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Aluminum, Indium, and Mixed Yttrium−Lithium Complexes Supported by a Chiral Binap-Based Fluorinated Dialkoxide: Structural Features and Heteroselective ROP of Lactide

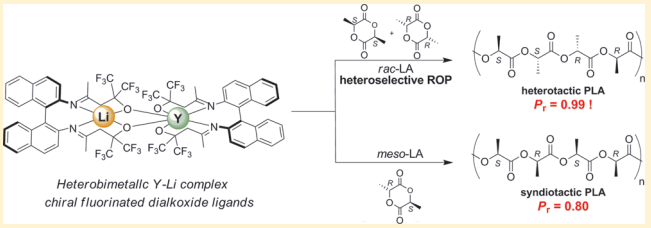
Nicolas Maudoux,[†] Thierry Roisnel,[‡] Jean-François Carpentier,*[,†] and Yann Sarazin*[,†]

[†]Institut des Sciences Chimiques de Rennes, Organometallics: Materials and Catalysis Laboratories, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes Cedex, France

[‡]Institut des Sciences Chimiques de Rennes, Centre de Diffraction X, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes Cedex, France

Supporting Information

ABSTRACT: The new chiral Binap-based fluorinated dialcohol proteo-ligand {ONNO}H_2 has been prepared under its enantiomerically pure and racemic forms following reaction of (*R*)- or (*rac*)-1,1′-binaphthyl-2,2′-diamine with 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)pentan-2-one. The racemic proteo-ligand reacts with the trivalent metallic precursors $AlEt_2Cl$ and $In(CH_2SiMe_3)_3$ to yield the complexes (*rac*)-{ONNO}-AlCl (**1**) and (*rac*)-{ONNO}$In(CH_2SiMe_3)$ (**2**), while the reaction of (*R*)-{ONNO}H_2 with a 1:1 mixture of $Y(N(SiMe_3)_2)_3$ and $LiN(SiMe_3)_2$ gives the enantiomerically pure heterobimetallic [((*R*)-{ONNO}$)_2$Y·Li] (**3**). Complex **3** acts as a single-component initiator for the near-perfect heteroselective ring-opening polymerization (ROP) of *racemic* lactide, yielding polymers with P_r up to 0.99 under mild conditions. It also produces syndiotactic-enriched polylactide (P_r = 0.80) by ROP of *meso* lactide.



INTRODUCTION

Isotactic poly(lactide) (*i*PLA), a crystalline polymer accessed by ring-opening polymerization (ROP) of L-lactide, is the archetype of a "green" polymer featuring good physical properties.[1] Because it can produce *i*PLA with improved properties (T_m up to 220 °C) compared to commercially available PLAs (T_m = 170−180 °C), the isoselective ROP of *racemic* lactide (*rac*-LA) has become the focus of intense investigations.[2] Catalysts affording isospecific ROP reactions leading to *i*PLA have been sought for 20 years. Breakthroughs have been achieved with aluminum-salen initiators,[3] and recently promising results have also been obtained with indium,[4] gallium,[5] zinc,[6] yttrium,[7] and group 4 metals.[8] The supporting ligands are often dianionic aryloxides (salen,[3] salan,[9] or salalen[10]), and the use of a chiral SalBinap backbone in Spassky's and Coates' seminal contributions gave isoselective catalysts that have not been surpassed.[11]

We and others have developed rare-earth complexes that display high *hetero*selectivity toward the ROP of *rac*-LA using a variety of bis(aryloxide) ligands incorporating amino[12] or dithiaalkanediyl bridges.[13,14] Although amorphous heterotactic PLA (*h*PLA) is not used yet for any specific application, highly heteroselective catalysts for the ROP of *rac*-LA are of interest because they can also produce crystalline (T_m = 152 °C) *syndio*tactic PLA (*s*PLA) by stereocontrolled polymerization of *meso* lactide (*meso*-LA).[3b,15] We have also shown that fluorinated (di)alkoxides with CF_3 groups in α-position to the $O_{alkoxide}$ atoms[16] afford complexes that show comparable efficiency as ROP catalysts to their aryloxide analogues.[11a,b,d,17] We report here on three aluminum, indium, and mixed yttrium−lithium complexes supported by a new chiral Binap-based fluorinated dialkoxide. It is shown that the Y−Li complex is a catalyst for the heteroselective ROP of *rac*-LA that yields near-perfect *h*PLA and also generates syndiotactic-enriched PLA by ROP of *meso*-LA.

RESULTS AND DISCUSSION

Synthesis and Structure of Fluorinated Diol Proligand and Related Al, In, and Y Complexes. The enantiomerically pure Binap-based proteo-ligand (*R*)-{ONNO}H_2 was isolated in 45% yield upon reaction of the commercially available (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine with 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)pentan-2-one (prepared in 79% yield by nucleophilic addition of acetone onto hexafluoroacetone under forcing conditions)[18] in refluxing toluene (Scheme 1). The identity and purity of (*R*)-{ONNO}H_2 were established by NMR spectroscopy, elemental analysis, mass spectrometry, and X-ray diffraction analysis. The methylene C*HH* hydrogen atoms are diastereotopic, giving rise to an AB spin system ($^2J_{HH}$

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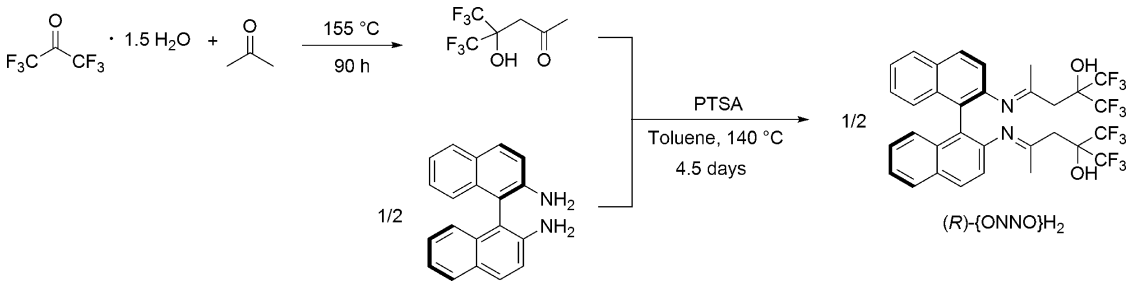
Scheme 1. Synthesis of (*R*)-{ONNO}H$_2$



= 16.6 Hz). Due to the chiral backbone, the two CF_3 groups carried by the same C_{sp3} atom are not equivalent, and each gives rise to a quartet ($^4J_{FF}$ = 9.8 Hz) in the $^{19}F\{^1H\}$ NMR spectrum of the proteo-ligand. The two halves of the proteo-ligand are otherwise magnetically equivalent, as a single set of resonances is detected in each of the ^1H, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra. The *racemic* version of the proteo-ligand, (*rac*)-{ONNO}H$_2$, was obtained from (*rac*)-(±)-1,1′-binaphthyl-2,2′-diamine following the same procedure, and the analytical data for the racemate were strictly identical to those of (*R*)-{ONNO}H$_2$.

The molecular solid-state structure of (*S*)-{ONNO}H$_2$ obtained from a scalemic mixture is depicted in Figure 1. It shows the proteo-ligand to be in the *S* configuration, with an angle of 79.5° between the two mean planes defined by the naphthalene units. The imino-alcohol tethers, which exhibit typical internal O−H···N hydrogen bonding, are located away from each other to minimize steric congestion.

