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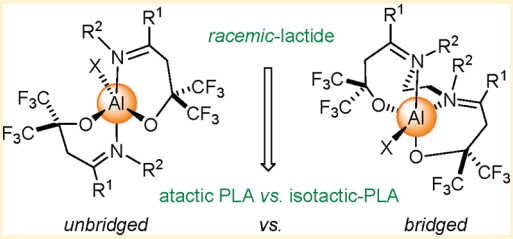
Aluminum Complexes of Bidentate Fluorinated Alkoxy-Imino Ligands: Syntheses, Structures, and Use in Ring-Opening Polymerization of Cyclic Esters

Miloud Bouyahyi, Thierry Roisnel, and Jean-François Carpentier*

Catalysis and Organometallics, UMR 6226 Sciences Chimiques de Rennes, CNRS-University of Rennes 1, 35042 Rennes Cedex, France

Supporting Information

ABSTRACT: The coordination chemistry of bidentate fluorinated alkoxy-imino ligands onto Al(III) centers has been studied. The proligands $(CF_3)_2C(OH)CH_2C(R^1)$=N−R^2 ({ON^{R1,R2}}H; R^1 = Me, Ph; R^2 = Ph, CH_2Ph, cyclohexyl; **1a−d**) react selectively with $AlMe_3$ (0.5 or 1.0 equiv) and $AlMe_2(OiPr)$ or $Al(OiPr)_3$ (0.5 equiv) to give the corresponding monoligand compounds {ON^{R1,R2}}$AlMe_2$ (**2a−d**) and the bis-ligand compounds {ON^{R1,R2}}$_2$AlMe (**3a−d**) and {ON^{R1,R2}}$_2$Al(O*i*Pr) (**4a−c**). X-ray diffraction studies revealed that {ON^{Ph,Bn}}$AlMe_2$ (**2a**), {ON^{Me,Bn}}$AlMe_2$ (**2b**), {ON^{Me,Bn}}$_2$AlMe (**3b**), {ON^{Ph,Ph}}$_2$AlMe (**3c**), {ON^{Me,Bn}}$_2$Al(O*i*Pr) (**4b**), and {ON^{Ph,Ph}}$_2$Al(O*i*Pr) (**4c**) all adopt a mononuclear structure in the solid state; four-coordinate {ON^{R1,R2}}$AlMe_2$ and five-coordinate {ON^{Me,Bn}}$_2$Al(O*i*Pr) feature respectively distorted-tetrahedral and trigonal-bipyramidal geometries. The ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR data indicate that the structures observed in the solid state are retained in CD_2Cl_2 or C_6D_6 solution at room temperature. The binary systems {ON^{R1,R2}}$AlMe_2$ (**2**)/BnOH and discrete {ON^{R1,R2}}$_2$Al(O*i*Pr) (**4**) are effective catalysts for the controlled ROP of *ε*-caprolactone and *rac*-lactide, both in bulk molten monomer and in toluene solution/slurry. In contrast to the case for {ON^{R}NO}Al(O*i*Pr), having a bridged tetradentate fluorinated dialkoxy-diimino ligand that provides isotactic-enriched polylactides, the unbridged compounds {ON^{R1,R2}}$_2$Al(O*i*Pr) (**4**) produce atactic PLAs. The key element which appears to be at the origin of the absence of stereocontrol is the lack of bridge between the two imino-alkoxy moieties, possibly via a decrease in the rigidity of the compounds and/or a different positioning of N,O vs N,N heteroatoms in axial sites.

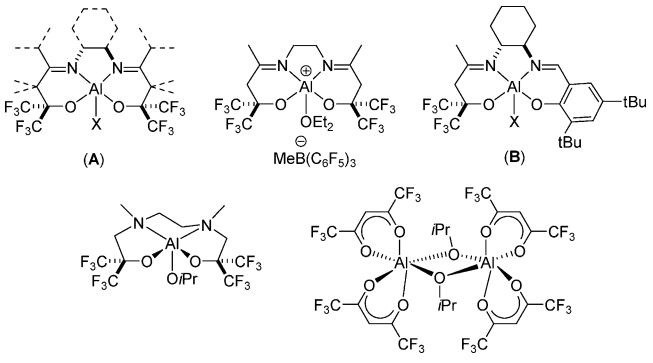


INTRODUCTION

Discrete aluminum complexes modified by ancillary ligands have attracted much interest in recent years as catalysts/initiators for the ring-opening polymerization (ROP) of cyclic esters[1] such as *ε*-caprolactone (*ε*-CL)[2] and lactide (LA),[3] a highly topical renewable resource. Numerous studies have evidenced that the nature of the ancillary ligand in the Al coordination sphere allows fine control of the molecular features of the polymerization. One notable such example is the formation of isotactic-rich polylactides from *rac*-lactide.[3a,d,e,4] The search for new ancillaries which allow tuning of the steric and electronic properties, and in turn the catalytic performances of these Al complexes, has therefore been permanent in the past decade.

Along these lines, our group has developed new families of ancillary ligands in which the phenolate groups—almost ubiquitous to the chemistry of oxophilic elements—have been replaced by alkoxides having strongly electron withdrawing α-CF_3 groups.[5] We have thus prepared a variety of neutral and cationic aluminum complexes derived from these "fluorinated" alkoxy ligands (Chart 1) and shown that they promote the efficient ROP of cyclic esters, eventually affording polymers with controlled architectures.[6] Interestingly, some neutral Al complexes supported by tetradentate fluorinated dialkoxy-diimino ligands (Chart 1, **A**) or mixed fluorinated alkoxy-diimino-phenolate (**B**) related to salen-type ligands,[7] based either on chiral or nonchiral backbones, PLAs with a

Chart 1. Examples of Aluminum Complexes (X = Me, Cl, O*i*Pr) Supported by Fluorinated Alkoxide Ligands Used in ROP of Cyclic Esters[6]



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highly isotactic-enriched stereoblock microstructure (P_{meso} up to 0.87)[8] were produced from *rac*-lactide.[6b,c]

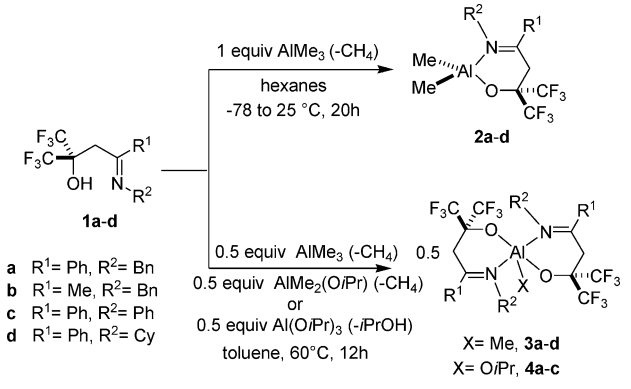
To explore the origin of the stereocontrol in those polymerizations, we have undertaken a comparative study of the analogous Al(III) compounds that incorporate *unlinked bidentate* fluorinated alkoxy-imino ligands of the type $\{OC(CF_3)_2{=}NR\}^-$ (hereafter abbreviated as $\{ON^{R1,R2}\}^-$). Those ligands can be viewed as the fluorinated analogues of the famous phenoxy-imine (FI) ligands that have met much success in the oligo-/polymerization of olefins.[9,10] The coordination chemistry of *bidentate* $\{ON^{R1,R2}\}^-$ ligands[11,12] has been studied for metal-organic chemical vapor deposition (MOCVD) applications in microelectronics with late transition metals (Ru,[13] Ir,[14] Pd,[13] Cu[15]); their chemistry with oxophilic elements (Ga,[16] Zn[17]) remains largely unexplored.

We report herein the preparation and structural characterization of new Al(III) complexes supported by bidentate fluorinated alkoxide-imino ligands ($\{ON^{R1,R2}\}^-$). The possibility of accessing heteroleptic complexes $\{ON^{R1,R2}\}AlX_2$ and $\{ON^{R1,R2}\}_2AlX$ having one or two nucleophilic ligands X (X = Me, O*i*Pr), which could be of potential interest for ROP catalysis, has been explored. Studies on the use of such complexes as initiators/catalysts for the ROP of ε-caprolactone and *rac*-lactide are reported and show that the unbridged bis(alkoxide-imino)-Al systems, although effective, are essentially nonstereoselective, in contrast to their bridged bis(alkoxide-imino)-Al analogues.

