

Article

Gallium and Indium Complexes with Bulky Pyridine-Bis(phenolate) Ligands: Synthesis, Structure, and Activity in Ring-Opening Polymerization of Cyclic Esters

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Abstract

A series of gallium and indium complexes bearing pyridine-2,6-bis(phenolate) ligands with *ortho*-substituents of increasing steric bulk (^tBu, SiMe₃, SiPh₃) was synthesized via SiMe₄ elimination from M(CH₂SiMe₃)₃ (M = Ga, In). The gallium complexes **2a–c** were structurally characterized by X-ray diffraction, revealing monomeric four-coordinate distorted trigonal pyramidal geometries. DOSY NMR studies revealed that the indium complexes **3a** (^tBu) and **3b** (SiMe₃) are dimeric in solution, whereas the bulkier **3c** (SiPh₃) is monomeric. All complexes were tested as initiators for ring-opening polymerization (ROP) of ϵ -caprolactone, L-lactide, and *rac*-lactide in the presence of benzyl alcohol. The M-CH₂SiMe₃ bond is inert toward alcohols, pointing to an activated monomer mechanism. Indium complexes exhibited higher activity than their gallium analogues, and the activity strongly depends on the ligand steric bulk: the most hindered SiPh₃ derivative **3c** showed the highest activity, reaching full ϵ -CL conversion in 24 h at 80 °C, whereas the analogous gallium complex **2c** was almost inactive.

Keywords: gallium complexes; indium complexes; ring-opening polymerization; ϵ -caprolactone; lactide

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1. Introduction

Gallium and indium complexes have attracted great interest from researchers over the past two decades. These derivatives are used as starting materials for the production of inorganic materials containing indium and gallium, as well as catalysts and/or initiators for various organic processes [1,2]. One important application of these complexes as polymerization initiators is the ring-opening polymerization (ROP) of cyclic esters, carbonates, and related compounds. The polymers derived from such monomers are biodegradable and find widespread use in medicine and pharmaceuticals. Currently, the most common method for obtaining these polymers is ROP in the presence of metal complexes

that act as polymerization initiators. The mechanism of ROP implies that the metal atoms of the initiator become covalently bonded to the polymer and remain in it after the polymerization process is complete. In this context, gallium and indium compounds are of particular interest as initiators, partly because they have been explored for medical applications and are generally considered less toxic than some other heavy metals [1].

The literature describes a considerable number of gallium and indium compounds that are effective initiators for the ROP of two basic monomers used in the synthesis of biodegradable polymers—lactide (LA) and ϵ -caprolactone (CL) (Figure 1) [2–11]. In some cases, the copolymerization of these monomers has been investigated. It is evident that the activity of the initiator, as well as the properties of the resulting polymer, directly depend on the initiator structure (the nature of the metal atom and the electronic and steric properties of the ligand) [3,6,8,9]. Several articles have been devoted to comparing the behavior of structurally analogous aluminum, gallium, and indium complexes in the ROP of cyclic esters [2,11,12]. Interestingly, the relative activity of Ga and In complexes depends strongly on the ligand structure and reaction conditions. Indium compounds, having a larger ionic radius, might be expected to display different reactivity, but the Lewis acidity of gallium is generally higher. Important factors are the ligand structure, which must allow free access of organic substrates to the metal atom, as well as the reaction medium. For example, indium compounds can form more bonds with solvent molecules than gallium compounds under the same conditions. This reduces the activity of indium compounds compared to gallium derivatives in the actual catalytic reaction [12]. It is worth noting, however, that the relative activity of Ga and In complexes depends strongly on the ligand structure and reaction conditions [12]. In systems with less sterically demanding ligands, the higher Lewis acidity of gallium often leads to higher activity, whereas for bulky ligand frameworks, the larger ionic radius of indium may become the dominant factor, as observed in the present work.