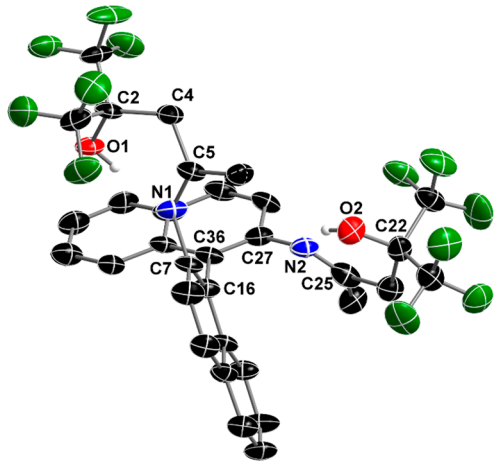


Figure 1. ORTEP representation of the molecular solid-state structure of (*S*)-{ONNO}H$_2$. Ellipsoids are drawn at the 50% probability level. Only one of the two independent and crystallographically equivalent molecules in the asymmetric unit is depicted. Hydrogen atoms (except OH) are omitted for clarity. Color code: red, O; blue, N; black, C; dark green, F. Selected bond lengths (Å): N(1)−C(5) = 1.263(11), N(1)−C(7) = 1.427(10), C(2)−C(4) = 1.539(13), C(4)−C(5) = 1.513(11), O(1)−C(2) = 1.395(10).

The stoichiometric reactions of (*R*)-{ONNO}H$_2$ or (*rac*)-{ONNO}H$_2$ with Al_2Me_6, $[Al(OiPr)_3]_4$, or $AlMe_2(OiPr)$ failed to give clean species, as unidentifiable products or intractable mixtures of compounds were obtained regardless of the reaction conditions. By contrast, (*rac*)-{ONNO}H$_2$ reacted cleanly and quantitatively with $AlEt_2Cl$ to afford the expected (*rac*)-{ONNO}AlCl (**1**) upon protonolysis and release of ethane (Scheme 2). Complex **1** was characterized by NMR spectroscopy and combustion analysis. At room temperature, the ^1H and $^{19}F\{^1H\}$ NMR spectra feature very broad resonances, indicative of fluxional behavior. The dynamic phenomenon was frozen at 213 K. At this temperature, the ^1H NMR spectrum shows the absence of symmetry in this complex, with in particular two singlets for the nonequivalent CH_3 groups and two sets of resonances for independent AB systems ($^2J_{HH}$ = 15.0 and 16.3 Hz) assigned to methylene C*HH* hydrogens. This is corroborated by the $^{19}F\{^1H\}$ NMR data, where four distinct quartets indicate that all CF_3 ($^4J_{FF}$ = 9.0 and 10.3 Hz) are nonequivalent. Reaction of **1** with KO*i*Pr failed to deliver the targeted (*rac*)-{ONNO}Al(O*i*Pr).

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane. Both enantiomers of the complex are found in the asymmetric unit in a 1:1 ratio. The representation of the *R* enantiomer displayed in Figure 2 shows the aluminum atom to rest in a five-coordinated trigonal bipyramidal environment in this monometallic complex, with one $O_{alkoxide}$ and one N_{imine} atom occupying the apical positions. However, poor refinement precludes discussion of the metric parameters in this complex.

The hydrocarbyl complex (*rac*)-{ONNO}In(CH_2SiMe_3) (**2**) was isolated in 66% yield[19] upon reaction of $In(CH_2SiMe_3)_3$ with 1 equiv of (*rac*)-{ONNO}H$_2$ and concomitant release of $SiMe_4$. The NMR data recorded in benzene-d_6 or THF-d_8 show that **2** is highly fluxional in solution at 298 K. In particular, in addition to a sharp singlet, the $^{19}F\{^1H\}$ NMR spectrum in THF-d_8 exhibits a very broad, almost flat resonance spreading over nearly 8 ppm. The fluxional behavior is frozen at 213 K, where the $^{19}F\{^1H\}$ NMR spectrum shows four broad singlets of equal intensities (Figure 3). The ^1H NMR spectrum of the complex is well resolved at this temperature and features an AB spin system at high field for the In*CHH*SiMe$_3$ hydrogens ($^2J_{HH}$ = 12.0 Hz) and two other AB systems for the *CHH*C(CF$_3$)$_2$ ($^2J_{HH}$ = 14.4 and 14.7 Hz). All hydrogens are in a unique environment, and thus the pseudochiral molecule has no symmetry at this temperature.

The NMR-scale reaction of (*R*)-{ONNO}H$_2$ with strictly 1 equiv of $Y(N(SiMe_3)_2)_3$ afforded an unidentified compound (**C**) featuring three distinct ligand environments on the basis of NMR spectroscopic data, but which a priori did not correspond to a putative (*R*)-{ONNO}Y(N(SiMe$_3$)$_2$). Besides, resonances for free $HN(SiMe_3)_2$ and unreacted $Y(N(SiMe_3)_2)_3$ were detected in the NMR spectrum of the crude product, while all the proteo-ligand had reacted.[18] The spectroscopic data suggested the presence of a protic NH or OH moiety could not be ruled out, yet we were unable to reconcile them with a zwitterion of the type {ONNO}Y$^-${ONN(H)$^+$O} akin to the bis(aryloxide)amine samarium(III) zwitterion reported by Mountford and co-workers.[20]

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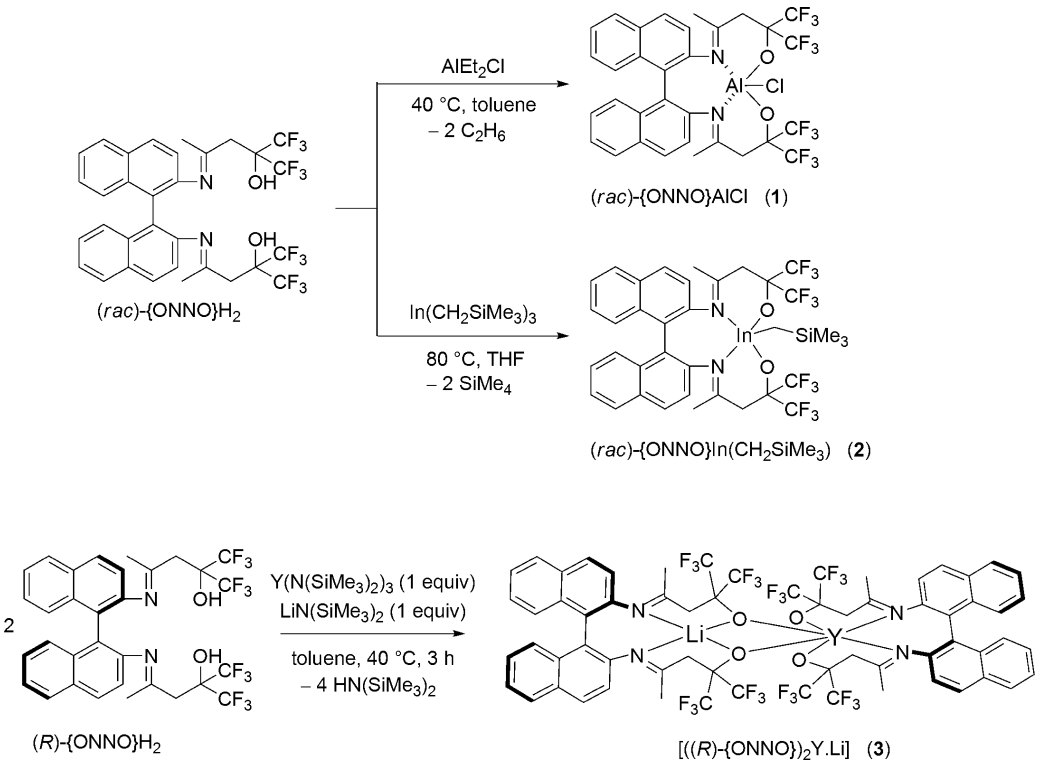
Scheme 2. Synthesis of Complexes 1−3 by Protonolysis Reactions



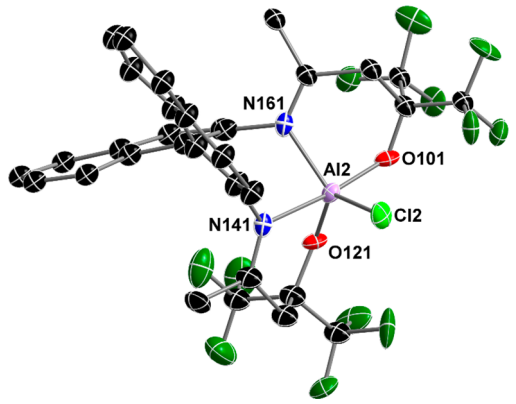


Figure 2. ORTEP representation of the molecular solid-state structure of the *R* enantiomer of (*rac*)-{ONNO}AlCl (**1**). Hydrogen atoms are omitted for clarity. Color code: red, O; blue, N; black, C; dark green, F; bright green, Cl; lavender, Al. Ellipsoids are drawn at the 50% probability level. Discussion of metric parameters is not pertinent owing to R_1 = 17.2%.