RESULTS AND DISCUSSION

Synthesis of Aluminum-{Fluorinated Alkoxy-Imino} Complexes. To explore the potential influence on structural and reactivity features, a set of fluorinated imino-alcohol proligands $\{ON^{R1,R2}\}H$ (**1a**–**d**) bearing various substituents at the imino function was used.[12] Synthetic routes similar to those employed for the preparation of aluminum complexes bearing salen-like fluorinated dialkoxy-diimino ligands[6b,c] were explored to prepare aluminum compounds supported by one or two $\{ON^{R1,R2}\}^-$ ligands. First, the dimethyl complexes $\{ON^{R,1R2}\}$-$AlMe_2$ (**2a**–**d**) were synthesized straightforwardly in high yields (>80%) by an alkane elimination reaction from $AlMe_3$ and the corresponding proligands at room temperature (Scheme 1).

Scheme 1. Synthesis of Aluminum-{Fluorinated Alkoxy-Imino} Complexes



Recrystallization of the white solids in hexanes gave crystals of **2a**,**b** that proved suitable for X-ray diffraction (vide infra).

Methyl and isopropoxide compounds bearing two $\{ON^{R1,R2}\}^-$ ligands were prepared by alkane elimination from $AlMe_3$ and $AlMe_2(OiPr)$, respectively. The reactions proceeded smoothly in toluene at 60 °C and afforded the corresponding complexes $\{ON^{R1,R2}\}_2AlMe$ (**3a**–**d**) and $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4a**–**c**) in >60% isolated yields. The latter isopropoxide complexes could also be prepared from $Al(OiPr)_3$ (Scheme 1).[18] All those compounds are soluble in dichloromethane and sparingly so in aliphatic hydrocarbons (pentane, hexanes). Crystals of **3b**,**c** and **4b**,**c** suitable for X-ray diffraction studies were grown from concentrated toluene/hexane or dichloromethane/pentane solutions at −30 °C.

Solid-State Structures of Aluminum-{Fluorinated Alkoxy-Imino} Complexes. The molecular structures of $\{ON^{Ph,Bn}\}AlMe_2$ (**2a**), $\{ON^{Me,Bn}\}AlMe_2$ (**2b**), $\{ON^{Me,Bn}\}_2AlMe$ (**3b**), $\{ON^{Ph,Ph}\}_2AlMe$ (**3c**), $\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**), and $\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4c**) are shown in Figures 1–3. Selected angles and distances characteristic of those compounds are gathered in Table 1, while crystallographic details are summarized in Table S1 (see the Supporting Information). All compounds adopt a mononuclear structure in the solid state.

Compounds $\{ON^{Ph,Bn}\}AlMe_2$ (**2a**) and $\{ON^{Me,Bn}\}AlMe_2$ (**2b**) both feature a four-coordinated metal center in a distorted-tetrahedral geometry with angles ranging from 94.8° (C(1)–Al(1)–C(2)) to 119.7° (O(1)–Al(1)–N(1)) for **2a** and from 97.2° (C(1)–Al(1)–C(2)) to 119.5° (O(1)–Al(1)–N(1)) for **2b** (Figure 1, Table 1). These complexes have strong structural similarities with aluminum-{phenoxy-imino} and other aluminum-Schiff base complexes reported in the literature.[2,10] For instance, the bond distances Al(1)–O(1) in **2a** (1.778(2) Å) and in **2b** (1.771(2) Å) compare well those in $[\{Salen^{(tBu)}\}AlEt_2]$ (1.772(1) Å), $[\{Salen^{(tBu)}\}Al(Me)Cl]$ (1.750(5) Å),[19] and $[Me_2AlOC(Ph)CH\{(3,5\text{-}Me_2C_3HN_2)\text{-}1\}]$ (1.747(3) Å).[20] This is also true for the Al(1)–N(1) distances in **2a** (1.999(2) Å) and in **2b** (1.988(2) Å), which are similar to that in $[\{OC(Me)CHC(Me)N(2,6\text{-}iPr_2C_6H_3)\}AlEt_2]$ (1.958 Å).[21] Minimal differences were observed in the geometrical features of **2a**,**b**, indicating no significant influence of the R^1 substituent.

On the other hand, the complexes $\{ON^{R1,R2}\}_2AlMe$ (**3b**,**c**) and $\{ON^{R1,R2}\}_2AlOiPr$ (**4b**,**c**) feature a pentacoordinated metal center. In each case, the geometry is best described as distorted trigonal bipyramidal (calculated values for the trigonal index τ: 0.95, 0.69, 0.91 and 0.85, respectively),[22] with the two nitrogen atoms occupying the axial positions (range for the N(1)–Al–N(2) angles 164.7–178.6°). This situation is significantly different from that for aluminum compounds bearing salen-like fluorinated diimino-dialkoxy ligands, namely $\{ON^{R}NO\}AlX$ (X = Me, O*i*Pr, Cl), where the trigonal-bipyramidal geometry is more distorted (τ: 0.85, 0.71, 0.48, and 0.42) and in which the axial positions are occupied by one nitrogen and one oxygen atoms of the ligand;[6b] the latter differences obviously result from the bridged nature of the dianionic ligand $\{ON^{R}NO\}^{2-}$, as compared to the coordination of two independent monoanionic $\{ON^{R1,R2}\}^-$ moieties. It is noteworthy also that the structure of the $\{ON^{Ph,Ph}\}_2AlX$ compounds **3c** and **4c** (τ: 0.69 and 0.85) is significantly more distorted than that of $\{ON^{Me,Bn}\}_2AlX$ compounds **3b** and **4b** (τ: 0.95 and 0.91), apparently as a direct consequence of the ligand substituents (Ph vs Me). The bond distances between the metal center and the nitrogen and oxygen atoms of the imino-alkoxide ligands in **3b**,**c** and **4b**,**c** span over ca. 0.8 Å (Al–O(1), Al–O(2) = 1.70–1.78 Å; Al–N(1), Al –N(2) = 2.06–2.14 Å). The latter Al–N bonds are significantly longer than those observed in

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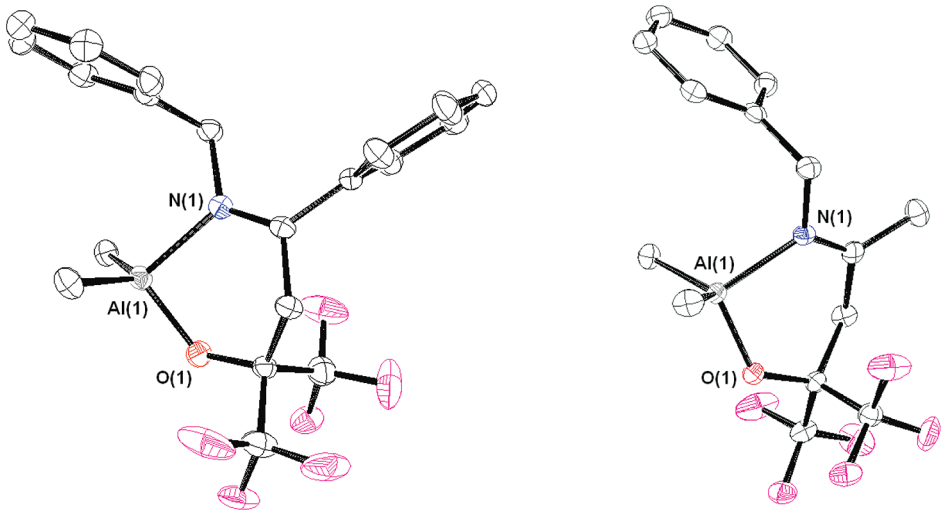

Figure 1. ORTEP structures of $\{ON^{Ph,Bn}\}AlMe_2$ (**2a**, left) and $\{ON^{Me,Bn}\}AlMe_2$ (**2b**, right) (ellipsoids drawn at the 50% probability level; all hydrogen atoms omitted for clarity).

