

# Bimetallic Aluminum Complexes Bearing Binaphthyl-Based Iminophenolate Ligands as Catalysts for the Synthesis of Polyesters

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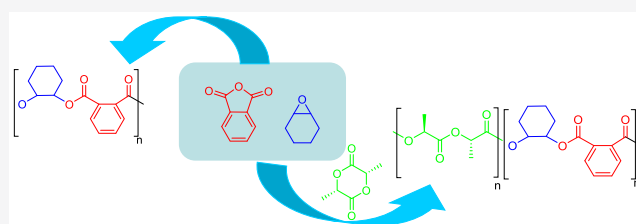
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**ABSTRACT:** Two dinuclear aluminum complexes bearing dinaphthalene bridging Schiff bases have been synthesized and investigated as catalysts in ring-opening polymerization (ROP) of cyclic esters such as *rac*-lactide (*rac*-LA) and  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and in the copolymerization (ROCOP) of phthalic anhydride (PA) with cyclohexene oxide (CHO) and limonene oxide (LO). The polymerizations of cyclic esters were living, producing polymers with narrow molar mass distributions. Kinetic studies showed that the polymerizations were first order with respect to the monomers. Cooperative effects between two metal centers, located in proximal positions, are invoked to rationalize the high activities toward both monomers, although the rigid backbone of the complexes enhances the reactivity of less encumbered caprolactone in comparison to lactide. Good activities were achieved also in the copolymerization of phthalic anhydride with cyclohexene epoxide and with the bioderived limonene oxide.



## INTRODUCTION

In the last two decades, synthetic aliphatic polyesters, because of their biodegradability and their efficient barrier properties, have attracted much interest as materials alternative to the oil-derived polymers.<sup>1–3</sup> The traditional synthetic route to produce commodity polyesters is the step-growth copolymerization of diols with diacid or diesters.<sup>4</sup> However, because of the drastic reaction conditions, the control degree over the polymerization process is generally low; thus this method is not adequate for the production of sophisticated polymeric architectures. Alternatively, these materials can be synthesized via ring-opening polymerization (ROP) of cyclic esters.<sup>5</sup> This method offers the advantage of an accurate control over the structures of the produced polymers,<sup>6,7</sup> but the restricted chemical and structural diversity of available monomers confines the properties of obtained materials within limited ranges.

Recently, the alternating ring-opening copolymerization (ROCOP) of cyclic anhydrides with epoxides has been emerging as a powerful alternative synthetic strategy to structurally diverse polyesters.<sup>8,9</sup> The accessibility of two distinct monomer libraries allows for the synthesis of materials with properties and functionalities not accessible by the strict ROP of lactones.

In 2014, Williams et al. described the first example of a single catalyst able to switch between these two distinct polymerization processes, selectively producing block polyesters by a new type of chemoselective control.<sup>10</sup> The possibility to combine ROP and ROCOP into a single

synthetic procedure allows extension to infinity the range of materials that can be obtained.<sup>11–13</sup> For example, polyether–polyester copolymers<sup>13</sup> have been obtained by chemoselective processes promoted by a single catalytic system.

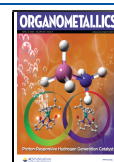
While a plethora of metal complexes, most of them based on phenoxy-based ligands,<sup>14–22</sup> have been reported as efficient catalysts for the ROP of cyclic esters,<sup>23,24</sup> a much lower number has been described for the ROCOP of epoxides<sup>25</sup> and anhydrides, and the examples of metal catalysts that are active in both catalytic processes are even less numerous.<sup>26,27</sup>

Among these, multinuclear catalysts showed the most interesting results.<sup>28,29</sup> Because of cooperative effects between reactive centers,<sup>30–34</sup> unexpected activities<sup>31–33,35–38</sup> and selectivity<sup>35</sup> have been often observed.<sup>39–43</sup>

In a previous work we reported that dinuclear salen aluminum complexes are efficient catalysts for the polymerization of cyclic esters and the copolymerization of epoxides and anhydrides.<sup>44–46</sup> These studies revealed that the distance between the coordinative pockets that host the aluminum atoms is a crucial parameter to have cooperation between them. Several papers put in evidence that higher ROP activities

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were found for dialuminum complexes with Al–Al distances in the range 5.8–6.6 Å.<sup>30,32</sup>

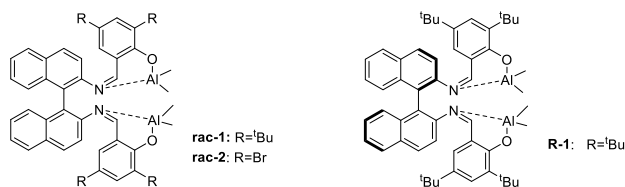
In this work we extended this study introducing a binaphthyl rigid bridge between the two imine functionalities with the aim to force the two reactive centers into coordinative environments conformationally inflexible at opportune distance from one another.