The reaction of $Y(N(SiMe_3)_2)_3$ with 2 equiv of (*R*)-{ONNO}H_2 gave an intractable mixture of compounds and did not provide useful information toward the identification of compound **C**. On the other hand, the one-pot reaction of (*R*)-{ONNO}H_2, $Y(N(SiMe_3)_2)_3$, and $LiN(SiMe_3)_2$ in 2:1:1 proportions returned cleanly and quantitatively the heterobimetallic [((*R*)-{ONNO})$_2$Y·Li] (**3**) (see Scheme 1). The formulation for **3** was established on the basis of spectroscopic (^{1}H, ^{19}F, and ^{7}Li NMR in C_6D_6) and crystallographic data, and its purity was corroborated by elemental analysis. The ^{7}Li NMR spectrum of **3** shows the presence of a single resonance at $\delta_{^7Li}$ = 0.86 ppm. In the ^{19}F{^{1}H} NMR spectrum, four resonances of equal intensity (three broad signals and a sharp quartet) are identified, each corresponding to two CF_3 groups and indicating partial symmetry in solution; this is further attested by ^{1}H NMR spectroscopy (only two AB systems for all backbone methylene C*HH* hydrogens and two singlets for all CH_3 moieties). The molecular solid-state structure of **3** was elucidated by X-ray crystallography (Figure 4). The two, nonequivalent ligand fragments in the complex retain their original *R* configuration. One of these is κ^2-coordinated to the yttrium atom (corresponding to O(1) and O(48)), while the other one (viz., O(51) and O(98)) acts as a μ^2:κ^2,κ^2 ligand bridging the two metal atoms. The six-coordinated yttrium atom lies in a slightly distorted octahedral environment, with all four $O_{alkoxide}$ atoms located at approximately the same distance from the metal, in the range 2.162(2)−2.209(2) Å. The lithium atom is also six-coordinated, with two Li−$O_{alkoxide}$ and two Li−N_{imine} bonds being complemented by two nonequivalent Li···F secondary interactions (2.175(6) and 2.412(6) Å); the geometry about the Li atom forms a much distorted tetrahedron. The Y−Li distance is too long for potential Y···Li interactions.[21] NMR data for **3** recorded in C_6D_6 or THF-d_8 did not provide evidence that the Li···F interactions are maintained in solution, but DOSY NMR measurements and diffusion molecular weight analysis (*D*-fw) demonstrated that the heterobimetallic structure of the complex is preserved in THF-d_8.[18,22] This is confirmed by comparison of the hydrodynamic radii of the complex determined by PGSE NMR spectroscopy (r_{PGSE} = 6.72 Å) and from the crystallographic data (r_{XRD} = 7.28 Å).[18]

Ring-Opening Polymerization Catalysis. Although by itself, or in combination with benzyl alcohol (BnOH), the aluminum complex **1** does not polymerize *rac*-LA, we have found that both the indium and yttrium−lithium complexes **2** and **3** mediate the heteroselective ROP of *rac*-LA under mild conditions (Table 1). Complex **2** requires the addition of 1 equiv of BnOH to catalyze the polymerization of 100 equiv of

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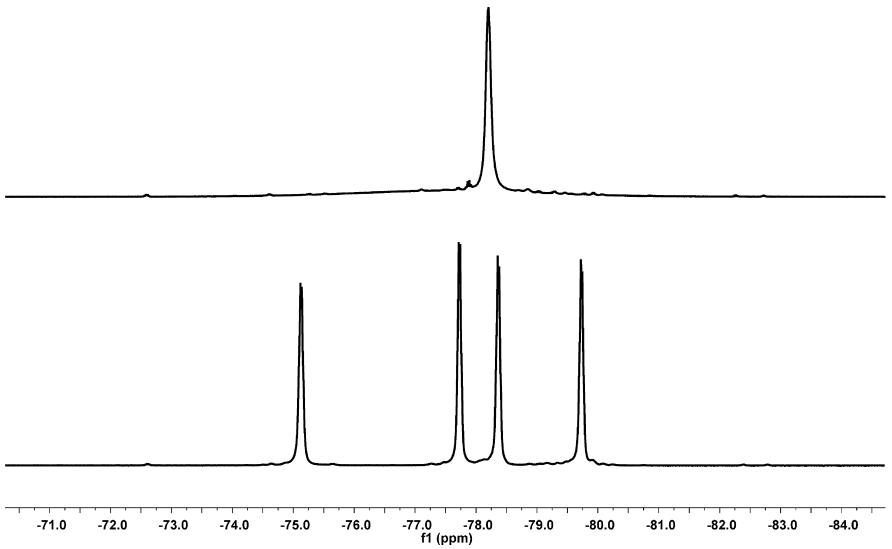

Figure 3. $^{19}F\{^{1}H\}$ NMR spectra of (*rac*)-{ONNO}In(CH_2SiMe_3) (**2**) (THF-d_8, 376.49 MHz) recorded at 298 K (top) and 213 K (bottom).