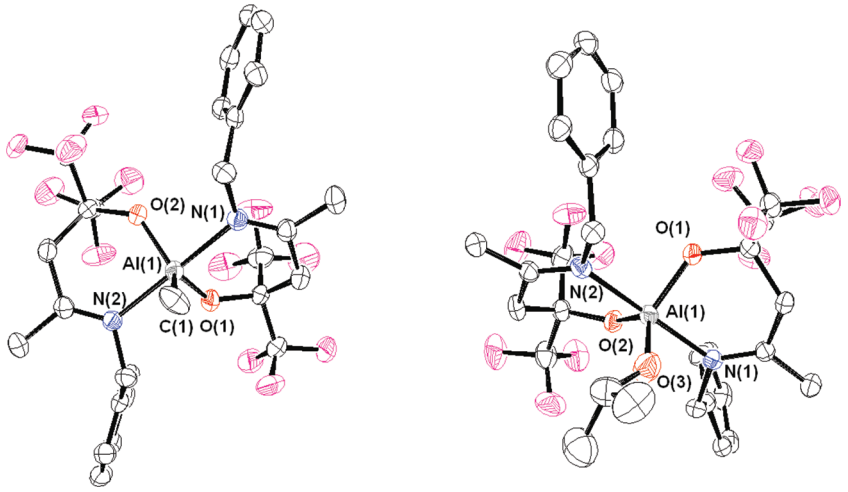

Figure 2. ORTEP structures of $\{ON^{Me,Bn}\}_2AlMe$ (**3b**, left) and $\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**, right) (ellipsoids drawn at the 50% probability level; all hydrogen atoms omitted for clarity).

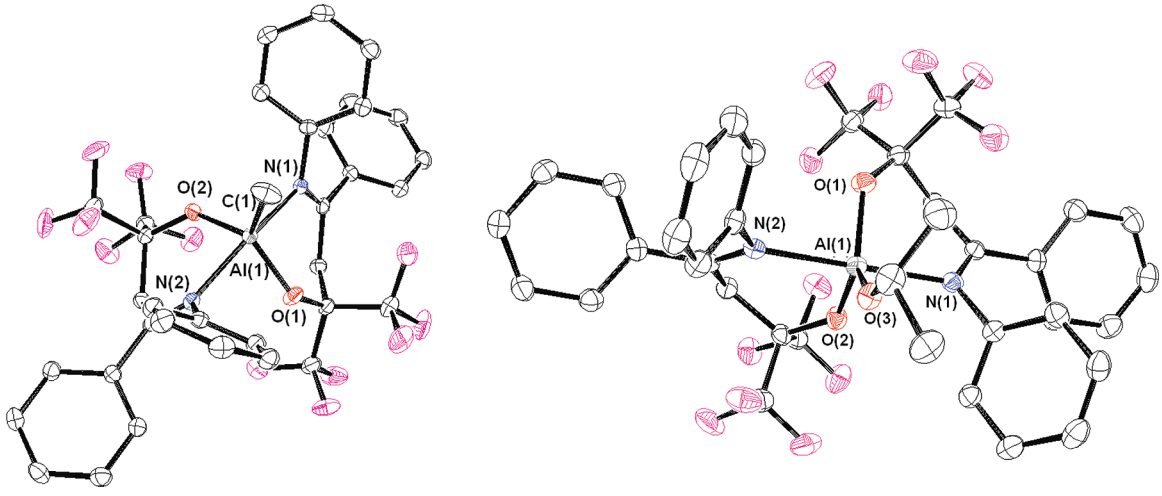

Figure 3. ORTEP structures of $\{ON^{Ph,Ph}\}_2AlMe$ (**3c**, left) and $\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4c**, right) (ellipsoids drawn at the 50% probability level; all hydrogen atoms omitted for clarity).

$\{ON^{R1,R2}\}AlMe_2$ complexes **2a**,**b** (vide supra); this probably reflects the greater steric crowding in the bis-ligand complexes. Bond distances between the Al center and the methyl or isopropoxide ligands compare well with those in $\{ON^{R1,R2}\}$-

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Table 1. Main Bond Distances (Å) and Angles (deg) in Complexes 2a,b, 3b,c, and 4b,c

	{ON^{Ph,Bn}}AlMe$_2$ (**2a**)		
Al−O(1)	1.778(2)	Al−C(1)	1.957(2)
Al−N(1)	2.000(2)	Al−C(2)	1.965(2)
O(1)−Al−C(1)	114.04(9)	O(1)−Al−N(1)	94.79(7)
O(1)−Al−C(2)	109.34(9)	C(1)−Al−N(1)	108.63(9)
C(1)−Al−C(2)	119.77(10)	C(2)−Al−N(1)	107.12(8)
	{ON^{Me,Bn}}AlMe$_2$ (**2b**)		
Al−O(1)	1.771(2)	Al−C(1)	1.958(2)
Al−N(1)	1.988(2)	Al−C(2)	1.963(2)
O(1)−Al−C(1)	112.15(8)	O(1)−Al−N(1)	97.19(7)
O(1)−Al−C(2)	108.82(8)	C(1)−Al−N(1)	108.36(8)
C(1)−Al−C(2)	119.54(9)	C(2)−Al−N(1)	108.39(8)
	{ON^{Me,Bn}}$_2$AlMe (**3b**)		
Al−O(1)	1.764(2)	Al−N(1)	2.070(2)
Al−O(2)	1.770(2)	Al−N(2)	2.080(2)
Al−C(1)	1.983(3)		
O(1)−Al−O(2)	115.39(11)	C(1)−Al−N(1)	90.97(11)
O(1)−Al−C(1)	122.11(14)	O(1)−Al−N(2)	87.52(9)
O(2)−Al−C(1)	122.50(13)	O(2)−Al−N(2)	91.71(9)
O(1)−Al−N(1)	91.61(9)	C(1)−Al−N(2)	90.36(11)
O(2)−Al−N(1)	87.72(9)	N(1)−Al−N(2)	178.65(10)
	{ON^{Ph,Ph}}$_2$AlMe (**3c**)		
Al−O(1)	1.772(1)	Al−N(1)	2.137(1)
Al−O(2)	1.772(1)	Al−N(2)	2.137(1)
Al−C(1)	1.944(2)		
O(1)−Al−O(1)	123.41(7)	C(1)−Al−N(1)	97.63(3)
O(1)−Al−C(1)	118.30(4)	O(1)−Al−N(2)	88.59(4)
O(1)−Al−C(1)	118.30(4)	O(1)−Al−N(2)	84.19(4)
O(1)−Al−N(1)	84.19(4)	C(1)−Al−N(2)	97.63(3)
O(1)−Al−N(1)	88.59(4)	N(1)−Al−N(2)	164.74(6)
	{ON^{Me,Bn}}$_2$Al(O*i*Pr) (**4b**)		
Al−O(3)	1.738(3)	Al−N(2)	2.064(3)
Al−O(1)	1.763(2)	Al−N(1)	2.084(3)
Al−O(2)	1.767(2)		
O(3)−Al−O(1)	123.84(14)	O(2)−Al−N(2)	91.94(11)
O(3)−Al−O(2)	119.45(14)	O(3)−Al−N(1)	93.14(13)
O(1)−Al−O(2)	116.65(12)	O(1)−Al−N(1)	91.00(11)
O(3)−Al−N(2)	88.03(13)	O(2)−Al−N(1)	88.15(11)
O(1)−Al−N(2)	87.71(11)	N(1)−Al−N(2)	178.61(12)
	{ON^{Ph,Ph}}$_2$Al(O*i*Pr) (**4c**)		
Al−O(3)	1.701(2)	Al−N(1)	2.107(2)
Al−O(2)	1.770(2)	Al−N(2)	2.111(2)
Al−O(1)	1.774(2)		
O(3)−Al−O(2)	122.26(7)	O(1)−Al−N(1)	90.77(6)
O(3)−Al−O(1)	121.32(7)	O(3)−Al−N(2)	94.78(7)
O(2)−Al−O(1)	116.41(7)	O(2)−Al−N(2)	90.08(6)
O(3)−Al−N(1)	91.86(7)	O(1)−Al−N(2)	84.28(6)
O(2)−Al−N(1)	87.86(6)	N(1)−Al−N(2)	173.14(7)

AlMe$_2$ and {ON^{R}NO}AlX (X = Me, O*i*Pr; R = ethylene, 1,2-cyclohexylene)[6b] derivatives.