## RESULTS AND DISCUSSION

**Synthesis of the Aluminum Complexes.** Two salen proligands were synthesized by condensation of the racemic ( $\pm$ )-1,1'-bi(2-naphthylamine) with salicyl aldehydes bearing different substituents (<sup>t</sup>Bu and Br) on the *ortho* and *para* positions of the phenoxy ring. The reactions were performed in absolute ethanol according to the literature.<sup>47</sup> A chiral proligand was also prepared by using (*R*)-1,1'-bi(2-naphthylamine).

The reactions between the salen proligands and 2 equiv of AlMe<sub>3</sub> afforded the desired bimetallic aluminum alkyl complexes [L–Al<sub>2</sub>Me<sub>4</sub>] in almost quantitative yields (Scheme 1). The complexes were all soluble in *n*-hexane, toluene, and tetrahydrofuran. They were characterized by multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, COSY, and NOESY).

### Scheme 1. Structures of Complexes *rac-1*, *rac-2*, and *R-1*

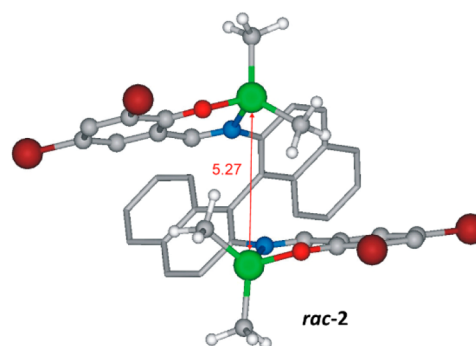


In the <sup>1</sup>H NMR spectra, the disappearance of the O–H signal of the proligands and the appearance of sharp singlets in the high-field region (between  $\delta$  –1.75 and –0.65 ppm), assigned to 12 protons of the diastereotopic methyls bound to Al centers, demonstrated the formation of the desired complexes. Diagnostic resonances in the low-field region of protonic spectra include singlets ( $\delta$  7.82 and 7.23 ppm) for the equivalent imine protons. A single set of signals for the two phenolate and the CH=N moieties point to C<sub>2</sub>-symmetric structures in solution. All data were consistent with the presence of two aluminum atoms per ancillary ligand.

To estimate the distance between metals in these bimetallic species, the minimum energy structure of *rac-2* was located by DFT calculations (computational details are reported in the Supporting Information). As reported in Figure 1, a distance of 5.27 Å was obtained, a value coherent with the optimal range of Al–Al distances to have cooperative effects

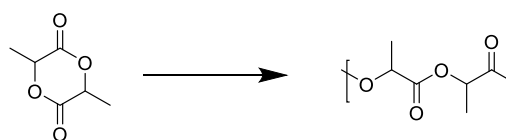
**Polymerization of Lactides.** Complexes *rac-1*, *rac-2*, and *R-1* were tested as catalysts for the ROP of *rac*-LA (Scheme 2). All polymerization reactions were performed at 70 °C in toluene solution. Representative results are summarized in Table 1.

Initially, the complex *rac-1* was tested as a catalyst in the ROP of *rac*-LA showing a very low activity: the quantitative conversion of the monomer was achieved only after 5 days at 70 °C (run 1, Table 1). The molecular masses of the obtained polymer showed a monomodal distribution with narrow dispersity and values coherent with the formation of a single polymer chain for the catalyst unit.



**Figure 1.** Minimum energy structure of *rac-2* by DFT calculations. The Al–Al distance is given in Å. Hydrogens, except for methyls, are omitted for clarity.

### Scheme 2. Polymerization of Lactide



This poor activity suggested a very slow initiation step because of the scarce nucleophilicity of the alkyl group as an initiating group. In fact, when the polymerization of *rac*-LA was carried out in the presence of isopropyl alcohol,<sup>48</sup> the activity increased significantly (run 2 of Table 1) and a conversion of 160 equiv of monomer was achieved until 14 h (run 3 of Table 1). In this case the molecular mass values were lower and were in agreement with the amount of added alcohol. Subsequently, to evaluate the degree of control over the molecular masses, different polymerization experiments were performed, changing the amount of alcohol or the amount of monomer (runs 3–6 of Table 1). In all cases, the molecular masses of the obtained polymers were in good agreement with the [LA]/[<sup>i</sup>PrOH] ratio.

In terms of activity, complex *rac-1* showed a high turnover frequency (TOF) of 11.2 h<sup>–1</sup>, comparable to that achieved with a bimetallic complex bearing an *n*-propyl backbone.<sup>44</sup> The hypothesis of a bimetallic cooperativity may be supported by comparison with the activities of related phenoxy-imine aluminum monometallic complexes already reported in the literature.<sup>31</sup> The same activity was showed by the chiral form of complex *R-1* (run 7 of Table 1), while a slightly higher activity (TOF = 13.4 h<sup>–1</sup>), was obtained with complex *rac-2*, in which electron-withdrawing substituents were introduced on the phenoxy rings of the ancillary proligand (compare run 8 vs run 9 of Table 1).