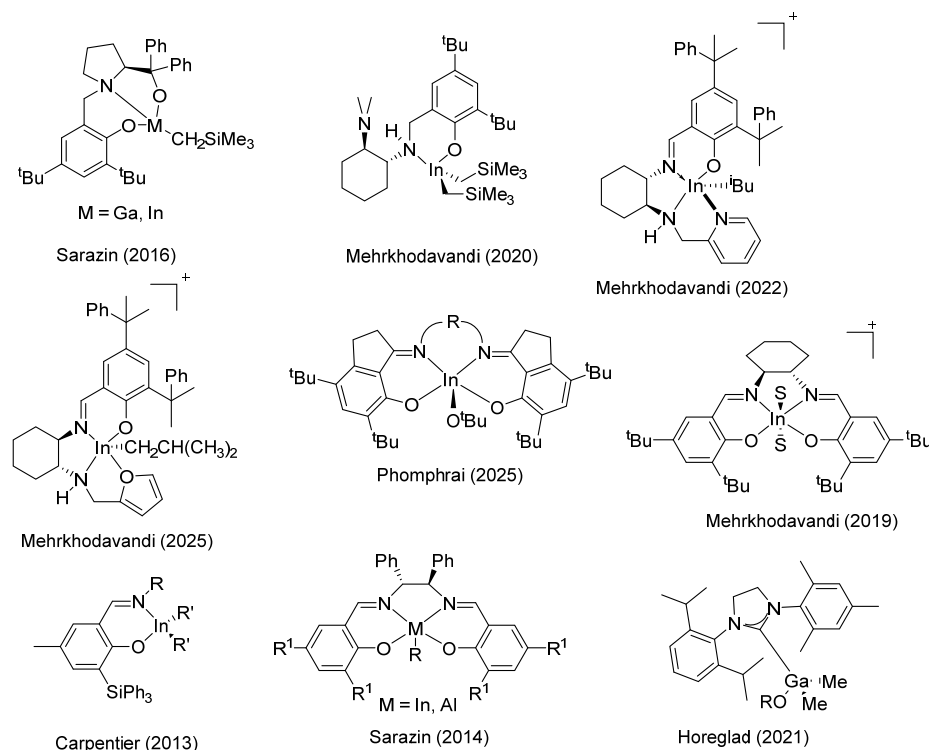


Figure 1. Gallium and indium complexes described in the literature as effective initiators for the ring-opening polymerization of cyclic esters [2–11].

Thus, the synthesis of new indium and gallium derivatives to expand the types of ligand structures and investigate their ROP activity is of considerable interest. Recently, we have shown that gallium complexes based on dianionic ONO ligands—aminobisphenolates—exhibit extremely high activity in the ROP of CL and high activity in the ROP of LA [13]. These compounds contain an amino group on the gallium atom. Complexes containing a *tert*-butoxide group exhibit lower activity. In addition to aminobisphenolates, pyridine-2,6-bis(phenols) bearing various substituents on the phenolic rings, which determine the activity of the entire complex, are highly interesting ligands. We have obtained the corresponding aluminum complexes, which proved to be extremely effective for the synthesis of statistical copolymers of CL and LA [14,15]. It seemed important to obtain indium and gallium complexes based on these ligands and to determine the main characteristics of the ROP processes involving these compounds. Traditional concepts in the field of biodegradable polymer synthesis based on cyclic esters indicate that the most effective groups, whose migration from the metal atom to the organic substrate initiates the ROP process, are the alkoxy and amino groups. However, it has recently been established that the trimethylsilylmethyl group also migrates quite efficiently [12].

Therefore, the aim of this work was the synthesis and structural investigation of gallium and indium complexes based on substituted 2,6-bis(2-hydroxyphenyl)pyridine containing a trimethylsilylmethyl group, and the study of ROP and copolymerization processes.

2. Results and Discussions

2.1. Ligands

In continuation of our previous studies [14,15], we employed three pyridine-2,6-bis(phenol) pro-ligands differing in the steric bulk of the *ortho*-substituents relative to the phenolic OH groups (Figure 2). These substituents (*tert*-butyl, trimethylsilyl, and triphenylsilyl) are located in close proximity to the metal center upon complexation and are expected to significantly influence the geometry, stability, and catalytic activity of the resulting gallium and indium complexes.