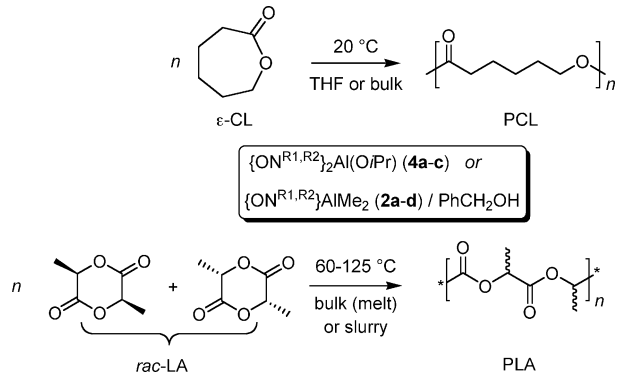
Solution Structures of Aluminum-{Fluorinated Alkoxy-Imino} Complexes. The ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR data obtained in CD_2Cl_2 or C_6D_6 at room temperature all indicate that the structures observed in the solid state are retained in solution. The NMR spectra for all prepared compounds contain a single set of resonances, indicative of the existence of a single highly symmetric species on the NMR time scale.

Complexes of the type Al{ON^{R1,R2}}Me$_2$ feature only one singlet in the ^{19}F{^{1}H} NMR spectra for two magnetically equivalent CF_3 groups. The two Al*Me*$_2$ methyl groups as well as the backbone methylene C*H*$_2$C═N each appear as one singlet in the ^{1}H NMR spectra. When a benzyl substituent is present (i.e., in **2a**,**b**), the C*H*$_2$Ph hydrogens are also equivalent and appear as a sharp singlet.

The ^{1}H, ^{19}F{^{1}H}, and ^{13}C{^{1}H} NMR spectra for the Al{ON^{R1,R2}}$_2$X complexes are all similar and indicative of two magnetically equivalent {ON^{R1,R2}}$^-$ ligands. For instance, in {ON^{Me,Bn}}$_2$AlX compounds **3b** and **4b**, a single sharp singlet resonance is observed for the NC*Me* groups. In C_6D_6, the hydrogens of the backbone C*HH*C═N group and, when present (i.e., in **3a**,**b** and **4a**,**b**), the C*HH*Ph hydrogens of the benzyl substituents are diastereotopic and each appear as an AB system. In CD_2Cl_2, the hydrogens of the backbone C*HH*C═N group also sometimes come out as a singlet (see the Experimental Section). The CF_3 groups within each OC(CF$_3$)$_2$ moiety are inequivalent and appear in the ^{19}F{^{1}H} NMR spectra as two sharp quartets (see the Supporting Information). No significant change (except slight variations in the chemical shifts) was noted in the high-temperature (100 °C) ^{1}H and ^{19}F{^{1}H} NMR spectra of **4c** in toluene-d_8; note that the complex proved stable for several days at this temperature.

Polymerization of ε-Caprolactone and *rac*-Lactide. The catalytic abilities of the prepared compounds were evaluated in the ROP of ε-caprolactone and *rac*-lactide (Scheme 2). For bis-ligand derivatives, {ON^{R1,R2}}$_2$Al(O*i*Pr) compounds (**4a**−**c**) which contain a nucleophilic isopropoxide group were used directly as single-site initiators. On the other hand, for monoligand derivatives, in situ combinations of {ON^{R1,R2}}AlMe$_2$ compounds (**2a**−**d**) with 1 equiv of benzyl alcohol were used.[10b,e,23] In fact, in the absence of benzyl alcohol, the {ON^{R1,R2}}AlMe$_2$ compounds do not initiate the ROP of ε-caprolactone at room temperature or that of lactide at 60 °C.[10b,e]

Scheme 2



All the aforementioned systems were found to readily polymerize ε-caprolactone at room temperature. Representative results are reported in Table 2. The reactions proceeded either in 2.0 M toluene solutions or in the bulk monomer. The latter solvent-free conditions afforded activities ca. 1 order of magnitude higher (TOF = 325−355 h^{-1}) than those under the former solution conditions (TOF = 12−19 h^{-1}). A similar effect, in line with the increase in concentration, was observed with salicylaldiiminato-aluminum alkoxide complexes, which featured activities somewhat higher than those of the present

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Table 2. ROP of ε-Caprolactone Mediated by $\{ON^{R1,R2}\}_2Al(OiPr)$ Complexes and Binary Systems $\{ON^{R1,R2}\}AlMe_2/BnOH$[a]

entry	compound	$[CL]_0:[Al]_0:[BnOH]_0$	[CL] (mol L^{-1})	time[b] (h)	conversion[c] (%)	M_n(calcd)[d] (kg mol^{-1})	M_n(exptl)[e] (kg mol^{-1})	M_w/M_n[e]	TOF (h^{-1})[f]
1	$\{ON^{Ph,Bn}\}AlMe_2$ (**2a**)	100:1:1	2.0	6	95	10.83	12.60	1.8_4	16
2	$\{ON^{Ph,Bn}\}AlMe_2$ (**2a**)	100:1:5	2.0	6	87	1.98	1.92	1.3_4	14
3	$\{ON^{Ph,Bn}\}AlMe_2$ (**2a**)	250:1:1	9.0[g]	0.5	65	18.52	14.48	1.9_5	325
4	$\{ON^{Me,Bn}\}AlMe_2$ (**2b**)	100:1:1	2.0	3	57	6.49	6.20	1.3_2	19
5	$\{ON^{Me,Bn}\}AlMe_2$ (**2b**)	100:1:1	2.0	6	98	11.17	12.40	1.5_1	16
6	$\{ON^{Ph,Ph}\}AlMe_2$ (**2c**)	100:1:1	2.0	6	89	10.14	7.25	1.3_3	15
7	$\{ON^{Ph,Cy}\}AlMe_2$ (**2d**)	100:1:1	2.0	6	93	10.60	8.95	1.7_0	15
8	$\{ON^{Ph,Cy}\}AlMe_2$ (**2d**)	250:1:1	9.0[g]	0.5	71	20.23	17.20	1.7_9	355
9	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	100:1:0	2.0	6	91	10.37	10.60	1.6_6	15
10	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	200:1:0	2.0	12	75	17.10	12.50	1.7_7	12
11	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	400:1:0	2.0	16	49	22.34	15.65	1.8_3	12
12	$\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**)	100:1:0	2.0	2	31	3.53	2.30	1.3_2	15
13	$\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**)	100:1:0	2.0	6	90	10.26	9.54	1.6_2	15
14	$\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4b**)	100:1:0	2.0	6	93	10.60	9.40	1.7_6	15
15	$\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4b**)	200:1:0	2.0	6	55	12.54	8.30	1.6_3	18

[a]Reactions performed in THF at 20 °C and at least duplicated. [b]Reaction times were not necessarily optimized. [c]Conversion of CL as determined by ^1H NMR. [d]Number-average molecular weight calculated from $[CL]_0/[BnOH \text{ or } OiPr]_0 \times$ conversn × 114.4. [e]Experimental number-average molecular weight (corrected with a factor of 0.56[28]) and molecular weight distribution determined by GPC in THF vs polystyrene standards. [f]Turnover frequency determined from the conversion and reaction time. [g]Reaction performed in bulk CL, without solvent.

Table 3. ROP of *rac*-Lactide Mediated by $\{ON^{R1,R2}\}_2Al(OiPr)$ Complexes and Binary Systems $\{ON^{R1,R2}\}AlMe_2/BnOH$[a]

entry	compound	$[LA]_0:[Al]_0:[BnOH]_0$	[LA] (mol L^{-1})	temp (°C)	time[b] (h)	conversion[c] (%)	M_n(calcd)[d] (kg mol^{-1})	M_n(exptl)[d] (kg mol^{-1})	M_w/M_n[e]	TOF (h^{-1})[f]
1	$\{ON^{Me,Bn}\}AlMe_2$ (**2b**)	100:1:1	2.0 in tol	100	3	61	8.78	6.12	1.5_9	20
2	$\{ON^{Ph,Ph}\}AlMe_2$ (**2c**)	100:1:1	2.0 in tol	100	3	96	13.82	11.72	1.6_1	32
3	$\{ON^{Ph,Cy}\}AlMe_2$ (**2d**)	100:1:1	2.0 in tol	100	3	73	10.51	7.26	1.6_9	24
4	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	100:1:0	2.0 in tol	70	120	88	12.60	15.80	1.1_5	≤1
5	$\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**)	100:1:0	2.0 in tol	70	48	79	11.30	11.08	1.2_0	1
6	$\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**)	100:1:0	2.0 in tol	60	48	83	11.95	9.57	1.2_2	1
7	$\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4c**)	100:1:0	2.0 in tol	70	48	75	10.80	8.61	1.1_1	1
8	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	100:1:0	bulk, melt	125	0.5	80	11.50	9.30	1.5_0	160
9	$\{ON^{Ph,Bn}\}_2Al(OiPr)$ (**4a**)	400:1:0	bulk, melt	125	0.5	55	31.68	22.74	1.5_5	440
10	$\{ON^{Me,Bn}\}_2Al(OiPr)$ (**4b**)	100:1:0	bulk, melt	125	0.5	100	14.40	11.18	1.5_6	200
11	$\{ON^{Ph,Ph}\}_2Al(OiPr)$ (**4c**)	100:1:0	bulk, melt	125	0.5	100	14.40	12.04	1.5_7	200
12	$Al(OiPr)_3$	200:1:0	2.0 in tol	70	48	60	5.8	4.3	2.4	1[g]