The microstructures of the resulting obtained PLAs were determined by the analysis of the methine regions of the homonuclear decoupled <sup>1</sup>H NMR spectra.<sup>49,50</sup> The spectrum of the poly(*rac*-LAs) obtained by *rac-1* and *rac-2* (runs 8 and 9, Table 1) indicated an atactic microstructure with *P<sub>m</sub>* = 57% (where *P<sub>m</sub>* is the probability of a *meso* linkage between lactide units).<sup>51</sup> The same tacticity was observed in the case of the PLA obtained by the chiral complex *R-1* (run 7, Table 1).

It is well-known that the alcohol plays a dual role in the ROP of cyclic esters: it can cause the alcoholysis of the Al–methyl bonds to form the related alkoxide derivative, and at the same time, when it is in excess, it can act as a chain transfer agent to promote an “immortal” process, allowing the production of

Table 1. Polymerization of Lactide Promoted by *rac*-1, *R*-1, and *rac*-2<sup>a</sup>

run	cat.	[LA]/[cat.]	<sup>i</sup> PrOH (equiv)	time (h)	conversn (%)	TOF (h <sup>-1</sup> )	M <sub>n</sub> <sup>GPC</sup> (KDa) <sup>b</sup>	M <sub>n</sub> <sup>th</sup> (KDa) <sup>c</sup>	D <sup>b</sup>
1	<i>rac</i> -1	100		168	100		15.5	14.4	1.18
2	<i>rac</i> -1	100	4	24	97	4.0	3.9 <sup>d</sup>	3.6	nd
3	<i>rac</i> -1	200	4	14	78	11.2	4.8	4.6	1.14
4	<i>rac</i> -1	200	3	24	97	8.0	9.1	9.3	1.13
5	<i>rac</i> -1	200	1	48	99	4.2	26.6	28.8	1.11
6	<i>rac</i> -1	300	3	24	94	12.0	14.0	13.0	1.11
7	<i>R</i> -1	200	4	14	79	11.2	6.0	5.6	1.08
8	<i>rac</i> -1	200	4	10	54	10.8	4.1	3.9	1.03
9	<i>rac</i> -2	200	4	10	68	13.4	6.4	4.9	1.07
10	<i>rac</i> -1 ( <sup>t</sup> OPr)	100		12	97	8.1	14.7	13.2	1.06

<sup>a</sup>All reactions were carried out at 70 °C with 10 μmol of cat. in toluene (2 mL). <sup>b</sup>Experimental M<sub>n</sub> (corrected using a factor of 0.58) and D values were determined by GPC analysis in THF using polystyrene standards. <sup>c</sup>Calculated M<sub>n</sub> (KDa) = 144.14([LA]/[<sup>i</sup>PrOH]) × conversion of LA. <sup>d</sup>Estimated by <sup>1</sup>H NMR.

several polymer chains per metal center. To rationalize this point, the alkoxide aluminum derivative was purposely synthesized by alcoholysis of alkyl precursor *rac*-1 with 4 equiv of 2-propanol. The reaction, performed in C<sub>6</sub>D<sub>6</sub> and monitored by <sup>1</sup>H NMR spectroscopy, was revealed to be very slow. The exhaustive alcoholysis of all the methyl groups was achieved only after 24 h (see the experimental details in the Supporting Information). Subsequently the isopropoxide derivative was tested as a catalyst in the polymerization of *rac*-LA under the reaction conditions described in Table 1 (run 10, Table 1). The molecular masses of PLA obtained, evaluated by NMR analysis and GPC analysis, indicated the formation of a single polymer chain for the catalyst unit. This was already observed for a similar bimetallic aluminum complex bearing an *n*-propyl bridge between the imine functionalities because of the high steric encumbrance of the active sites, in combination with a chelation effect between the two aluminum centers by the O-lactate propagating species (see Figure S21 in the Supporting Information).<sup>44</sup>

These observations suggest that the alcoholysis of the complex is slow in comparison to the propagation rate of the polymerization reaction; thus, it is reasonable to suppose that, after the alcoholysis of the first alkyl group of the aluminum complex *rac*-1, the polymerization can start and the residual alcohol acts simply as a chain transfer agent. However, a monomer-activated ROP mechanism cannot be excluded.

Additional information about the polymerization mechanism were obtained by kinetic investigations. For complex *rac*-1, kinetic studies showed that the polymerization of *rac*-LA obeyed first-order kinetics in monomer with instantaneous initiation and with  $k_{app} = 0.148 \text{ h}^{-1}$  (Figure 2).

**Polymerization of Heterocyclic Monomers.** Complexes *rac*-1 and *rac*-2 were tested as catalysts for the ROP of lactones such as  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and  $\beta$ -butyrolactone ( $\beta$ -BL) and of epoxides such as cyclohexene oxide (CHO) and propylene oxide (PO) (Scheme 3). All polymerization reactions were performed under the reaction conditions optimized for ROP of lactide. Representative results are summarized in Table 2.

In the ROP of  $\epsilon$ -CL (see runs 1 and 2, Table 2), both complexes showed very high activity. At 70 °C, the turnover frequency (TOF) was higher than 6000 h<sup>-1</sup> for the complex *rac*-2.