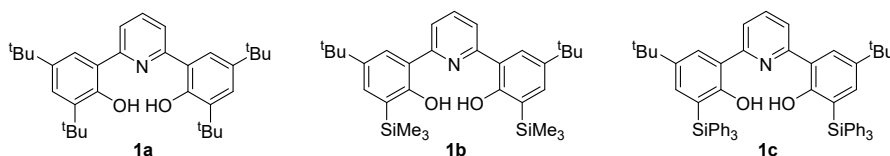


Figure 2. Pyridine-2,6-bis(phenol) *pro*-ligands **1a** (R = *t*Bu), **1b** (R = SiMe₃), and **1c** (R = SiPh₃) used in this study.

The *pro*-ligands **1a** (R = *t*Bu), **1b** (R = SiMe₃), and **1c** (R = SiPh₃) were synthesized according to the procedures reported by us earlier [15,16].

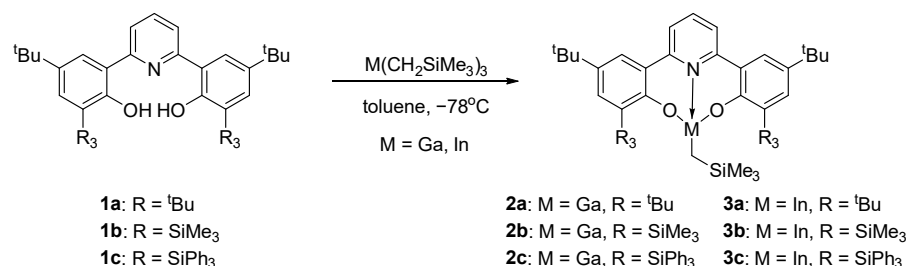
2.2. Synthesis of the Complexes and Their Characterization

The tris(trimethylsilyl)methyl compounds M(CH₂SiMe₃)₃ (M = Ga, In) were chosen as metal sources because they are stable, readily available precursors that react cleanly with the *pro*-ligands via SiMe₄ elimination, giving the desired mono(alkyl) complexes in high yields [12,17]. Moreover, unlike their aluminum analogues, the resulting Ga-CH₂SiMe₃ and In-CH₂SiMe₃ moieties are inert toward alcohols (e.g., *i*PrOH, BnOH) even at elevated temperatures [2,12]. This inertness has been instrumental in establishing an “activated monomer” mechanism for the ROP of lactide with indium initiators, as opposed to the classical coordination-insertion pathway [2]. Consequently, when an alcohol is added as a co-initiator, the metal-carbon bond remains intact, and the polymerization

proceeds via monomer activation by the Lewis acidic metal center followed by nucleophilic attack of the external alcohol. This mechanistic understanding explains why the polymerization is controlled even in the presence of excess alcohol and why no metal-alkoxide species are formed prematurely.

Based on the three O,N,O-type pro-ligands (ligands **1a**, **1b** and **1c**), three gallium complexes (**2a**, **2b**, **2c**) and three indium complexes (**3a**, **3b**, **3c**) were successfully synthesized and characterized.

The synthesis of gallium complexes (**2a–c**) and indium complexes (**3a–c**) was carried out under an argon atmosphere, using solvents dried by standard procedures. The reactions were performed in toluene at -78°C (Scheme 1). As starting metal sources, we employed tris(trimethylsilylmethyl)gallium ($\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$) and tris(trimethylsilylmethyl)indium ($\text{In}(\text{CH}_2\text{SiMe}_3)_3$). $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (or $\text{In}(\text{CH}_2\text{SiMe}_3)_3$) was added dropwise to a solution of the corresponding ligand. It is important to maintain a low temperature during the addition, because at higher temperatures the formation of undesirable bimetallic gallium (or indium) by-products may occur [12].