[a]Reactions were at least duplicated. [b]Reaction times were not necessarily optimized. [c]Conversion of *rac*-LA as determined by ^1H NMR from the methyl LA and PLA resonances. [d]Number-average molecular weight calculated from $[LA]_0/[BnOH \text{ or } OiPr]_0 \times$ conversn × 144.0. [e]Experimental number-average molecular weight (corrected with a factor of 0.58[28]) and molecular weight distribution determined by GPC in THF vs polystyrene standards. [f]Turnover frequency determined from the conversion and reaction time. [g]Calculated on the basis of three active isopropoxide groups.

fluorinated alkoxy-imino compounds (TOF = 300 h^{-1} at [CL] = 0.90 M and TOF > 1000 h^{-1} at [CL] = 4.7 M).[2g] No major influence of the ligand imino substituents on activity was observed. The reactions proceeded in a controlled fashion, leading to polymers with monomodal, relatively narrow molecular weight distributions (M_w/M_n = 1.3−1.9) and experimental number average molecular weights generally in good agreement with the values calculated from the conversion and initial monomer-to-initiator ratio. In particular, a good control over the molecular features was obtained with the binary systems $\{ON^{R1,R2}\}AlMe_2$ (**2a**−**d**)/BnOH, with which effective living-immortal ROP could be demonstrated with 1−5 equiv of BnOH as initiator/chain transfer agent (entries 1−8). Analysis by MALDI-ToF-MS of a PCL sample generated from the **2a**/BnOH (1:1) system showed a major population of signals unambiguously assignable to linear [H-(PCL)-OBn]·Na^+ cations (see the Supporting Information); in addition, a minor set of signals assigned to linear [H-(PCL)-OH]·Na^+ cations, most likely produced by hydrolysis of the former population under ionization conditions,[25c] was observed. No cyclic isomers could be detected, suggesting that transesterification/backbiting processes occurred to a minor extent. Overall, the activity and degree of control of the $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4a**−**c**) compounds in the ROP of ε-caprolactone compare well with those observed under similar conditions with the tetradentate bridged fluorinated diimino-dialkoxy ligands, namely $\{ON^{R}NO\}Al(OiPr)$.[6b]

The ROP of *rac*-lactide was investigated under conditions similar to those used for the $\{ON^{R}NO\}Al(OiPr)$:[6b] that is, in toluene slurry at 60−100 °C or in bulk molten lactide at 125 °C. Representative results are reported in Table 3. The binary systems $\{ON^{R1,R2}\}AlMe_2$ (**2a**−**d**)/BnOH showed modest activity[23] with nonoptimized turnover frequencies in the range 20−32 h^{-1} at full conversion (entries 1−3). These TOF values are similar to those achieved with binary systems based on Al-{phenoxy-imine} complexes of the type [O-2-*t*Bu-6-(RN=CH)C_6H_3]$AlMe_2$ associated to BnOH (TOF < 100 h^{-1}).[10b]

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Discrete complexes $\{ON^{R1,R2}\}_2Al(OiPr)$ **4a−c** were less active in toluene slurry at 60−70 °C (TOF = ca. 1 h^{-1}) but offered PLAs with narrow molecular weight distributions (M_w/M_n = 1.1−1.2) and molecular weights in good agreement with calculated M_n values (entries 4−7). They are just as active but definitively much better controlled than simple $Al(OiPr)_3$, which leads under similar conditions to PLAs with much broader polydispersities (Table 3, entry 12). When **4a−c** were used in bulk molten monomer at 125 °C, their activities were significantly increased (TOF = 160−440 h^{-1}). These activities are of the same order of magnitude as those observed with the $\{ON^RNO\}Al(OiPr)$ compound bearing an ethylene-bridged fluorinated diimino-dialkoxy ligand (R = C_2H_4; TOF = ca. 6 h^{-1} in slurry at 70 °C and 180−1000 h^{-1} at 120 °C in the melt).[6b] Although the PLAs produced with $\{ON^{R1,R2}\}_2Al(OiPr)$ in the melt at 120 °C had broader polydispersities (M_w/M_n = 1.50−1.57) than those obtained in slurry at 60−70 °C—as expected from the higher concentration and temperature—a good match between experimental and calculated M_n values was still observed. This is a remarkable feature, since the PLAs produced in the melt from $\{ON^RNO\}Al(OiPr)$ had most generally a molecular weight lower than that expected.[6b] All those PLAs derived from **4a−c** were end-capped by isopropoxycarbonyl (from the initiator) and hydroxyl (from eventual hydrolytic cleavage during workup) groups, as revealed by ^1H NMR analysis.

Homodecoupled ^1H NMR analyses revealed also that the PLAs produced from *rac*-lactide with $\{ON^{R1,R2}\}AlMe_2$/BnOH systems and $\{ON^{R1,R2}\}_2Al(OiPr)$ discrete complexes were all essentially atactic. This is in striking contrast with the significantly isotactic-enriched microstructure of PLAs produced under similar conditions with achiral or chiral $\{ON^RNO\}Al(OiPr)$ compounds (R = C_2H_4, *rac,trans*-1,2-cyclohexylene; P_m = 0.78−0.81)[6b] and the related compound based on a tetradentate mixed fluorinated alkoxy-diimino-phenolate unsymmetrical Schiff base ligand, namely $\{^{Ar}ON^RNO^{CF3}\}Al(OiPr)$ (R = *rac,trans*-1,2-cyclohexylene; P_m = 0.87).[6c]

One aim of this work was to discuss possible structure−stereoselectivity relationships by comparing the new unbridged compounds $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4a−c**) disclosed herein with their aforementioned bridged analogues $\{ON^RNO\}Al(OiPr)$[6b] and $\{^{Ar}ON^RNO^{CF3}\}Al(OiPr)$.[6c] Apparently, the *initial* gross geometry at the metal center in the initiator is not a determining factor: indeed, both $\{ON^{Cy}NO\}Al(OiPr)$ (quite stereoselective) and $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4b,c**; both non-stereoselective) feature trigonal-bipyramidal geometries with similar extents of distortion (τ = 0.85 vs. 0.91 and 0.85, respectively). One further argument for a minimally discriminating role of this factor is the high stereoselectivity provided by the mixed fluorinated alkoxy-diimino-phenolate compound $\{^{Ar}ON^{Cy}NO^{CF3}\}Al(OiPr)$, which features an Al center in an almost perfectly square pyramidal environment (τ = 0.12).[24] On the other hand, a striking difference between $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4a−c**) and $\{ON^RNO\}Al(OiPr)$ compounds, despite their quite similar overall trigonal-bipyramidal geometry, is the positioning of heteroatoms: in the former compounds the axial sites are occupied by two nitrogen atoms, while in the latter these are occupied by one oxygen and one nitrogen atom (likely due to the unbridged/bridged nature of the $\{ON^{R1,R2}\}^-$ vs $\{ON^RNO\}^{2-}$ ligands; vide infra). Of course, it is noteworthy that these are *initial* geometries observed in the starting complexes and one does not know how these evolve in the course of the polymerization reaction when the isopropoxide initiating group progressively builds up in the propagating polylactide chain, with probable coordination on the metal center of additional moieties (i.e., ester group of the growing polymer chain and/or lactide monomer).[25] In this regard, it seems obvious that the ethylene and cyclohexylene bridges in $\{ON^RNO\}Al(OiPr)$ and $\{^{Ar}ON^RNO^{CF3}\}Al(OiPr)$, which have been removed in the scaffold of unbridged compounds $\{ON^{R1,R2}\}_2Al(OiPr)$ (**4a−c**), should make the former systems more conformationally rigid than the latter ones. This should contribute to limit the extent of distortion and global geometry changes over the reaction pathway in the intermediates and transition states; however, this can be difficult to quantify.