This activity is significantly higher than those of related monometallic complexes.<sup>18</sup> Considering the well-known scarce activity of aluminum catalysts, we were delighted to observe a

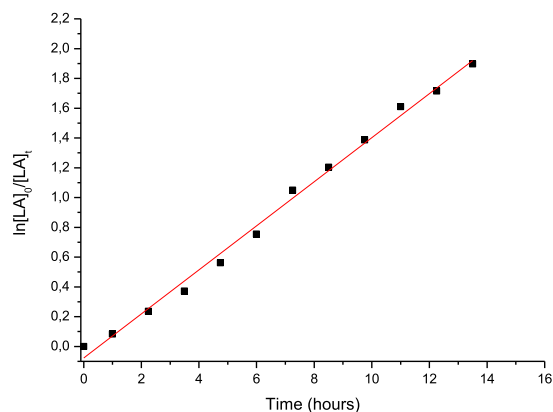
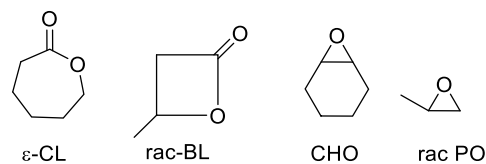


Figure 2. Kinetic plot for ROP of *rac*-LA promoted by *rac*-1 depicting a reaction order of unity with respect to monomer concentration. The pseudo-first-order rate constant is  $k_{app} = 0.148 \text{ h}^{-1}$  ( $R^2 = 0.9939$ ). Reaction conditions: [cat.] = 0.01 M; [LA]/[cat.] = 100;  $T = 343 \text{ K}$ ; 0.5 mL of toluene-*d*<sub>8</sub> as solvent.

### Scheme 3. Monomers Investigated in This Work



good activity even at room temperature with a TOF of 106 h<sup>-1</sup> (run 3, Table 2). A few other examples have been recently reported.<sup>20,52</sup>

These very good activities are due to an efficient cooperation between the two reactive centers of the dinuclear complexes enhanced by the rigid architecture of the binaphthyl bridge that forces the two coordinative pockets in proximal and fixed positions. Reasonably, this effect is more advantageous for ROP of caprolactone in comparison to lactide, because of less encumbrance of the monomer and higher flexibility of the growing polymer chain.

The polymerization process was generally well controlled, as evidenced by narrow distributions of the molecular weights with dispersities lower than 1.18 and by the good agreement between the experimental molecular masses and the theoretical values (calculated on the basis of the equivalents of alcohol added).

Table 2. Polymerizations of Heterocyclic Monomers Promoted by *rac-1* and *rac-2*<sup>a</sup>

run <sup>a</sup>	cat.	mon (equiv)	T (°C)	<sup>i</sup> PrOH (equiv)	time (min)	conversion (%)	TOF (h <sup>-1</sup> )	M <sub>n</sub> <sup>GPC</sup> (KDa) <sup>b</sup>	M <sub>n</sub> <sup>th</sup> (KDa) <sup>c</sup>	D <sup>b</sup>
1	<i>rac-1</i>	$\epsilon$ -CL (500)	70	4	5	88	5280	21.9	14.3	1.13
2	<i>rac-2</i>	$\epsilon$ -CL (500)	70	4	5	100	6000	17.0	14.3	1.12
3	<i>rac-1</i>	$\epsilon$ -CL (500)	25	4	240	85	106	14.4	12.1	1.11
4	<i>rac-1</i>	$\beta$ -BL (100)	70	4	9000	30	2			
5 <sup>d</sup>	<i>rac-1</i>	CHO (250)	70	4	10	92	1350	6.2	5.6	1.23
6	<i>rac-1</i>	CHO (250)	25	4	900	85	14	11.3	5.2	1.81

<sup>a</sup>All reactions were carried out with 10  $\mu$ mol of *rac-1* in toluene (2 mL). <sup>b</sup>Experimental M<sub>n</sub> (corrected using factor of 0.56 for PCL) and D values were determined by GPC analysis in THF using polystyrene standards. <sup>c</sup>Calculated M<sub>n</sub> (KDa) = MM<sub>monomer</sub>  $\times$  ([Monomer]/[<sup>i</sup>PrOH])  $\times$  conversion of monomer. <sup>d</sup>Solvent free.

As expected, kinetics studies, performed at 70 °C, showed that the polymerization rate had a first-order dependence on the monomer concentration (Figure 3).<sup>53</sup> At room temper-

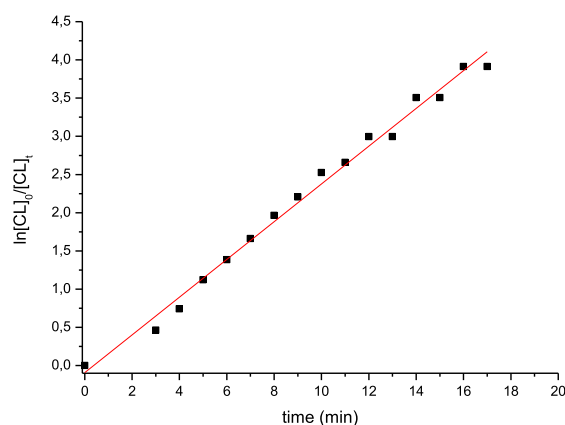


Figure 3. Kinetic plot for ROP of  $\epsilon$ -CL by *rac-1* depicting a reaction order of unity with respect to monomer concentration. The pseudo-first-order rate constant is  $K_{app} = 0.245 \text{ min}^{-1}$  ( $R^2 = 0.9903$ ). Reaction conditions: [*rac-1*] = 0.01 M; [ $\epsilon$ -CL]/[*rac-1*] = 100;  $T = 343 \text{ K}$ ; 0.5 mL of toluene- $d_8$  as solvent.