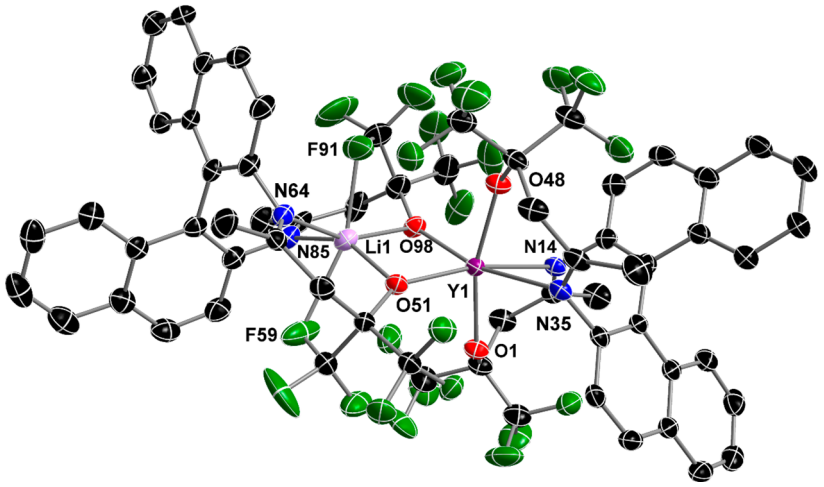

Figure 4. ORTEP representation of the molecular solid-state structure of [((*R*)-{ONNO})$_2$Y·Li] (**3**). Hydrogen atoms are omitted for clarity. Color code: red, O; blue, N; black, C; dark green, F; lavender, Li; violet, Y. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Y(1)−O(48) = 2.162(2), Y(1)−O(1) = 2.170(2), Y(1)−O(98) = 2.1899(19), Y(1)−O(51) = 2.209(2), Y(1)−N(14) = 2.518(3), Y(1)−N(35) = 2.531(2), Y(1)−Li(1) = 3.075(6), O(51)−Li(1) = 1.998(5), F(59)−Li(1) = 2.412(6), N(64)−Li(1) = 2.121(6), N(85)−Li(1) = 2.089(6), F(91)−Li(1) = 2.175(6), O(98)−Li(1) = 2.108(6); O(48)−Y(1)−O(1) = 164.91(8), O(48)−Y(1)−O(98) = 92.09(8), O(1)−Y(1)−O(98) = 99.08(8), O(48)−Y(1)−O(51) = 96.61(8), O(1)−Y(1)−O(51) = 94.71(8), O(98)−Y(1)−O(51) = 83.53(7), O(48)−Y(1)−N(14) = 94.64(8), O(1)−Y(1)−N(14) = 73.94(8), O(98)−Y(1)−N(14) = 97.61(8), O(51)−Y(1)−N(14) = 168.64(8), O(48)−Y(1)−N(35) = 74.37(8), O(1)−Y(1)−N(35) = 93.56(8), O(98)−Y(1)−N(35) = 165.82(8), O(51)−Y(1)−N(35) = 101.91(7), N(14)−Y(1)−N(35) = 79.66(8), O(51)−Li(1)−N(85) = 151.0(3), O(98)−Li(1)−N(64) = 155.0(3), F(91)−Li(1)−F(59) = 161.5(3).

Table 1. Ring-Opening Polymerization Data[a]

entry	cat	LA	$[LA]_0/[Cat]_0/[BnOH]_0$	solv	T (°C)	t (h)	conv (%)	$M_{n,theo}$[b] (g·mol^{-1})	$M_{n,SEC}$[c] (g·mol^{-1})	M_w/M_n	P_r[d]
1	**2**	*rac*-	100:1:1	Tol	70	7	57	8300	5000	1.04	0.53
2	**2**	*rac*-	100:1:1	THF	70	7	68	9900	5900	1.05	0.70
3[e]	**3**	*rac*-	170:1:0	THF	30	5	100	24 600	21 900	1.45	0.99
4	**3**	*rac*-	300:1:0	THF	30	5	75	32 400	19 500	1.74	0.99
5	**3**	L-	170:1:0	THF	30	7	18	4400	nd	nd	0.00
6	**3**	D-	170:1:0	THF	30	7	16	3900	nd	nd	0.00
7	**3**	*meso*-	300:1:0	THF	30	5	100	43 200	20 800	1.16	0.80

[a] $[rac\text{-LA}]_0$ = 0.8 M; see the SI for complementary results. [b] $M_{n,theo} = [rac\text{-LA}]_0/[Cat]_0 \times$ conversion ×144.13 (+108.14 when BnOH was employed); reactions quenched with MeOH unless otherwise specified. [c] Determined by size exclusion chromatography vs polystyrene standards and corrected by a factor of 0.58. [d] Probability of *racemic* enchainments for consecutive lactide units, determined by selective $^{1}H\{^{1}H\}$ NMR spectroscopy. [e] Reaction quenched with EtOH. nd: not determined.

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rac-LA (entries 1, 2), as otherwise no controlled reaction is taking place (*vide infra*). Partial conversions (50−70%) are obtained after 7 h with moderate control of the molecular weights but very narrow molecular weight distributions. End-group analysis by NMR spectroscopy confirms the presence of the expected termini, BnOC(═O)CH(CH_3)− and −CH-(CH_3)OH. The reaction is slightly faster in THF than in toluene, an observation already made with other indium-based ROP initiators.[4] Interestingly, reactions in THF afford PLA with a heterotactic bias (P_r = 0.70),[23] whereas the polymers produced in toluene are atactic, suggesting that THF may play a noninnocent role as a coligand.

An independent NMR experiment showed the total absence of reaction between **2** and BnOH (1−10 equiv) in THF-d_8, at either 25 or 70 °C; the [In]−CH_2SiMe_3 moiety did not undergo any alcoholysis, and complex **2** remained stable for several hours under these conditions. Similar observations have been reported before with related indium-carbyl complexes[11d,24] and strongly suggest that the **2**/BnOH system here operates via an activated monomer mechanism, in which **2** acts as a Lewis acidic catalyst that activates the monomer toward nucleophilic attack by external (macro)alcohol molecules.

The polymerization of *rac*-LA mediated by **3** takes place in THF under mild conditions (30 °C, [*rac*-LA]$_0$ = 0.8 M) without the need for any exogenous nucleophile (Table 1, entries 3, 4), readily converting 170−300 equiv of monomer. Under these conditions, the reactions are not controlled, as experimental $M_{n,SEC}$ values are lower than the calculated $M_{n,theo}$ ones and the molecular weights of the resulting polymers are not narrowly dispersed. Monomer consumption follows first-order kinetics in [*rac*-LA]. Monitoring of an NMR-scale polymerization of *rac*-LA[25] showed that a long induction period preceded the steady-state regime, which in this case prevented accurate and reliable determination of the observed rate constant by a simple first-order analysis.[18] The initiation and propagation rate constants k_i = (1.83 ± 0.20) × 10^{-4} L·mol^{-1}·s^{-1} and k_p = (156.6 ± 12.5) × 10^{-4} L·mol^{-1}·s^{-1} were determined by fitting the experimental data to a nonlinear regression model for living ROP reactions.[18,26] Most gratifyingly, near-perfect heterospecific *h*PLA is obtained (Figure 5), with values of P_r very close to 1 (entries 3, 4 in Table 1); this compares favorably with other heteroselective catalysts for the ROP of *rac*-LA disclosed in the literature.[12−14] Complex **3** polymerizes *rac*-LA faster than the enantiomerically pure L-LA (compare entries 3 and 5), consistently with the heteroselectivity displayed by the initiator toward *rac*-LA. Moreover, the polymerization of D-LA, the other enantiomer of lactide, takes place at the same rate as that of L-LA (entries 5 and 6). Note that the value of P_r decreases to 0.90−0.95 if the polymerization is carried in CH_2Cl_2 instead of THF, if the reaction temperature is increased to 60−80 °C (to enhance the reaction rate), or if the reaction is not quenched as soon as full monomer consumption is reached (presumably due to deleterious transesterification processes).[18,27]

End-group analysis by ^{1}H NMR spectroscopy and MALDI-ToF MS demonstrated the presence of −CH(CH_3)OH and MeOC(═O)CH(CH_3)− termini (Figure 6 and the SI). If the former is to be expected, a MeOC(═O)CH(CH_3)− chain-end is unusual in the present context. We surmise that these observations result from (i) initial (i.e., for the first insertion) nucleophilic attack of the coordinated monomer by one of the $O_{alkoxide}$ atoms in **3**, where therefore the ligand would act not only as an *ancillary* group but also as a *reactive* nucleophile,

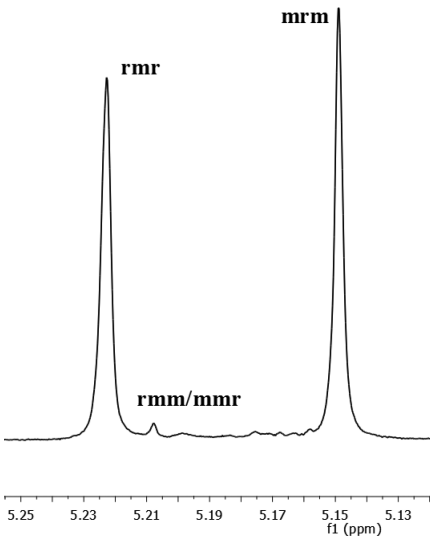

Figure 5. Methine region of the ^{1}H homodecoupled NMR spectrum (500.13 MHz, $CDCl_3$ with calibration at 7.26 ppm, 298 K) of a PLA sample prepared by polymerization of *rac*-LA mediated by **3** (Table 1, entry 4; P_r = 0.99).

followed by (ii) transesterification of the initial chain-end in the presence of methanol during quenching of the reaction and precipitation of the polymer, both carried out with methanol.[28] In fact, in a control experiment, quenching of the polymerization with EtOH instead of the customary MeOH resulted in the formation of an EtOC(═O)CH(CH_3)− end-capped polylactide.[18] Our attempts to isolate or unambiguously identify a putative {ONNO}-capped PLA before quenching were unsuccessful.