CONCLUSIONS

Binary systems $\{ON^{R1,R2}\}AlMe_2$/BnOH and discrete complexes $\{ON^{R1,R2}\}_2Al(OiPr)$ are effective catalysts for the controlled ROP of ε-caprolactone and *rac*-lactide both in bulk molten monomer and in toluene solution/slurry. No significant influence of the ligand imino substituents was observed. The polymers obtained feature experimental molecular weights in quite good agreement with calculated values. The catalytic activities of these systems are comparable to those achieved with non-fluorinated {phenoxy-imine}-$AlMe_2$/BnOH combinations or discrete compounds $\{ON^RNO\}Al(OiPr)$ having a tetradentate fluorinated dialkoxy-diimino ligand. In contrast to the latter systems that provide isotactic-enriched polylactides, the polymers produced from the unbridged compounds $\{ON^{R1,R2}\}_2Al(OiPr)$ were all atactic. These observations shed further light on the major influence played by the molecular architecture of the organometallic catalyst/initiator in stereoselective ring-opening polymerizations of *rac*-lactide proceeding under chain-end control.[3,26,27] The present results indicate that the gross geometry (i.e., trigonal bipyramidal or square pyramidal) at the metal center does not play a determining role. Rather, the key element which appears to be at the origin of the absence of stereocontrol is the lack of a bridge between the two imino-alkoxy moieties. At this stage, it cannot be concluded yet whether this proceeds via a decrease in the rigidity of the compounds and/or a different positioning of N,O vs N,N heteroatoms in axial sites.

EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under purified argon using standard Schlenk techniques or in a glovebox (<1 ppm O_2, 5 ppm of H_2O). Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were distilled from Na/K alloy under argon and degassed by freeze−thaw−vacuum cycles prior to use. Chlorinated solvents were distilled from calcium hydride. Deuterated solvents (>99.5% D, Eurisotop) were freshly distilled from the appropriate drying agent under argon and degassed prior to use. Fluorinated imino-alcohol proligands $\{ON^{R1,R2}\}H$ (**1a−d**) were prepared following a previously reported procedure.[12] $AlMe_3$ (2.0 M solution in heptane, Aldrich), $AlMe_2(OiPr)$ (98%, Strem Chemicals), and $Al(OiPr)_3$ (98%, Aldrich) were purchased and used as received. *rac*-Lactide (Aldrich) was recrystallized twice from dry toluene and then sublimed under vacuum at 50 °C before use. ε-Caprolactone (Acros) was dried over calcium hydride and then distilled under reduced pressure (2 mmHg, 85 °C) before use. Polymerizations of ε-caprolactone and *rac*-lactide were performed as previously reported.[6b]

NMR spectra of aluminum compounds were recorded in Teflon-valved NMR tubes on Bruker AM 300 MHz and AM 500 MHz spectrometers at 298 K, unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported in ppm vs $SiMe_4$ and were determined by

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reference to the residual solvent resonances. Assignment of signals was made from 2D ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC and HMBC NMR experiments. ^{19}F chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. NMR coupling constants are reported in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

Size exclusion chromatography (SEC) analyses of PLAs and PCLs were performed in THF (1.0 mL min^{-1}) at 20 °C using a Polymer Laboratories PL-GPC 50 plus apparatus equipped with a PLgel 5 μm MIXED-C 300 × 7.5 mm column and RI and dual angle LS (PL-LS 45/90) detectors. The number-average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the polymers were calculated with reference to a universal calibration vs polystyrene standards. The M_n values of PCLs and PLAs were corrected with factors of 0.56 and 0.58, respectively, to account for the difference in hydrodynamic volumes with polystyrene.[28]

MALDI-ToF mass spectra of PCL were obtained with a Bruker Daltonic MicroFlex LT, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: 1 μL of a 2:1 mixture of a saturated solution of α-cyano-4-hydroxycinnamic acid (Bruker Care) in HPLC-quality acetonitrile and a 0.1% solution of trifluoroacetic acid in ultrapure water was deposited on the sample plate. After total evaporation, 1 μL of a 5−10 mg mL^{-1} solution of the polymer in HPLC-quality THF was deposited. Bruker Care Peptide Calibration Standard and Protein Calibration Standard I were used for external calibration.

The microstructures of PLAs were determined by homodecoupling ^{1}H NMR spectroscopy at 20 °C in $CDCl_3$ on a Bruker AC-500 spectrometer.

{ON^{Ph,Bn}}AlMe$_2$ (2a). In a Schlenk flask, a solution of proligand {ON^{Ph,Bn}}H (**1a**; 200 mg, 0.53 mmol) in hexanes (2 mL) was added dropwise onto a solution of $AlMe_3$ (0.27 mL of a 2.0 M solution in heptane, 0.54 mmol) in hexanes (3 mL), precooled at −80 °C. The solution was slowly warmed to room temperature and stirred overnight. Volatiles were removed under vacuum, and the residue was washed with cold hexanes (3 mL) and dried under vacuum. Compound **2a** was isolated as a yellowish solid (0.184 g, 80%). Single crystals of **2a** suitable for X-ray diffraction analysis were obtained from a concentrated hexanes solution at −30 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ −0.92 (s, 6H, Al(CH_3)$_2$), 3.41 (s, 2H, CH_2C═N), 4.85 (s, 2H, ArCH_2), 7.09−7.15 (m, 3H$_{Ar}$), 7.34−7.37 (m, 5H$_{Ar}$), 7.56−7.59 (m, 2H$_{Ar}$). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −79.05 (s, 6F). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ −10.53 (Al(CH_3)$_2$), 38.37 (CH_2C(CF_3)$_2$), 56.42 (ArCH_2), 126.78 (q, $^1J_{CF}$ = 281.1, CF_3), 128.22, 128.42, 128.68, 129.42, 131.11, 134.41, 135.72 (all C$_{aro}$), 181.47 (C═N). Anal. Calcd for $C_{20}H_{20}AlF_6NO$: C, 55.69; H, 4.67; N, 3.25. Found: C, 55.6; H, 4.7; N, 3.1.

{ON^{Me,Bn}}AlMe$_2$ (2b). This compound was prepared as described for **2a**, starting from proligand {ON^{Me,Bn}}H (**1b**; 300 mg, 0.95 mmol) and $AlMe_3$ (0.48 mL of a 2.0 M solution in heptane, 0.96 mmol). Crystals of **2b** suitable for X-ray diffraction were prepared by prolonged crystallization from a hexane solution (3 mL) at −30 °C to yield colorless crystals of **2b** (110 mg, 31%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ −0.90 (s, 6H, Al(CH_3)$_2$), 2.30 (s, 3H, N═CCH_3), 3.06 (s, 2H, CH_2C═N), 4.83 (s, 2H, ArCH_2), 7.16−7.49 (m, 5H$_{Ar}$). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.49 (s, 6H, Al(CH_3)$_2$), 1.11 (s, 3H, N═CCH_3), 2.42 (s, 2H, CH_2C═N), 4.04 (s, 2H, ArCH_2), 6.78−7.03 (m, 5H$_{Ar}$). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −79.31 (s, 6F). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ −11.20 (Al(CH_3)$_2$), 37.96 (CH_2C(CF_3)$_2$), 53.96 (ArCH_2), 121.86, 123.70 (q, $^1J_{CF}$ = 295.0, CF_3), 125.45, 127.39, 128.09, 128.97, 134.50 (all C$_{aro}$), 183.78 (C═N). Anal. Calcd for $C_{15}H_{18}AlF_6NO$: C, 48.79; H, 4.91; N, 3.79. Found: C, 48.9; H, 4.9; N, 3.9.