ature, the reaction showed an induction time of about 90 min (Figure 4). After this time, as shown by the second stage of the plot, the conversion of the monomer describes a polymerization that was first order in monomer concentration with a  $k_{app}$  value of  $0.0155 \text{ min}^{-1}$ . The existence of an induction

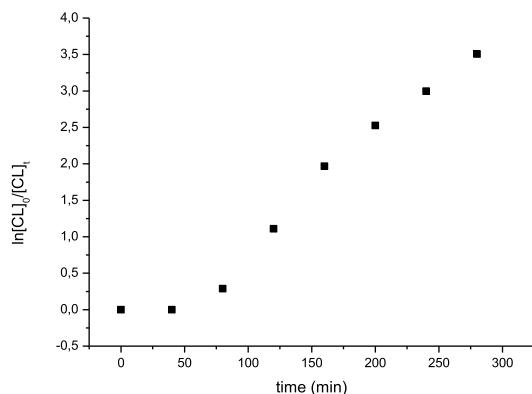


Figure 4. Kinetic plot for ROP of  $\epsilon$ -CL by *rac-1* depicting a reaction order of unity with respect to monomer concentration after the initial induction period. The pseudo-first-order rate constant is  $K_{app} = 0.0155 \text{ min}^{-1}$  ( $R^2 = 0.985$ ). Reaction conditions: [*rac-1*] = 0.01 M; [ $\epsilon$ -CL]/[*rac-1*] = 100;  $T = 298 \text{ K}$ ; toluene- $d_8$  as solvent.

period is due to a slow reaction between the isopropyl alcohol and the metal complex, in agreement with that observed by an NMR study of the alcoholysis reaction.

In the ROP of  $\beta$ -BL the activity of complex *rac-1* was extremely low; after 15 h the conversion of only 30 equiv of monomer was observed (run 4, Table 2). The presence of isopropoxide chain end groups was observed by NMR analysis and allowed us to estimate the molecular masses of the obtained sample (see Figures S7 and S8).

Since the polymerization of epoxides follows a bimetallic pathway,<sup>54,55</sup> we extended the use of these catalysts to the ROP of epoxides.

In the ROP of cyclohexene oxide (CHO), complex *rac-1* showed a very high activity when the reaction was performed in bulk (run 5, Table 2), while the monomer conversion dropped dramatically when the reaction was performed in toluene solution (run 6, Table 2).

The microstructure of the obtained poly(1,2-cyclohexene oxide) was investigated by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In the <sup>1</sup>H NMR spectrum, the presence of three peaks ( $\delta$  3.52, 3.39, and 3.36 ppm), attributable to syndiotactic (*rr*), heterotactic (*mr* and *rm*), and isotactic (*mm*) triads of the methine protons suggests a stereoirregular microstructure. Correspondingly, three main signals were found in the <sup>13</sup>C NMR spectrum for the methine carbons at  $\delta$  80.0, 78.7, and 75.6 ppm.

In the polymerization of propylene oxide (PO), both catalysts failed to enable isolation of any significant quantity of polymer, even after prolonged reaction times and performance of the reactions up to 60 °C. Although there are several examples of aluminum complexes, especially cationic species, that are reported as active catalysts for PO polymerization,<sup>56</sup> the complexes described did not show any activity.

**Copolymerizations of Cyclohexene Oxide with Cyclic Esters and/or Phthalic Anhydride.** Subsequently, complex *rac-1* was tested in the copolymerization of CHO with cyclic esters.

In the CHO/ $\epsilon$ -CL copolymerization, after 10 min, a complete conversion of  $\epsilon$ -CL was achieved but, despite the high activity observed in the related homopolymerizations, no reaction of CHO was observed within 2 h (run 1, Table 3). Similarly, in the copolymerization of CHO with L-LA, a complete conversion of the cyclic ester was obtained after 18 h. In both cases, no evidence of incorporation of cyclohexene oxide in the polyester sequences was observed, i.e., no ether linkages, or a separate polyether was observed (run 2, Table 3). These results were in agreement with those previously obtained by Williams, who revealed that the chemical nature of the metal–polymer chain end group plays a central role in