It has been shown that highly heteroselective catalysts polymerize *meso*-LA to syndiotactic *s*PLA.[15] The polymerization of *meso*-LA promoted by **3** is stereoselective, as it generates narrowly dispersed syndiotactic *s*PLA (Table 1, entry 7, P_r = 0.80; Figure 7). Yet, the level of selectivity is lower for *meso*-LA than for *rac*-LA, which as observed by Hillmyer and Tolman suggests that the configuration of *both* stereocenters of the last inserted lactide molecule is determinant for the stereochemistry of the insertion of the next monomer.[14g] Qualitative comparison of the data for entries 4 and 7 in Table 1 indicates that *meso*-LA is polymerized a little more rapidly than *rac*-LA; in similar cases, it has been said that this could result from the greater ring strain in *meso*-LA.[15e] Again, the kinetics of the polymerization exhibit first-order dependence in monomer concentration, with k_{obs} = 7.00 × 10^{-5} s^{-1}. Monitoring of an NMR-scale reaction did not show the presence of a detectable induction period, k_i = (304.7 ± 127.7) × 10^{-4} L·mol^{-1}·s^{-1} and k_p = (143.4 ± 1.19) × 10^{-4} L·mol^{-1}·s^{-1}. Comparisons of the plots of monomer consumption and of the respective values of k_i and k_p under otherwise strictly identical conditions indicates that the ROP of *meso*-LA is overall marginally faster than that of *rac*-LA, but essentially in the present scenario due to the long induction period detected in the case of *rac*-LA (see above).[18,24]

CONCLUSION

In summary, we have shown that the heterobimetallic complex [((*R*)-{ONNO})$_2$Y·Li] (**3**) bearing a fluorinated dialkoxo ligand is available quantitatively and under its enantiomerically pure form by simple concomitant, one-pot protonolysis

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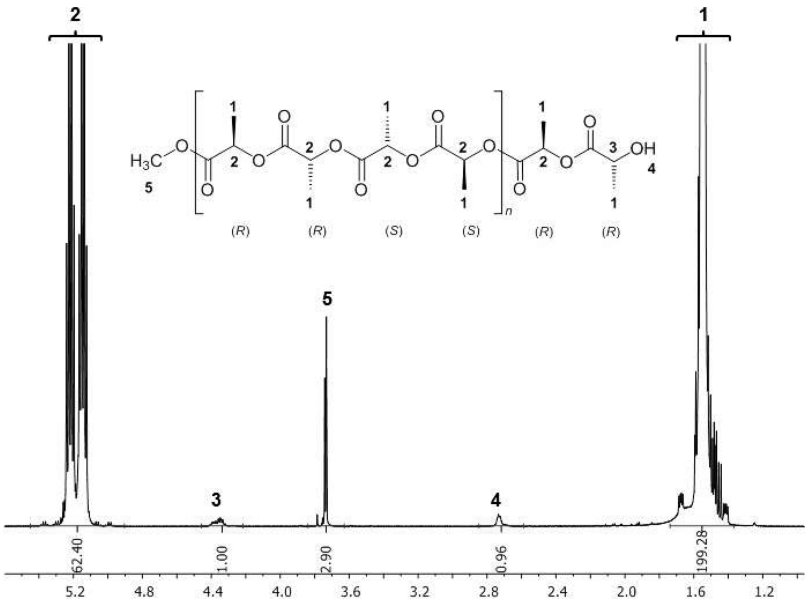

Figure 6. ^{1}H NMR spectrum (500.13 MHz, $CDCl_3$, 298 K) of an *h*PLA prepared by ROP of *rac*-LA mediated by **3** and quenched by MeOH.

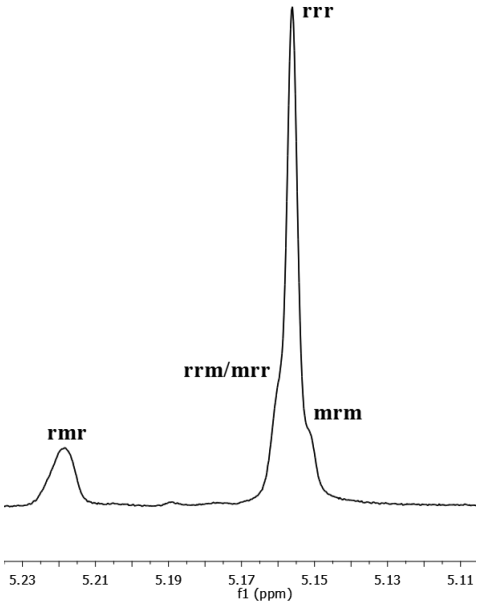

Figure 7. Methine region of the ^{1}H homodecoupled NMR spectrum (500.13 MHz, $CDCl_3$ with calibration at 7.26 ppm, 298 K) of an *s*PLA sample prepared by polymerization of *meso*-LA mediated by **3** (Table 1, entry 7; P_r = 0.80).

reactions. This complex polymerizes *racemic* lactide to an unusual[12] near-perfect heterotactic polylactide with P_r = 0.99, while it also gives syndiotactic polylactide (P_r = 0.80) from *meso* lactide. Although the reactions are not entirely controlled and the mechanisms have not been fully unraveled, these results open up new directions in the area of ligand design for stereoselective ROP catalysis.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O_2 < 1 ppm, H_2O < 5 ppm) for catalyst loading. Solvents (THF, Et_2O, CH_2Cl_2, pentane, and toluene) were purified and dried (water contents all below 10 ppm) over alumina columns (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze−thaw−vacuum cycles. *Racemic* lactide (Acros) was purified by recrystallization from a hot (80 °C), concentrated *i*PrOH solution, followed by two subsequent recrystallizations in hot (105 °C) toluene; after purification, it was stored at −30 °C under the inert atmosphere of the glovebox. Benzyl alcohol and 2-propanol (Aldrich) were dried and distilled over magnesium turnings and stored over 3 Å molecular sieves.

NMR spectroscopic data were recorded on Bruker AM-400 and AM-500 spectrometers. All ^{1}H and $^{13}C\{^{1}H\}$ chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated vs $SiMe_4$. Assignment of the signals was carried out using 1D (^{1}H, $^{13}C\{^{1}H\}$) and 2D (COSY, HMBC, HMQC) NMR experiments. Coupling constants are given in hertz. $^{19}F\{^{1}H\}$ chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. DOSY NMR experiments were carried out on a Bruker Avance III 400 MHz spectrometer equipped with a BBOF pulsed field-gradient probe using a bipolar gradient pulse stimulated echo sequence. Each experiment was performed on a 0.021 M solution at 298 K using a spectral width of 4807 Hz, a 90° pulse width of 11.5 μs, a diffusion delay time of 0.05 s, and a total diffusion-encoding pulse width of 0.0016 s. The diffusion encoding pulse strength was arrayed from 0 to 35 G·cm^{-2} over 12 or 16 increments with four dummy scans and eight scans per increment.

Elemental analyses were performed on a Carlo Erba 1108 elemental analyzer instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements.

