F} = 6.5 Hz, 3F). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 20 °C): δ 169.33 (N=C(CH₃)), 165.78 (N=CH), 157.78, 140.25, 136.34, 126.96, 126.20, 117.63 (C aro), 72.82 (CHC=NH), 63.31 (CHC=N(CH₃)), 34.97 (C(CH₃)₃), 34.11 (C(CH₃)₃), 33.08 (CH₂C=N(CH₃)), 32.82, 31.60, 31.44, 29.36 (CH₂ Cy), 24.15 (C(CH₃)₃), 24.01 (C(CH₃)₃), 22.65 (C(CH₃)₃), 20.59 ((CH₃)C=N). ESI-HRMS: *m/z* calcd for C₂₇H₃₈N₂O₂F₆ 536.28; found 536.27. Anal. Calcd for C₂₇H₃₈N₂O₂F₆: C, 60.43; H, 7.14; N, 5.22. Found: C, 60.5; H, 7.3; N, 5.2.

{ArONCyNO^{CF3}}AlCl (5**).** A solution of pro-ligand **1** (100 mg, 0.186 mmol) in toluene (5 mL) was added to a solution of AlMe₂Cl (186 μL of a 1 M solution in hexanes, 0.186 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 14 h and then heated at 80 °C for 4 h. Volatiles were removed under vacuum, and the solid residue was washed with cold hexane (1 mL) to give complex **5** as a pale yellow powder (102 mg, 92%). Single crystals suitable for X-ray diffraction studies were grown from a benzene solution at room temperature. ¹H NMR (C₆D₆, 300 MHz, 20 °C): δ 7.84 (d, 1H, *J* = 3 Hz, *H* aro), 7.54 (s, 1H, N=CH), 7.03 (d, 1H, *J* = 3 Hz, *H* aro), 3.69 (m, 1H, CH–N=C(CH₃)), 3.22 (d, 1H, *J* = 15 Hz, CHHC(CF₃)₂), 2.57 (d, 1H, *J* = 15 Hz, CHHC(CF₃)₂), 2.42 (m, 1H, CH–N=CH), 1.90 (s, 9H, *t*Bu), 1.46 (s, 9H, *t*Bu), 1.44 (s, 3H, CH₃), 0.44–1.13 (m, 8H, CH₂ Cy). ¹⁹F{¹H} NMR (C₆D₆, 188 MHz, 20 °C): δ –76.78 (q, ⁴*J*_{F–F} = 10 Hz, 3F), –79.02 (q, ⁴*J*_{F–F} = 10 Hz, 3F). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 20 °C): δ 179.16 (N=C(CH₃)), 166.38 (N=CH), 164.70, 142.09, 138.21, 131.88, 127.31, 117.71 (C aro), 64.49 (CHN=CH), 63.04 (CHN=CC(CH₃)), 37.48 (CH₂C(CH₃)=N), 35.81 (C(CH₃)₃), 34.23 (C(CH₃)₃), 31.66, 31.07, 29.75, 27.49 (CH₂ Cy), 26.03 (C(CH₃)₃), 25.11 (C(CH₃)₃), 25.08 (C(CH₃)₃), 24.55 ((CH₃)C=N), 24.20 (C(CH₃)₃). Anal. Calcd for C₂₇H₃₆AlClF₆N₂O₂: C, 54.32; H, 6.08; N, 4.69. Found: C, 54.6; H, 6.3; N, 4.6.

{ArONCyNO^{CF3}}AlO*i*Pr (6**).** In a Schlenk flask, a solution of pro-ligand **1** (100 mg, 0.186 mmol) and Al(O*i*Pr)₃ (38.1 mg, 0.186 mmol) in toluene (10 mL) was stirred at 80 °C for 3 days. After

(23) It is noteworthy that MALDI-TOF-MS analysis of the PLA produced with the 7/*i*PrOH (1:1) system revealed the presence of cyclic oligomers, indicating that intramolecular transesterification ("back-biting") does occur in this system; see ref 22a.