Table 3. Copolymerization Tests Promoted by *rac-1*<sup>a</sup>

run	CHO (equiv)	Mon (equiv)	cocat. (equiv)	time (h)	T (°C)	conversion <sub>CHO</sub> (%)	conversion <sub>Mon</sub> (%)	ester (%)	M <sub>n</sub> <sup>GPC</sup> (KDa) <sup>b</sup>	M <sub>n</sub> <sup>th</sup> (KDa) <sup>c</sup>	Đ <sup>b</sup>
1	CHO (250)	ε-CL (500)	<sup>1</sup> PrOH (4)	2	70		>99		12.7	14.3	1.17
2	CHO (250)	L-LA (200)	<sup>1</sup> PrOH (4)	24	70		>99		8.3	7.02	1.04
3	CHO (100)	PA (100)	PPNCl (1)	7	110	>99	75	81	9.6	20.9	1.30
4	CHO (100)	PA (100)	PPNCl (2)	4	110	55	53	>99	2.6	6.8	1.11
5	CHO (100)	PA (50)	PPNCl (2)	4	110	51	>99	>99	2.4	6.2	1.17
6	CHO (100)	PA/LA (50/50)	PPNCl (2)	24	110	53	>99	>99	6.1	9.8	1.44

<sup>a</sup>All reactions were carried out with 10 μmol of *rac-1*, with  $[rac-1]_0/[^1PrOH] = 1/4$  in toluene (2 mL). <sup>b</sup>Experimental M<sub>n</sub> (corrected using a factor of 0.56 for PCL and 0.58 for PLA) and Đ values were determined by GPC analysis in THF using polystyrene standards. <sup>c</sup>Calculated M<sub>n</sub> =  $[MM_{CHO} \times ([CHO]/[Cocat]) \times \text{conversion of CHO} + MM_{monomer} \times ([Monomer]/[Cocat]) \times \text{conversion of monomer}]$ .

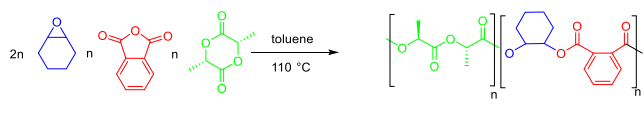
controlling the monomer selectivity, from a complex mixture, during polymerization.<sup>10</sup>

Subsequently, we explored the catalytic behavior of complex *rac-1* in the ROCOP of CHO with phthalic anhydride (PA). The copolymerization reaction CHO/PA was performed at 110 °C in toluene solution, in the presence of 1 equiv of bis(triphenylphosphine)iminium chloride (PPNCl) as cocatalyst and with an epoxide/anhydride/catalyst ratio of 100/100/1. Under these conditions, after 7 h, complex *rac-1* produced a poly(ester-ether), with 81% of ester functionalities (run 3, Table 3).<sup>57</sup>

When the amount of cocatalyst was increased, no significant effect in terms of activity was observed, but the selectivity improved substantially, producing a polyester with a perfect alternating structure (run 4, Table 3), even though there was a significant reduction of the molecular masses probably because of its behavior as a chain transfer agent. Similar effects were previously observed by Duchateau.<sup>58</sup>

Finally, we explored the possibility of promoting a combined ROP/ROCOOP catalysis. A ter-polymerization experiment was performed in the presence of equal amounts of phthalic anhydride (PA) and L-LA (50 equiv) and an excess of cyclohexene oxide (100 equiv) (Scheme 4). For comparison a

Scheme 4. ROCOP/ROP from a Mixture of CHO, PA, and L-LA

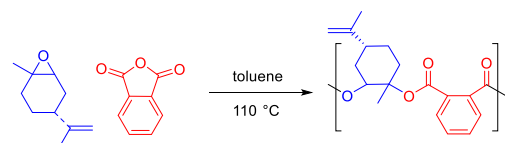


ROCOOP experiment was performed by using the same amounts of CHO and PA (runs 5 and 6, Table 3). After 24 h, the diblock copolymer poly(cyclohexene phthalate)-*co*-polylactide was obtained, as demonstrated by the <sup>1</sup>H NMR and DOSY analysis (Figures S11 and S12 in the Supporting Information). As expected, the molecular masses showed a monomodal distribution and were higher than those obtained for the control experiment, preserving a low dispersity (Figure S13 in the Supporting Information).

As previously observed for analogous systems,<sup>46</sup> complex *rac-1* showed the ability to selectively promote the copolymerization of CHO/PA followed by the ROP of lactide.

**Copolymerizations of Limonene Oxide with Cyclic Esters and/or Phthalic Anhydride.** Successively, the catalytic behavior of complex *rac-1* in the ROCOP of (+)-LO with phthalic anhydride (PA) was explored (Scheme 5). The copolymerization reactions were performed at 110 °C

Scheme 5. Synthesis of Polyesters from Phthalic Anhydride (PA) and Limonene Oxide (LO)



in 1 mL of toluene, in the presence of bis-(triphenylphosphine)iminium chloride (PPNCl) or 4-dimethylaminopyridine (DMAP) as a cocatalyst at different epoxide/anhydride/catalyst/cocatalyst ratios. In order to improve the molecular weight and the glass transition temperature (*T<sub>g</sub>*) of the poly(LO-*co*-PA), a precontact between the catalyst and cocatalyst was performed.<sup>59</sup>

The results of the performance of complex *rac-1* in the ROCOP of (+)-LO with phthalic anhydride (PA) and thermal and molecular properties are reported in Table 4.