Size exclusion chromatography (SEC) measurements were performed on an Agilent PL-GPC50 equipped with two PLgel 5 Å MIXED-C columns and a refractive index detector. The column was eluted with THF at 30 °C at 1.0 mL·min^{-1} and was calibrated using 11 monodisperse polystyrene standards in the range 580 to 380 000 g·mol^{-1}. The molecular weights of all PLAs were corrected by a factor of 0.58.[29]

Typical Schlenk-Scale Polymerization Procedure. In the glovebox, the metal catalyst (ca. 5.0−15.0 mg) was placed in a Schlenk flask together with the monomer (ca. 0.1−1.0 g). The Schlenk flask was sealed and removed from the glovebox. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of solvent (THF or toluene) was added with a syringe to the catalyst and the monomer, followed when

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necessary by addition of alcohol (*i*PrOH or BnOH, 3−10 μL). The resulting mixture was immerged in an oil bath preset at the desired temperature, and the polymerization time was measured from this point. The reaction was terminated by addition of MeOH, and the polymer was precipitated in methanol or a methanol/pentane mixture. The polymer was then dried to constant weight in a vacuum oven at 55 °C under dynamic vacuum (<5 × 10^{-2} mbar).

Typical NMR-Scale Polymerization Procedure. All NMR-scale ROP reactions were conducted in THF-d_8. In a typical experiment, the catalyst and the monomer were loaded in an NMR tube in the glovebox. The NMR tube was placed in a Schlenk flask, which was then removed from the glovebox and connected to the vacuum manifold. All subsequent operations were performed using Schlenk techniques. The appropriate amount of THF-d_8 was added to the NMR tube in this order at room temperature. The NMR tube was then sealed, gently heated to ensure complete dissolution of the monomer, and introduced in the spectrometer preset at the desired temperature. Time measurement started at this point. Data points were collected at regular intervals (typically 30−480 s, with D1 = 0.5 s and NS = 8−16 scans) until conversion of the monomer stopped (this usually coincided with near-full conversion). The conversion was reliably determined by integrating the methine region of PLA vs that of the monomer.

Curve-Fitting Methods. For kinetic experiments, the values of k_i and k_p were determined with the software Origin and Datafit by curve-fitting of experimental data as described in ref 24.

X-ray Diffraction Crystallography. Single crystals of (*R*)-{ONNO}H_2 and [((*R*)-{ONNO})$_2$Y·Li] (**3**) suitable for X-ray diffraction analysis were obtained by recrystallization of the purified compound. Diffraction data were collected at 150(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 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 direct methods; remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).[30] Carbon- and oxygen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. 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. Crystal data and details of data collection and structure refinement for all compounds structurally characterized (CCDC 997544 and 997545) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

MALDI-ToF Mass Spectrometry. MALDI-TOF mass spectra were recorded at the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems) equipped with a pulsed N_2 laser source (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and with an accelerating voltage of 20 kV. A THF solution (1 mL) of the matrix (*trans*-3-indoleacrylic acid (Aldrich, 99%)) and a MeOH solution of the cationization agent (NaI, 10 mg·mL^{-1}) were prepared. A fresh solution of the polymer samples in THF (10 mg·mL^{-1}) was then prepared. The three solutions were then rapidly combined in a 1:1:10 volume ratio of matrix-to-sample-to-cationization agent. One to two microliters of the resulting solution was deposited onto the sample target and vacuum-dried.

5,5,5-Trifluoro-4-hydroxy-4-(trifluoromethyl)pentan-2-one. A sealed 100 mL stainless steel autoclave was charged with hexafluoroacetone sesquihydrate (12.5 g, 64.7 mmol) and acetone (57.5 mL, 775 mmol). The autoclave was heated at 155 °C for 90 h and then cooled to room temperature. Diethyl ether (20 mL) was added, the mixture was dried over Na_2SO_4 and filtered, and the solvents were pumped off. The residual oil was distilled under reduced pressure (2 mmHg, 32 °C) to give the desired product as a colorless liquid. Yield: 11.4 g, 79%. ^{1}H NMR ($CDCl_3$, 298 K, 400.16 MHz): δ 6.72 (s, 1H, O*H*), 2.97 (s, 2H, CH_2), 2.36 (s, 3H, CH_3) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$, 298 K, 376.49 MHz): δ −78.3 (s, CF_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, 100.62 MHz): δ 209 (s, *C*═O), 122.6 (q, $^1J_{CF}$ = 287 Hz, CF_3), 76.2 (hept, $^2J_{CF}$ = 30 Hz, $C(CF_3)_2$), 37.0 (s, CH_2), 32.0 (s, CH_3) ppm.

(*R*)-{ONNO}H_2. 5,5,5-Trifluoro-4-hydroxy-4-(trifluoromethyl)-pentan-2-one (1.64 g, 7.32 mmol) was dissolved in dry toluene (ca. 45 mL). (*R*)-(+)-1,1′-Binaphthyl-2,2′-diamine (0.91 g, 3.18 mmol) and then *p*-toluenesulfonic acid (36 mg, 6 mol %) were added. The mixture was refluxed at 140 °C for 4.5 days in a setup equipped with a Dean−Stark apparatus. The volatiles were then removed *in vacuo* to afford a brown solid, which was extracted with Et_2O. Filtration followed by evaporation of the solvent gave a solid, which was purified by chromatography over silica (petroleum ether/ethyl acetate = 92:8). Recrystallization in petroleum ether yielded the enantiomerically pure title compound as an off-white solid (1.0 g, 45%). ^{1}H NMR (C_6D_6, 298 K, 400.16 MHz): δ 8.04 (s, 2H, O*H*), 7.70 (d, 4H, $^3J_{HH}$ = 8.5 Hz, $C_{arom}H$), 7.19 (t, 2H, $^3J_{HH}$ = 7.7 Hz, $C_{arom}H$), 7.10 (d, 2H, $^3J_{HH}$ = 8.4 Hz, $C_{arom}H$), 6.97 (t, 2H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 6.75 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 2.12−1.96 (AB system, 4H, $^2J_{HH}$ = 16.6 Hz, CH_2), 1.37 (s, 6H, CH_3) ppm. ^{19}F{^{1}H} NMR (C_6D_6, 298 K, 376.49 MHz): δ −77.8 (q, $^4J_{FF}$ = 9.8 Hz, CF_3), −78.4 (q, $^4J_{FF}$ = 9.8 Hz, CF_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 100.62 MHz): δ 171.3 (C═N), 143.3, 133.6, 132.1, 129.6, 128.7, 127.2, 125.7, 125.6 (all C_{arom}), 123.6 (q, $^1J_{CF}$ = 286 Hz, CF_3), 124.8 (C_{arom}), 120.5 (C_{arom}), 76.5 (hept, $^2J_{CF}$ = 29.4 Hz, $C(CF_3)_2$), 33.5 (CH_2), 22.7 (CH_3) ppm. Anal. Calcd for $C_{32}H_{24}F_{12}N_2O_2$ (696.53 g·mol^{-1}): C, 55.2; H, 3.5; N, 4.0. Found: C, 54.7; H, 3.4; N, 4.0. ESI-HRMS: *m*/*z* calcd for [M + H]$^+$ 697.17189; found 697.1721 (0 ppm).[31]

(*rac*)-{ONNO}Al(Cl) (1). (*rac*)-{ONNO}H_2 (150 mg, 0.22 mmol) was dissolved in toluene (3 mL) and added dropwise to a solution of $AlEt_2Cl$ (240 μL, 0.22 mmol) in toluene (1.5 mL). The reaction mixture was stirred at 40 °C for 3 h, when a colorless solid precipitated. The solid was isolated by filtration, washed with pentane (3 × 5 mL), and dried *in vacuo* to afford **1** as a colorless powder (150 mg, 92%). ^{1}H NMR (CD_2Cl_2, 213 K, 400.16 MHz): δ 8.08−8.05 (m, 2H, $C_{arom}H$), 8.00 (dd, 2H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 3.0 Hz, $C_{arom}H$), 7.58−7.52 (m, 2H, $C_{arom}H$), 7.39−7.30 (m, 3H, $C_{arom}H$), 7.23 (m, 2H, $C_{arom}H$), 7.14 (d, 1H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 3.06 and 2.68 (AB system, 2H, $^2J_{HH}$ = 16.3 Hz, CH_2), 2.91 and 2.81 (AB system, 2H, $^2J_{HH}$ = 15.0 Hz, CH_2), 1.93 (s, 3H, CH_3), 1.79 (s, 3H, CH_3) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2, 213 K, 376.49 MHz): δ −75.68 (q, $^4J_{FF}$ = 10.3 Hz, CF_3), −76.93 (q, $^4J_{FF}$ = 10.3 Hz, CF_3), −79.28 (q, $^4J_{FF}$ = 9.0 Hz, CF_3), −80.50 (q, $^4J_{FF}$ = 9.0 Hz, CF_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 125.75 MHz): δ 133.38, 132.05, 129.38, 129.18, 127.90, 127.08, 125.88 (all C_{arom}), 30.1 (br, CH_2), 26.3 (br, CH_3) ppm. The resonances for N═*C*, $C(CF_3)_3$, and $C(CF_3)_3$ are not visible at 298 K. Anal. Calcd for $C_{32}H_{22}AlClF_{12}N_2O_2$ (756.94 g·mol^{-1}): C, 50.8; H, 2.9; N, 3.7. Found: C, 50.9; H, 3.0; N, 3.8.