Scheme 1. Synthesis of gallium complexes **2a–c** and indium complexes **3a–c**.

The subsequent work-up (evaporation of the solvent) was carried out under reduced pressure. Purification (recrystallization from a toluene/ n -hexane mixture) was performed under a stream of argon.

The synthesized O,N,O-type gallium and indium complexes were characterized by ^1H and ^{13}C NMR spectroscopy (**2a–c**, **3a–c**), ESI HRMS (**2a–c**, **3a–c**) and single-crystal X-ray diffraction (**2a–c**).

2.2.1. Single-Crystal X-Ray Diffraction Studies of **2a–2c**

The molecular structures of gallium complexes **2a**, **2b** and **2c** were determined by single-crystal X-ray diffraction analysis. Suitable crystals were obtained by recrystallization from a n -hexane/toluene mixture. The structures are shown in Figures 3–5 and selected bond lengths and angles are summarized in the corresponding captions.

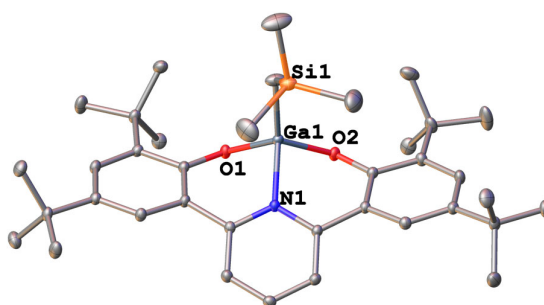


Figure 3. Molecular structure of **2a** (R = $t\text{Bu}$). All hydrogen atoms are hidden. Selected bonds distances($\text{\AA}$) and angles: Ga1–O1 1.847(8), Ga1–O2 1.846(1), Ga1–N1 1.976(1), Ga1–C34 1.940(2), O1–

Ga1–O2 107.3(5), O1–Ga1–N1 93.5(5), O2–Ga1–N1 93.7(5), O1–Ga1–C34 116.5(6), O2–Ga1–C34 119.1(6), N1–Ga1–C34 122.0(6).

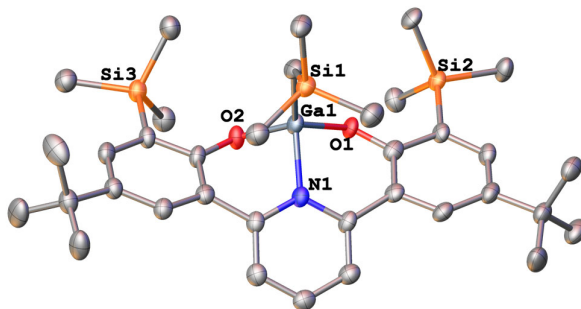


Figure 4. Molecular structure of **2b** (R = SiMe₃). All hydrogen atoms are hidden. Selected bonds distances (Å) and angles: Ga1–O1 1.837(3), Ga1–O2 1.854(3), Ga1–N1 1.971(3), Ga1–C24 1.945(4), O1–Ga1–O2 105.6(1), O1–Ga1–N1 95.4(1), O2–Ga1–N1 92.8(1), O1–Ga1–C24 119.4(2), O2–Ga1–C24 119.9(2), N1–Ga1–C24 118.3(2).