{ON^{Ph,Ph}}AlMe$_2$ (2c). This compound was prepared as described above for **2a**, starting from a solution of proligand {ON^{Ph,Ph}}H (**1c**; 200 mg, 0.55 mmol) in hexanes (4 mL) and a solution of $AlMe_3$ (0.27 mL of a 2.0 M solution in heptane, 0.55 mmol) in hexanes (1 mL). Workup afforded **2c** as a white powder (187 mg, 81%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.42 (s, 6H, Al(CH_3)$_2$), 3.12 (s, 2H, CH_2C═N), 6.62−6.37 (m, 10H$_{aro}$). ^{19}F{^{1}H} NMR (188 MHz, C_6D_6, 298 K): δ −78.19 (s, 6F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 1.18 (Al(CH_3)$_2$), 37.93 (CH_2C(CF_3)$_2$), 123.24, 127.13, 127.61, 127.66, 127.88, 127.93, 127.98, 128.25, 128.41, 129.23, 130.67, 135.69 (all C$_{aro}$), 175.26 (C═N); quartet resonances for CF_3 groups were not observed due to their low intensity. Anal. Calcd for $C_{19}H_{18}AlF_6NO$: C, 54.68; H, 4.35; N, 3.36. Found: C, 54.8; H, 4.4; N, 3.4.

{ON^{Ph,Cy}}AlMe$_2$ (2d). This compound was prepared as described above for **2a**, starting from a solution of proligand {ON^{Ph,Cy}}H (**1d**; 100 mg, 0.27 mmol) in hexanes (4 mL) and a solution of $AlMe_3$ (0.14 mL of a 2.0 M solution in heptane, 0.28 mmol) in hexane (1 mL). Workup gave **2d** as a white powder (102 mg, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ −0.67 (s, 6H, Al(CH_3)$_2$), 0.97−1.15 (m, 3H, cyclohexyl), 1.55−1.91 (m, 7H, cyclohexyl), 3.25 (s, 2H, CH_2C═N), 3.55−3.61 (m, 1H, cyclohexyl), 7.20 (m, 2H$_{aro}$), 7.53 (m, 2H$_{aro}$). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −78.96 (s, 6F). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K): δ −7.50 (Al(CH_3)$_2$), 25.40, 32.54 (cyclohexyl), 38.88 (CH_2C(CF_3)$_2$), 65.22 (CH cyclohexyl), 77.96 (C(CF_3)$_2$), 123.33, 125.36, 125.82 (q, $^1J_{CF}$ = 293.3, CF_3), 130.25, 131.19, 137.81 (all C$_{aro}$), 179.88 (C═N). Anal. Calcd for $C_{19}H_{24}AlF_6NO$: C, 53.90; H, 5.71; N, 3.31. Found: C, 53.9; H, 5.8; N, 3.2.

{ON^{Ph,Bn}}$_2$AlMe (3a). In a Schlenk flask, a solution of proligand {ON^{Ph,Bn}}H (**1a**; 200 mg, 0.53 mmol) in toluene (5 mL) was added dropwise onto a solution of $AlMe_3$ (0.13 mL of a 2.0 M solution in heptane, 0.26 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. Volatiles were removed under vacuum, and the solid residue was washed with cold hexanes (3 × 3 mL) and finally dried under vacuum for 12 h, to give **3a** as a white powder (92 mg, 45%). Single crystals of **3a** suitable for X-ray diffraction analysis were obtained from a concentrated hexanes/THF solution (2/1 mL) at −30 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ −0.98 (s, 3H, AlCH_3), 3.20 (s, 4H, CH_2C═N), 4.78 and 4.98 (2d, J = 14.4, 4H, ArCHH), 7.00−7.38 (m, 10H$_{Ar}$). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.40 (s, 3H, AlCH_3), 3.16 and 3.28 (2d, J = 17.3, 2 × 2H, CHHC═N), 4.98 and 5.18 (2d, J = 13.8, 2 × 2H, ArCHH), 6.77−7.28 (m, 10H$_{Ar}$). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −78.24 (q, J = 10.3, 6F), −79.02 (q, J = 10.3, 6F). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 13.86 (AlCH_3), 37.77 (CH_2C(CF_3)$_2$), 54.91 (ArCH_2), 124.26 (q, $^1J_{CF}$ = 284.5, CF_3), 124.97, 125.23, 125.92, 126.51, 127.04, 127.74, 128.19, 128.81, 128.96, 129.34, 138.01 (all C$_{aro}$), 176.90 (C═N). Anal. Calcd for $C_{37}H_{31}AlF_{12}N_2O_2$: C, 56.21; H, 3.95; N, 3.54. Found: C, 56.1; H, 4.0; N, 3.5.

{ON^{Me,Bn}}$_2$AlMe (3b). This compound was prepared as described for **3a**, starting from proligand {ON^{Me,Bn}}H (**1b**; 200 mg, 0.63 mmol) and $AlMe_3$ (0.16 mL of a 2.0 M solution in heptane, 0.32 mmol) in toluene (15 mL). Crystallization from a hexanes/toluene solution (5 mL; 3/2 v/v) at −30 °C yielded colorless crystals of **3b** (90 mg, 44%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ −0.89 (s, 3H, AlCH_3), 1.94 (s, 6H, N═CCH_3), 2.86 (s, 4H, CH_2C═N), 4.72 and 4.99 (2d, J = 15.0, 2 × 2H, ArCHH), 7.16−7.28 (m, 10H$_{aro}$). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.52 (s, 3H, AlCH_3), 1.22 (s, 6H, N═CCH_3), 2.57 (s, 4H, CH_2C═N), 4.72 and 5.00 (2d, J = 15.0, 2 × 2H, ArCHH), 7.14−7.27 (m, 10H$_{aro}$). ^{19}F{^{1}H} NMR (188 MHz, C_6D_6, 298 K): δ −77.82 (q, J = 10.3, 6F), −78.85 (q, J = 10.3, 6F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 14.28 (AlCH_3), 23.45 (N═CCH_3), 36.81 (CH_2C(CF_3)$_2$), 54.17 (ArCH_2), 78.18 (C(O)(CF_3)$_2$), 122.76, 127.07, 127.51, 128.22 (q, $^1J_{CF}$ = 289.8, CF_3), 128.61, 137.85 (all C$_{aro}$), 177.18 (C═N). Anal. Calcd for $C_{27}H_{27}AlF_{12}N_2O_2$: C, 48.66; H, 4.08; N, 4.20. Found: C, 48.6; H, 4.2; N, 4.1.

{ON^{Ph,Ph}}AlMe (3c). This compound was prepared as described above for **3a**, starting from a solution of proligand {ON^{Ph,Ph}}H (**1c**; 200 mg, 0.55 mmol) in toluene (5 mL) and $AlMe_3$ (0.14 mL of a 2.0 M solution in heptane, 0.27 mmol) in toluene (15 mL). Reaction for 24 h at 60 °C and workup afforded **3c** as colorless crystals (78 mg, 38%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.89 (s, 3H, AlCH_3), 3.26 and 3.42 (2d, J = 15.0, 2 × 2H, CHHC(O)(CF_3)$_2$), 6.66−6.98 (m, 20 H$_{aro}$). ^{19}F{^{1}H} NMR (188 MHz, C_6D_6, 298 K): δ −76.46 (q, J = 10.3, 6F), −79.48 (q, J = 10.3, 6F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 14.23 (AlCH_3), 37.32 (CH_2C(O)(CF_3)$_2$), 124.13, 125.98,

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126.17 (q, $^1J_{CF}$ = 156.1, CF_3), 127.52, 127.80, 128.51, 129.48, 147.46 (all C_{aro}), 175.26 (C=N). Anal. Calcd for $C_{35}H_{27}AlF_{12}N_2O_2$: C, 55.13; H, 3.57; N, 3.67. Found: C, 55.2; H, 3.6; N, 3.6.

{ON^{Ph,Cy}}AlMe (3d). This compound was prepared as described for **3a**, starting from proligand {ON^{Ph,Cy}}H (**1d**; 100 mg, 0.27 mmol) and $AlMe_3$ (0.07 mL of a 2.0 M solution in heptane, 0.14 mmol) in toluene (5 mL). Reaction for 24 h at 60 °C gave **3d** as a white powder (78 mg, 72%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ − 0.48 (s, 3H, $AlCH_3$), 1.14−1.20 (m, 6H, cyclohexyl), 1.81−1.93 (m, 14H, cyclohexyl), 3.05 and 3.19 (2d, J = 16.0, 2 × 2H, $CHHC(O)(CF_3)_2$), 3.63−3.65 (m, 2H, cyclohexyl), 7.17−7.51 (m, 10 H_{Ar}). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −76.40 (q, J = 10.4, 6F), −79.35 (q, J = 10.4, 6F). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 10.50 ($AlCH_3$), 22.32, 24.32, 32.54 (cyclohexyl), 39.15 ($CH_2C(O)(CF_3)_2$), 67.22 (CH cyclohexyl), 121.54, 123.78, 125.15, 127.80, 139.40 (all C_{aro}), 177.80 (C=N); quartet resonances for CF_3 groups were not observed due to their low intensity. Anal. Calcd for $C_{35}H_{39}AlF_{12}N_2O_2$: C, 54.27; H, 5.07; N, 3.62. Found: C, 54.4; H, 5.3; N, 3.5.