(*rac*)-{ONNO}In(CH_2SiMe_3) (2). (*rac*)-{ONNO}H_2 (200 mg, 0.29 mmol) and In(CH_2SiMe_3)$_3$ (109 mg, 0.29 mmol) were dissolved in 5 mL of THF, and the reaction medium was stirred at 80 °C for 15 h. Evaporation of the volatiles gave a solid, which was washed with pentane (3 × 2 mL) to afford **2** as a colorless powder (170 mg, 66%). ^{1}H NMR (THF-d_8, 213 K, 500.13 MHz): δ 8.17 (d, 1H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 8.13 (d, 1H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 8.06 (d, 2H, $^3J_{HH}$ = 7.9 Hz, $C_{arom}H$), 7.55−7.45 (m, 2H, $C_{arom}H$), 7.36−7.24 (m, 4H, $C_{arom}H$), 7.13 (d, 1H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 7.06 (d, 1H, $^3J_{HH}$ = 8.4 Hz, $C_{arom}H$), 3.07 and 2.58 (AB system, 2H, $^2J_{HH}$ = 14.4 Hz, $CH_2C(CF_3)_2$), 2.93 and 2.54 (AB system, 2H, $^2J_{HH}$ = 14.7 Hz, $CH_2C(CF_3)_2$), 2.07 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 0.13 (s, 9H, Si(CH_3)$_3$), −0.05 and −0.30 (AB system, 2H, $^2J_{HH}$ = 12.0 Hz, InCH_2) ppm. ^{19}F{^{1}H} NMR (THF-d_8, 213 K, 376.49 MHz): δ −75.13 (q, $^4J_{FF}$ = 8.4 Hz, CF_3), −77.73 (q, $^4J_{FF}$ = 9.0 Hz, CF_3), −78.37 (q, $^4J_{FF}$ = 9.0 Hz, CF_3), −79.73 (q, $^4J_{FF}$ = 8.4 Hz, CF_3) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 213 K, 100.25 MHz): δ 184.8 (N═C), 178.2 (N═C), 142.6, 141.7, 133.7, 133.6, 133.0, 132.6, 131.1, 131.0, 129.3 (all C_{arom}), 129.0−123.0 (2 q overlapping with other resonances, CF_3), 128.6, 128.4, 128.2, 127.6, 126.6, 126.5, 126.4, 126.2, 122.7, 122.1 (all C_{arom}), 90.0−79.4 (2 overlapping hept, $C(CF_3)_2$), 41.1 ($CH_2C(CF_3)_2$), 38.1 ($CH_2C(CF_3)_2$), 26.0 (CH_3), 25.0 (CH_3), 2.2 (Si(CH_3)$_3$), 1.2 (InCH_2)

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ppm. Anal. Calcd for $C_{36}H_{33}F_{12}InN_2O_2Si$ (896.54 g·mol^{-1}): C, 49.7; H, 3.8; N, 3.2. Found: C, 49.8; H, 4.3; N, 3.5.

[((*R*)-{ONNO})$_2$Y·Li] (3). (*R*)-{ONNO}H$_2$ (201 mg, 0.29 mmol), Y(N(SiMe$_3$)$_2$)$_3$ (82 mg, 0.14 mmol), and LiN(SiMe$_3$)$_2$ (24 mg, 0.14 mmol) were dissolved in toluene (3 mL) and stirred at 40 °C for 3 h. The volatiles were then pumped off to give a solid, which was washed with pentane (3 × 3 mL) and dried *in vacuo* to afford **3** as a colorless powder (206 mg, 96%). ^{1}H NMR (C_6D_6, 298 K, 500.13 MHz): δ 7.77 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 7.69−7.65 (m, 4H, $C_{arom}H$), 7.61 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.28 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $C_{arom}H$), 7.21−7.11 (m, 4H, $C_{arom}H$), 7.09−7.00 (m, 6H, $C_{arom}H$), 6.95 (m, 2H, $C_{arom}H$), 6.89 (m, 2H, $C_{arom}H$), 3.00 and 2.63 (AX system, 4H, $^2J_{HH}$ = 14.2 Hz, CH_2), 2.44 and 2.29 (AB system, 4H, $^2J_{HH}$ = 16.3 Hz, CH_2), 1.32 (s, 6H, CH_3), 1.20 (s, 6H, CH_3) ppm. ^{19}F{^{1}H} NMR (C_6D_6, 298 K, 376.49 MHz): δ −78.4 (br, CF_3), −77.9 (q, $^4J_{FF}$ = 9.7 Hz, CF_3), −74.9 (br, CF_3), −74.3 (br, CF_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 100.25 MHz): δ 179.7 (N=*C*), 172.0 (N=*C*), 145.8, 145.1, 133.7, 133.5, 132.9, 131.8, 130.4, 129.8, 129.0, 128.9 (all C_{arom}), 127.0−120.9 (4 q overlapping CF_3 + other C_{arom} resonances) 126.9, 126.5, 126.4, 126.0, 125.2, 125.1, 123.5, 123.1, 122.3, 121.2 (all C_{arom}H), 81.0 (2 overlapping hept, $C(CF_3)_2$), 41.3 (CH_2), 40.5 (CH_2), 25.4 (CH_3), 23.3 (CH_3). ^{7}Li NMR (C_6D_6, 298 K, 155.51 MHz): δ 0.86 ppm. Anal. Calcd for $C_{64}H_{44}F_{24}LiN_4O_4Y$ (1484.87 g·mol^{-1}): C, 51.8; H, 3.0; N, 3.8. Found: C, 51.8; H, 3.1; N, 3.8.

■ ASSOCIATED CONTENT

Supporting Information

General experimental procedures; table of X-ray diffraction data; NMR data; full polymerization data; DOSY NMR measurements; MALDI-ToF MS data; ROP kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jean-francois.carpentier@univ-rennes1.fr.
*E-mail: yann.sarazin@univ-rennes1

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1078. (b) *Poly(lactic acid): Synthesis, Structures, Properties, Processing and Applications*; Auras, R.; Lim, L.-T.; Selke, S. E. M.; Tsuji, H., Eds.; John Wiley and Sons Inc.: Hoboken, NJ, 2010.

(2) For reviews, see: (a) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486. (b) Dijkstra, P. J.; Du, H.; Feijen, J. *Polym. Chem.* **2011**, *2*, 520.

(3) (a) Wisniewski, M.; Le Borgne, A.; Spassky, N. *Macromol. Chem. Phys.* **1997**, *198*, 1227. (b) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (c) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (d) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4510. (e) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (f) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291. (g) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026. (h) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343. (i) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433.

(4) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 2290.

(5) Bakewell, C.; White, A. J. P.; Long, N. J.; Williams, C. K. *Inorg. Chem.* **2013**, *52*, 12561.