cooling to room temperature, volatiles were removed under vacuum and the solid residue was washed with cold hexanes (1 mL) to give complex **6** as a pale yellow solid (105 mg, 91%). ^1H NMR (C_6D_6 , 300 MHz, 20 °C): δ 7.85 (d, 1H, $J = 3$ Hz, H_{aro}), 7.66 (s, 1H, $\text{N}=\text{CH}$), 7.10 (d, 1H, $J = 3$ Hz, H_{aro}), 4.85 (m, 1H, $\text{OCH}(\text{CH}_3)_2$), 3.76 (m, 1H, $\text{CHN}=\text{C}(\text{CH}_3)$), 3.26 (d, 1H, $J = 15$ Hz, $\text{CHHC}(\text{CF}_3)_2$), 2.59 (d, 1H, $J = 15$ Hz, $\text{CHHC}(\text{CF}_3)_2$), 2.45 (m, 1H, $\text{CHN}=\text{CH}$), 1.94 (s, 9H, $t\text{Bu}$), 1.69 (d, $J = 6$ Hz, 3H, $(\text{CH}_3)_2\text{CHO}$), 1.52 (d, $J = 6$ Hz, 3H, $(\text{CH}_3)_2\text{CHO}$), 1.46 (s, 9H, $t\text{Bu}$), 1.43 (s, 3H, $\text{C}(\text{CH}_3)=\text{N}$), 0.61–1.18 (m, 8H, CH_2 Cy). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 188 MHz, 20 °C): δ -76.53 (q, $^4J_{\text{F-F}} = 11$ Hz, 3F), -78.91 (q, $^4J_{\text{F-F}} = 11$ Hz, 3F). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 20 °C): δ 176.61 ($\text{N}=\text{C}(\text{CH}_3)$), 165.22 ($\text{N}=\text{CH}$), 161.58, 141.99, 137.40, 131.24, 127.37, 118.12 (C_{aro}), 64.53 ($\text{CH}_2\text{CHC}=\text{NH}$), 63.72 ($\text{CH}_2\text{CHC}=\text{N}(\text{Me})$), 63.15 ($\text{OCH}(\text{CH}_3)_2$), 38.13 ($\text{CH}_2\text{CHC}=\text{N}(\text{Me})$), 35.83 ($\text{C}(\text{CH}_3)_3$), 34.18 ($\text{C}(\text{CH}_3)_3$), 31.69, 30.96, 29.95, 29.73 (CH_2 Cy), 28.80 ($\text{OCH}(\text{CH}_3)_2$), 28.52 ($\text{OCH}(\text{CH}_3)_2$), 26.17 ($\text{C}(\text{CH}_3)_3$), 24.65 ($\text{C}(\text{CH}_3)_3$), 24.49 ($\text{C}(\text{CH}_3)_3$), 24.21 ($(\text{CH}_3)\text{C}=\text{NCH}$), 24.18 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{AlF}_6\text{N}_2\text{O}_3$: C, 59.72; H, 7.59; N, 4.22. Found: C, 60.0; H, 7.7; N, 4.2.