Table 4. Copolymerization Results of LO and PA Promoted by *rac-1*<sup>a</sup>

run	cocat.	cat./cocat.	yield (%) <sup>d</sup>	M <sub>n</sub> (KDa) <sup>b</sup>	Đ <sup>b</sup>	T <sub>g</sub> (°C) <sup>c</sup>
1	DMAP	1/1	40.5	6.9	1.19	116
2	PPNCl	1/1	58.9	8.5	1.26	121
3	DMAP	0.5/1	63.6	9.0	1.26	117
4	PPNCl	0.5/1	81.8	9.2	1.28	125
5	DMAP	0.5/0.5	57.8	6.6	1.22	124
6	PPNCl	0.5/0.5	36.2	5.7	1.23	118
7	DMAP	1/2	84.7	7.7	1.21	127
8	PPNCl	1/2	85.6	8.1	1.27	128

<sup>a</sup>All reactions were carried out with 10 μmol of *rac-1*. <sup>b</sup>Experimental M<sub>n</sub> and Đ values were determined by GPC analysis in THF using polystyrene standards, precontact step 1 h, polymerization time 48 h, and an epoxide/anhydride ratio of 250/250, *T<sub>g</sub>* determined by Differential Scanning Calorimetry (DSC) analysis performed using cyclic heating and cooling rates of 20 °C per minute and heated from 20 to 200 °C. <sup>c</sup>The values of glass transition temperature *T<sub>g</sub>* were recorded during the second thermal cycle. <sup>d</sup>The yield (%) was calculated as  $\frac{\text{yield(g)}}{\text{g(LO)} + \text{g(PA)}} \times 100$ .

As reported in the literature for the salen-type catalysts,<sup>60</sup> PPNCl gives the best performance in terms of yield as well as in terms of molecular masses and thermal properties, except for the ratio catalyst/cocatalyst = 0.5/0.5.

No signals attributable to the ethereal LO–LO bond have been detected in the <sup>1</sup>H NMR spectra, as expected for the bulky nature of LO.

## CONCLUSIONS

Salen-type frameworks containing dinaphthaleneimine bridge were selected to prepare dinuclear aluminum complexes to feature two metal sites allocated in rigid coordinative pockets at an opportune distance from one another. All complexes, activated by isopropyl alcohol, promoted controlled homopolymerizations of lactide, caprolactone, and cyclohexene oxide, showing different activities depending on the nature of the substituents in the phenoxy moieties. The high activities achieved support the hypothesis of metallic cooperativity that is more efficient for a monomer with less encumbrance and/or a more flexible growing chain. Additionally, such complexes were revealed to be active in the copolymerization of phthalic anhydride with cyclohexene oxide and limonene oxide and in the terpolymerization of these monomers with lactide to produce diblock polyesters.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster glovebox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

**Reagents and Solvents.** Benzene, hexane, and toluene (Sigma-Aldrich) were distilled under nitrogen over sodium benzophenone. The aluminum precursor  $\text{AlMe}_3$  was purchased from Aldrich and was used as received. Deuterated solvents were dried over molecular sieves.  $\epsilon$ -Caprolactone, cyclohexene oxide were purchased from Aldrich, freshly distilled from  $\text{CaH}_2$  under nitrogen, and degassed thoroughly by freeze–vacuum–thaw cycles prior to use. *rac*-lactide and *L*-lactide were purchased from Aldrich, dried in vacuo over  $\text{P}_2\text{O}_5$  for 72 h, and stored afterward at –20 °C in a glovebox.  $\text{PPNCl}$  was dissolved in dichloromethane and precipitated with diethyl ether twice. DMAP was crystallized by toluene. All other chemicals were commercially available and were used as received unless stated otherwise.

**NMR Analysis.** The NMR spectra were recorded on Bruker Advance 300, 400, and 600 MHz spectrometers at 25 °C, unless stated otherwise. Chemical shifts ( $\delta$ ) are expressed as parts per million and coupling constants (*J*) in hertz.  $^1\text{H}$  NMR spectra are referenced using the residual solvent peak at  $\delta$  7.16 for  $\text{C}_6\text{D}_6$  and  $\delta$  7.27 for  $\text{CDCl}_3$ .  $^{13}\text{C}$  NMR spectra are referenced using the residual solvent peak at  $\delta$  128.06 for  $\text{C}_6\text{D}_6$  and  $\delta$  77.23 for  $\text{CDCl}_3$ .

**Synthesis of Proligands *rac*-L1 and *rac*-L2.** Both proligands were synthesized by modifying a procedure previously reported in the literature.<sup>61</sup> In a 100 mL two-neck round-bottom flask equipped with a reflux condenser, to a stirred solution containing *rac*-1,1'-binaphthyl-2,2'-diamine (0.510 g, 1.76 mmol) in ethanol (50 mL) was added 2 equiv (3.54 mmol) of the opportune aldehyde (3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 0.825 g; 3,5-dibromo-2-hydroxybenzaldehyde, 0.991 g). The solution was stirred at reflux for 12 h. The solid products were isolated by filtration and washed with fresh ethanol. Yields: 86% for *rac*-L1 and 84% for *rac*-L2.