{ON^{Ph,Bn}}$_2$Al(O*i*Pr) (4a). This compound was prepared by following a procedure similar to that described above for **3a**, starting from a solution of proligand {ON^{Ph,Bn}}H (**1a**; 200 mg, 0.53 mmol) in toluene (5 mL) and $AlMe_2$(O*i*Pr) (31 mg, 0.26 mmol). Reaction for 24 h at 60 °C and workup afforded **4a** as a white powder (80 mg, 38%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.12 (m, 3H, AlOCH(CH_3)), 1.19 (m, 3H, AlOCH(CH_3)), 3.17 and 3.26 (2d, J = 17.2, 2 × 2H, $CHHC(O)(CF_3)_2$), 4.17 (m, 1H, AlOC*H*), 4.99 and 5.17 (2d, J = 13.9, 2 × 2H, ArC*HH*), 6.77−7.30 (m, 20 H_{Ar}). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.01−1.10 (m, 3H, AlOCH(CH_3)), 1.37−1.41 (m, 3H, AlOCH(CH_3)), 3.14−3.29 (2d, J = 17.2, 2 × 2H, $CHHC(O)(CF_3)_2$), 4.97 and 5.19 (2d, J = 13.9, 2 × 2H, ArC*HH*), 6.77−7.30 (m, 20 H_{Ar}). ^{19}F{^{1}H} NMR (188 MHz, CD_2Cl_2, 298 K): δ −77.59 (q, J = 10.3, 6F), −78.28 (q, J = 10.3, 6F). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 14.09 (AlOCH(CH_3)), 22.81 (AlOCH-(CH_3)), 31.72 ($CH_2C(O)(CF_3)_2$), 37.87 (AlO*C*H), 55.27 ($ArCH_2$), 124.87 (q, $^1J_{CF}$ = 266.8, CF_3), 126.79, 127.66, 127.95, 128.35, 128,55, 128.68, 128.99, 137.99, 138.03 (all C_{aro}), 176.96 (C=N). Anal. Calcd for $C_{39}H_{35}AlF_{12}N_2O_3$: C, 56.12; H, 4.23; N, 3.36. Found: C, 56.0; H, 4.4; N, 3.3.

{ON^{Me,Bn}}$_2$Al(O*i*Pr) (4b). This compound was prepared as described above for **3a**, starting from a solution of proligand {ON^{Me,Bn}}H (**1b**; 200 mg, 0.63 mmol) in toluene (10 mL) and $AlMe_2$(O*i*Pr) (37 mg, 0.32 mmol). Reaction for 48 h at 50 °C in toluene (10 mL) afforded, after a similar workup, colorless crystals of **4b** (118 mg, 52%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.95 (d, J = 6.0, 6H, AlOCH(CH_3)$_2$), 1.94 (s, 6H, N=CCH_3), 2.86 (s, 4H, CH_2C=N), 3.58 (m, 1H, AlOC*H*), 4.70 and 5.13 (2d, J = 15.0, 2 × 2H, ArC*HH*), 7.16−7.36 (m, 10 H_{aro}). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.24 (s, 6H, N=CCH_3), 1.26 (d, J = 5.8, 3H, AlOCH(CH_3)$_2$), 1.34 (d, J = 5.8, 3H, AlOCH(CH_3)$_2$), 2.63 (s, 4H, CH_2C=N), 3.76 (m, 1H, AlOC*H*), 4.81 and 5.19 (2d, J = 14.0, 2 × 2H, ArC*HH*), 7.17 (m, 2H_{aro}), 7.32 (m, 4H_{aro}), 7.40 (m, 4H_{aro}). ^{19}F{^{1}H} NMR (188 MHz, C_6D_6, 298 K): δ −78.01 δ (q, J = 10.2, 6F), −78.68 (q, J = 10.2, 6F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 23.00 (AlOCH(CH_3)$_2$), 23.56 (AlOCH(CH_3)$_2$), 28.06 (N=CCH_3), 36.87 ($CH_2C(CF_3)_2$), 54.82 ($ArCH_2$), 62.84 (AlO*C*H), 127.05, 127.78, 128.10, 128.44, 128.51, 138.12 (all C_{aro}), 178.44 (C=N); quartet resonances for CF_3 groups were not observed due to their low intensity. Anal. Calcd for $C_{29}H_{31}AlF_{12}N_2O_3$: C, 49.02; H, 4.40; N, 3.94. Found: C, 49.2; H, 4.4; N, 3.9.

{ON^{Ph,Ph}}Al(O*i*Pr) (4c). This compound was prepared as described above for **3a**, starting from proligand {ON^{Ph,Ph}}H (**1c**; 200 mg, 0.55 mmol) and $AlMe_2$(O*i*Pr) (32 mg, 0.28 mmol) in toluene (5 mL). Workup and crystallization from a hexanes/toluene solution (3/1 mL) at −30 °C gave **4c** as colorless crystals (0.10 g, 47%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 0.60 (d, J = 5.8, 3H, AlOCH(CH_3)$_2$), 0.69 (d, J = 5.8, 3H, AlOCH(CH_3)$_2$), 3.23 (d, J = 17.2, 2H, $CHHC(O)(CF_3)_2$), 3.27 (m, 1H, AlOC*H*), 3.38 (d, J = 17.2, 2H, $CHHC(O)(CF_3)_2$), 6.72−6.78 (m, 10H_{Ar}), 6.96−7.00 (m, 10H_{Ar}). ^{19}F{^{1}H} NMR (188 MHz, C_6D_6, 298 K): δ −76.52 (q, J = 10.3, 6F), −79.42 (q, J = 10.3, 6F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 26.64 (AlOCH(CH_3)), 27.09 (AlOCH(CH_3)), 37.37 ($CH_2C(O)(CF_3)_2$), 63.03 (AlO*C*H), 125.90, 127.60 (q, $^1J_{CF}$ = 138.2 Hz, CF_3), 127.91, 128.10, 128.29, 128.52, 129.51, 138.06, 147.47, (all C_{aro}), 176.06 (C=N). Anal. Calcd for $C_{37}H_{31}AlF_{12}N_2O_3$: C, 55.09; H, 3.87; N, 3.47. Found: C, 55.2; H, 3.9; N, 3.4.

X-ray Diffraction Studies. Suitable single crystals were mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 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 direct methods using the SIR97 program[29] and then refined with full-matrix least-squares methods based on F^2 (SHELX-97)[30] with the aid of the WINGX program.[31] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and oxygen-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 magnitudes of the residual electron densities were of no chemical significance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 and CIF files giving X-ray crystallographic data for **2a**,**b**, **3b**,**c**, and **4b**,**c** and figures giving representative ^{1}H, ^{19}F{^{1}H}, and ^{13}C{^{1}H} NMR spectra for some complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+33)(0)223-236-939. E-mail: jean-francois.carpentier@univrennes1.fr.

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(24) It must be noted that $\{^{Ar}ON^{Cy}NO^{CF3}\}Y(N(SiHMe_2)_2)(THF)$, which has an yttrium center in a slightly distorted octahedral environment with the O,N,N,O atoms of the Schiff base ligand lying in the equatorial plane (τ = 0.04), proved completely non-stereoselective in the ROP of racemic lactide.[6c]

(25) Efforts to prepare Al-lactate or Al-(alkoxy-ester) compounds with these $\{ON^{R1,R2}\}$ ligands proved unsuccessful. For leading references related to model aluminum complexes that mimic the putative active species with a growing polyester chain, see: (a) Lewinski, J.; Zachara, J.; Justyniak, I. *Organometallics* **1997**, *16*, 4597. (b) Lewinski, J.; Horeglad, P.; Wojcik, K.; Justyniak, I. *Organometallics* **2005**, *24*, 4588. (c) Koller, J.; Bergman, R. G. *Organometallics* **2011**, *30*, 3217. See also refs 3j and 3p.

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