(6) (a) Wang, H.; Ma, H. *Chem. Commun.* **2013**, *49*, 8686. (b) Honrado, M.; Otero, A.; Fernandez-Baeza, J.; Sanchez-Barba, L. F.; Lara-Sanchez, A.; Tejeda, J.; Caarrion, M. P.; Martinez-Ferrer, J.; Garces, A.; Rodriguez, A. M. *Organometallics* **2013**, *32*, 3437.

(7) Bakewell, C.; Cao, T.-P.-A.; Long, N.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 20577.

(8) Whitelaw, E. L.; Davidson, M. G.; Jones, M. D. *Chem. Commun.* **2011**, *47*, 10004.

(9) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688.

(10) (a) Whitelaw, E. L.; Loraine, G.; Mahon, M. F.; Jones, M. D. *Dalton Trans.* **2011**, *40*, 11469. (b) Hancock, S. L.; Mahon, M. F.; Jones, M. D. *Dalton Trans.* **2013**, *42*, 9279.

(11) For other Al-ligand systems leading to isotactic PLA, see: (a) Bouyahi, M.; Grunova, E.; Marquet, N.; Kirillov, E.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2008**, *27*, 5815. (b) Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2009**, *28*, 1469. (c) Darensbourg, D. J.; Karroonnirun, O.; Wilson, S. J. *Inorg. Chem.* **2011**, *50*, 6775. (d) Normand, M.; Dorcet, V.; Kirillov, E.; Carpentier, J.-F. *Organometallics* **2013**, *32*, 1694.

(12) (a) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. *Chem. Commun.* **2004**, *40*, 330. (b) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169. (c) Amgoune, A.; Thomas, C. M.; Carpentier, J. F. *Macromol. Rapid Commun.* **2007**, *28*, 693. (d) Liu, X. L.; Shang, X. M.; Tang, T.; Hu, N. H.; Pei, F. K.; Cui, D. M.; Chen, X. S.; Jing, X. B. *Organometallics* **2007**, *26*, 2747. (e) Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. *Chem. Commun.* **2010**, *46*, 273. (f) Zhao, W.; Cui, D.; Liu, X.; Chen, X. *Macromolecules* **2010**, *43*, 6678. (g) Zhao, W.; Cui, D.; Liu, X.; Chen, X. *Macromolecules* **2010**, *43*, 6678. (h) Nie, K.; Gu, X.; Yao, Y.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2010**, *39*, 6832. (i) Dyer, H. E.; Huijser, S.; Susperregui, N.; Bonnet, F.; Schwarz, A. D.; Duchateau, R.; Maron, L.; Mountford, P. *Organometallics* **2010**, *29*, 3602. (j) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. *Chem.—Eur. J.* **2011**, *17*, 1872. (k) Nie, K.; Fang, L.; Yao, Y.; Zhang, Y.; Shen, Q.; Wang, Y. *Inorg. Chem.* **2012**, *51*, 11133.

(13) (a) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem.* **2006**, *118*, 7982. (b) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328.

(14) For other heteroselective ROP initiators, see ref 5 and: (a) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583. (b) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (c) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Chem. Commun.* **2003**, 48. (d) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280. (e) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293. (f) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115. (g) Pietrangelo, A.; Knight, S. C.; Gupta, A. K.; Yao, L. J.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2010**, *132*, 11649. (h) Cushion, M. G.; Mountford, P. *Chem. Commun.* **2011**, *47*, 2276. (i) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2011**, *50*, 7718. (j) Yang, S.; Nie, K.; Zhang, Y.; Xue, M.; Yao, Y.; Shen, Q. *Inorg. Chem.* **2014**, *53*, 105. (k) Bakewell, C.; Cao, T.-P.-A.; Le Goff, X. F.; Long, N. J.; Auffrant, A.; Williams, C. K. *Organometallics* **2013**, *32*, 1475. (l) Mou, Z.; Liu, B.; Liu, X.; Xie, H.; Rong, W.; Li, L.; Li, S.; Cui, D. *Macromolecules* **2014**, *47*, 2233.

(15) (a) Du, H.; Velders, A. H.; Dijkstra, P. J.; Sun, J.; Zhong, Z.; Chen, X.; Feijen, J. *Chem.—Eur. J.* **2009**, *15*, 9836. (b) Buffet, J.-C.; Kapelski, A.; Okuda, J. *Macromolecules* **2010**, *43*, 10201. (c) Buffet, J.-

C.; Okuda, J. *Chem. Commun.* **2011**, *47*, 4796. (d) Buffet, J.-C.; Okuda, J. *Polym. Chem.* **2011**, *2*, 2758. (e) Kapelski, A.; Buffet, J.-C.; Spaniol, T. P.; Okuda, J. *Chem.—Asian J.* **2012**, *7*, 1320.
(16) (a) Lavanant, L.; Chou, T.-Y.; Chi, Y.; Lehmann, C. W.; Toupet, L.; Carpentier, J.-F. *Organometallics* **2004**, *23*, 5450. (b) Carpentier, J.-F. *Dalton Trans.* **2010**, *39*, 37 and references therein.
(17) (a) Normand, M.; Kirillov, E.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2012**, *31*, 1448. (b) Bouyahyi, M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2012**, *31*, 1458.
(18) See the Supporting Information for details.
(19) The reaction is essentially quantitative. The lower isolated yield in the In-alkyl complex **2** in comparison with the other two complexes **1** and **3** is simply due to its much greater solubility in hydrocarbons, probably resulting in substantial losses during washings with pentane.
(20) Dyer, H. E.; Huijser, S.; Schwarz, A. D.; Wang, C.; Duchateau, R.; Mountford, P. *Dalton Trans.* **2008**, 32.
(21) Evans, W. J.; Shreeve, J. L.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1995**, *501*, 7.
(22) (a) Li, D.; Keresztes, I.; Hopson, R.; Williard, P. G. *Acc. Chem. Res.* **2009**, *42*, 270. (b) Kagan, G.; Li, W.; Li, D.; Hopson, R.; Williard, P. G. *J. Am. Chem. Soc.* **2011**, *133*, 6596.
(23) P_r, the probability of a *racemic* enchainment between two consecutive LA units, is the measure of heterotacticity. P_r is determined by examination of the methine region of the homodecoupled ^{1}H NMR spectrum. (a) Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, J. I.; Munson, E. J. *Macromolecules* **1997**, *30*, 2422. (b) Chisholm, M. H.; Iyer, S. S.; Matison, M. E.; McCollum, D. G.; Pagel, M. *Chem. Commun.* **1997**, 1999.
(24) Maudoux, N.; Roisnel, T.; Dorcet, V.; Carpentier, J.-F.; Sarazin, Y. *Chem.—Eur. J.* **2014**, *20*, 6131.
(25) Conditions: $[\text{lactide}]_0$ = 0.8 M in THF-d_8, $[\text{lactide}]_0/[\mathbf{3}]_0$ = 200:1, T = 30 °C.
(26) Wang, L.; Bochmann, M.; Cannon, R. D.; Carpentier, J.-F.; Roisnel, T.; Sarazin, Y. *Eur. J. Inorg. Chem.* **2013**, 5896.
(27) Comparison of entries 1 and 2 in Table S5 shows that when the reaction is carried out for an unduly long time after complete monomer conversion, P_m decreases from 0.91 to 0.85 and the PDI increases. Besides, the analogous reaction carried out under more controlled conditions at 40 °C for only 1.5 h yields a polymer featuring P_m = 0.94 in 96% yield.
(28) Note that the addition of 1 equiv of BnOH co-initiator to **3** suppresses all ROP catalytic activity.
(29) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.
(30) (a) Sheldrick, G. M. *SHELXS-97, Program for the Determination of Crystal Structures*; University of Goettingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Goettingen: Germany, 1997.
(31) The *racemic* (*rac*)-{ONNO}H_2 was obtained similarly and gave identical spectral and analytical data.

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