$\{\text{ArON}^{\text{Cy}}\text{NO}^{\text{CF}_3}\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$ (**7**). A solution of ligand **1** (50.0 mg, 0.093 mmol) in toluene (5 mL) was added onto solid $\text{Y}(\text{N}(\text{SiHMe}_2)_2)_3(\text{THF})_2$ (50.0 mg, 0.093 mmol). The reaction mixture was stirred at room temperature for 3 days, after which volatiles were removed under vacuum. The solid residue was washed with a minimal amount of cold hexane and dried under vacuum to give complex **7** as a white powder (45.0 mg, 58%). Single crystals suitable for X-ray diffraction studies were grown from a benzene solution at room temperature. ^1H NMR (C_6D_6 , 300 MHz, 20 °C): δ 8.14 (s, 1H, $\text{N}=\text{CH}$), 7.81 (m, 1H, H_{aro}), 7.37 (m, 1H, H_{aro}), 5.15 (m, 2H, $\text{SiH}(\text{CH}_3)_2$), 4.94 (m, 1H, $\text{CH}_2\text{CHN}=\text{C}(\text{Me})$), 4.37 (m, 4H, THF), 3.06 (d, 1H, $J = 12$ Hz, $\text{CHHC}(\text{CF}_3)_2$), 2.68 (d, 1H, $J = 12$ Hz, $\text{CHHC}(\text{CF}_3)_2$), 2.66 (m, 1H, $\text{CH}_2\text{CHN}=\text{CH}$), 1.83 (m, 4H, THF), 1.78 (s, 9H, $t\text{Bu}$), 1.49 (s, 9H, $t\text{Bu}$), 1.47 (s, 3H, $\text{C}(\text{CH}_3)=\text{N}$), 0.91–1.65 (m, 8H, CH_2 Cy), 0.45 (m, 6H, SiHMe_2), 0.42 (m, 6H, SiHMe_2). $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 188 MHz, 20 °C): δ -76.42 (q, $^4J_{\text{F-F}} = 11$ Hz, 3F), -78.82 (q, $^4J_{\text{F-F}} = 11$ Hz, 3F). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 20 °C): δ 180.17 ($\text{N}=\text{C}(\text{CH}_3)$), 170.71 ($\text{N}=\text{CH}$), 159.18, 144.69, 140.21, 135.62, 128.47, 118.94 (C_{aro}), 75.56 ($\text{CHC}=\text{NH}$), 71.38 ($\text{CHC}=\text{N}(\text{CH}_3)$), 69.77 ($\alpha\text{-CH}_2$, THF), 39.46 ($\text{CH}_2\text{C}=\text{N}(\text{CH}_3)$), 36.51 ($\text{C}(\text{CH}_3)_3$), 34.28 ($\text{C}(\text{CH}_3)_3$), 31.90, 31.82, 29.03, 27.57 (CH_2 Cy), 27.15 ($\text{C}(\text{CH}_3)_3$), 26.76 ($\text{C}(\text{CH}_3)_3$), 24.98 ($\text{C}(\text{CH}_3)_3$), 24.79 ($\beta\text{-CH}_2$, THF), 24.41 ($(\text{CH}_3)\text{C}=\text{NCH}$), 24.13 ($\text{C}(\text{CH}_3)_3$), 4.54 ($\text{SiH}(\text{CH}_3)(\text{CH}_3)$), 4.31 ($\text{SiH}(\text{CH}_3)(\text{CH}_3)$). Anal. Calcd for $\text{C}_{35}\text{H}_{58}\text{F}_6\text{N}_3\text{O}_3\text{Si}_2\text{Y}$: C, 50.77; H, 7.06; N, 5.08. Found: C, 50.9; H, 7.3; N, 4.8.

Crystal Structure Determinations. Suitable crystals for X-ray diffraction analysis of **5** and **7** were obtained by recrystallization of purified products. Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal

structures were solved by means of the Patterson method; remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).²⁴ Many hydrogen atoms could be found from the Fourier difference analysis. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystals of **5** and **7** were found to contain lattice disordered solvent molecules (benzene), which were modeled at best (the large maximum difference density of $1.588\text{ e}\cdot\text{Å}^{-3}$ in the case of complex **5** could be significantly decreased to $0.335\text{ e}\cdot\text{Å}^{-3}$ by removing the most disordered benzene molecules using the SQUEEZE procedure²⁵ implemented in the PLATON package;²⁶ however, the geometric features of the main molecule remained essentially the same). Crystal data and details of data collection and structure refinement for the different compounds are given in Table 1. Crystallographic data are also available as CIF files (see the Supporting Information).

Typical Procedure for *rac*-Lactide Polymerization. In an inert atmosphere glovebox, a Schlenk flask was charged with a solution of the metal complex (e.g., **7**, 5.9 mg, 7.1 μmol) in toluene (0.5 mL). To this solution, solid *rac*-lactide (0.102 g, 0.708 mmol, 100 equiv vs Y or Al) in toluene (1.0 mL) was rapidly added. The reaction mixture was stirred at the desired temperature for a given time period. Small aliquots of the reaction mixture were periodically sampled with a pipet for determining the conversion by ^1H NMR spectrometry. The reaction was quenched by adding ca. 1 mL of acidic methanol (1.2 M HCl solution in CH_3OH), and the polymer was precipitated with excess methanol (ca. 3 mL). Then, the supernatant solution was removed with a pipet and the polymer was dried under vacuum to constant weight.

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Supporting Information Available: Crystallographic data for **5** and **7** as CIF files. Homonuclear decoupled ^1H NMR spectrum of the methine region of isotactic-enriched PLA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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