***rac*-L1.**  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  13.23 (s, 2H), 8.31 (s, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 2.1 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 6.9 Hz, 2H), 6.88 (d, *J* = 2.2 Hz, 2H), 1.40 (s, 18H), 1.23 (s, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  163.2, 158.9, 144.3, 139.9, 136.9, 133.9, 133.0, 130.1, 129.8, 127.3, 127.1, 126.9, 126.0, 118.9, 117.7, 35.2, 34.1, 31.6, 29.5.

***rac*-L2.**  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  13.12 (s, 2H), 7.75 (s, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 2.1 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 6.9 Hz, 2H), 6.55 (d, *J* = 2.1 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  164.2, 157.3, 144.2, 139.5,

137.9, 132.7, 133.0, 130.7, 129.8, 127.3, 127.1, 126.3, 125.0, 118.4, 115.5.

**Synthesis of Proligand *R*-L1.** The synthetic procedure was the same as that described for the related chiral proligand *rac*-L1, but the chiral diamine was used. To (*R*)-1,1'-binaphthyl-2,2'-diamine (505 mg, 1.76 mmol) in ethanol (50 mL) was added 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (833 mg, 3.52 mmol). The solution was stirred at reflux for 12 h. The solid product was isolated by filtration and washed with fresh ethanol. Yield: 89%.  $[\alpha]_{25}^{\text{D}} = -432.28$ .

**Complex *rac*-1.** To a stirred solution containing  $\text{AlMe}_3$  (0.083 g, 1.1 mmol) in benzene (2 mL) was added dropwise a solution of the proligand precursor *rac*-L1 (0.400 g, 0.56 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (96%).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.82 (s, 2H, CH=N), 7.63 (d, *J* = 2.4 Hz, 2H, ArH), 7.51 (d, *J* = 8.4 Hz, 2H, ArH), 7.43 (d, *J* = 8.7 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 2H, ArH), 7.24 (d, *J* = 8.7 Hz, 2H, ArH), 7.14 (t, *J* = 7.4 Hz, 2H, ArH), 7.01 (t, *J* = 7.1 Hz, 2H, ArH), 6.36 (d, *J* = 2.4 Hz, 2H, ArH), 1.54 (s, 18H, *t*-Bu), 1.23 (s, 18H, *t*-Bu), –0.45 (s, 6H, Al–CH<sub>3</sub>), –0.75 (s, 6H, Al–CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  173.7, 163.0, 144.7, 140.8, 139.2, 134.9, 133.2, 132.7, 131.0, 130.1, 126.6, 125.4, 124.2, 119.6 (Ar or ArCNH), 35.5 (C(CH<sub>3</sub>)<sub>3</sub>), 34.0 (C(CH<sub>3</sub>)<sub>3</sub>), 31.4 (CH<sub>3</sub>), 29.7 (CH<sub>3</sub>), –9.1 (Al–CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{54}\text{H}_{66}\text{Al}_2\text{N}_2\text{O}_2$  (%): C, 78.23; H, 8.02; N, 3.38. Found: C, 78.44; H, 7.97; N, 3.30.

**Complex *R*-1.** To a stirred solution containing  $\text{AlMe}_3$  (0.044 g, 0.54 mmol) in benzene (2 mL) was added dropwise a solution of the proligand precursor *R*-L1 (0.193 g, 0.27 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (94%). The NMR characterization was reported for the complex *rac*-1. Anal. Calcd for  $\text{C}_{54}\text{H}_{66}\text{Al}_2\text{N}_2\text{O}_2$ : C, 78.23; H, 8.02; N, 3.38. Found: C, 78.13; H, 7.94; N, 3.41.

**Complex *rac*-2.** To a stirred solution containing  $\text{AlMe}_3$  (0.050 g, 0.62 mmol) in benzene (2 mL) was added dropwise a solution of the proligand precursor *rac*-L1 (0.250 g, 0.31 mmol) in benzene (4 mL). The solution was stirred for 3 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid in almost quantitative yield (97%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.56 (d, *J* = 2.3 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.23 (s, 2H), 7.10 (t, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.90 (t, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 2.3 Hz, 2H), –0.67 (s, 6H), –1.25 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  143.0, 142.7, 136.2, 134.3, 132.7, 131.4, 128.4, 128.3, 128.2, 128., 127.2, 127.1, 124.8, 123.3, 120.6, 120.6, 117.6, 108.9. Anal. Calcd for  $\text{C}_{38}\text{H}_{30}\text{Al}_2\text{Br}_4\text{N}_2\text{O}_2$ : C, 49.60; H, 3.29; N, 3.04. Found: C, 49.65; H, 3.32; N, 3.10.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00016>.

Cartesian coordinates of the calculated structure (XYZ)

NMR spectra of complexes, experimental details of the polymerization reactions; NMR spectra and GPC traces of polymers (PDF)

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## Notes

The authors declare no competing financial interest.

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