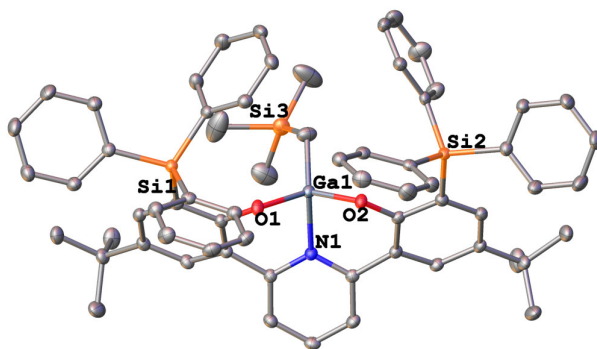


Figure 5. Molecular structure of **2c** (R = SiPh₃). All hydrogen atoms are hidden. Selected bonds distances (Å) and angles: Ga1–O1 1.853(1), Ga1–O2 1.842(2), Ga1–N1 1.991(2), Ga1–C63 1.928(4), O1–Ga1–O2 108.2(6), O1–Ga1–N1 92.1(7), O2–Ga1–N1 93.9(7), O1–Ga1–C63 118.8(9), O2–Ga1–C63 116.3(9), N1–Ga1–C63 122.8(1).

All three complexes are monomeric in the solid state. The gallium atom is four-coordinated by the tridentate O,N,O-ligand (two phenolate oxygens and the pyridine nitrogen) and one carbon atom from the remaining trimethylsilylmethyl group. The NMR spectra of ¹H and ¹³C **2a–2c** also correspond to the monomeric structure of these compounds in solution. For example, the ¹H NMR spectrum of **2a** contains a set of ligand signals that correspond to the symmetrical structure of the ligand in the complex: two singlets of H atoms of four *tert*-butyl groups; each signal, except for one, of aromatic protons corresponds to two protons from different parts of the ligand. The coordination polyhedron around Ga is best described as a distorted trigonal pyramid ($\tau_4 = 0.89–0.92$). For four-coordinate complexes, the τ_4 parameter is used, where $\tau_4 = 1$ corresponds to an ideal tetrahedron and $\tau_4 = 0$ to a perfect square plane. The observed τ_4 values of 0.89–0.92 indicate a geometry close to tetrahedral, which can be described as a distorted trigonal pyramid (see Figure 6 for a clearer view of the coordination environment). This geometry is typical for group 13 metal complexes with such dianionic pincer ligands [15].

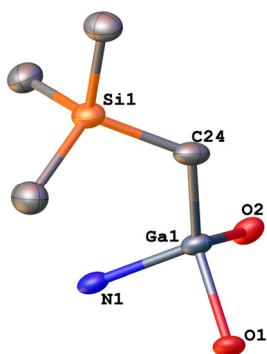


Figure 6. Coordination geometry of the gallium center in complexes **2a–c**.

The geometric parameters are very similar across the series **2a–2c**. The Ga–O bond lengths (1.837–1.854 Å) and Ga–N distances (1.971–1.991 Å) are essentially identical within experimental error, as are the O–Ga–O, O–Ga–N and O–Ga–C angles. Thus, the variation of the ortho-substituent (*t*Bu in **2a**, SiMe₃ in **2b**, SiPh₃ in **2c**) does not significantly change the coordination sphere of gallium.

For the same set of pro-ligands, the corresponding aluminum methyl complexes were previously reported by us [14,15]. Their solid-state structures also reveal monomeric, four-coordinate aluminum centers in a distorted trigonal pyramidal geometry. Thus, the overall structural motif is preserved upon replacing aluminum with gallium, which allows a direct comparison of their catalytic behavior without major geometric artefacts.

2.2.2. NMR Spectroscopy Studies of **3a–3c**

Despite numerous crystallization attempts, single crystals of indium complexes **3a–c** suitable for X-ray diffraction could not be obtained. However, their solution structures were thoroughly investigated by NMR spectroscopy, including diffusion-ordered spectroscopy (DOSY). The ¹H and ¹³C NMR spectra of **3a** and **3b** differ markedly from those of their gallium analogues **2a** and **2b**. While the gallium complexes display a single set of signals indicative of a symmetric structure (e.g., two *tert*-butyl singlets for **2a**), the indium complexes **3a** and **3b** exhibit multiple signals for chemically inequivalent groups, suggesting a loss of molecular symmetry. To clarify the aggregation state, DOSY NMR experiments were performed in CDCl₃ at 298 K. The molecular structures of **3a–c** were investigated by DOSY NMR spectroscopy to determine the association of the complexes (see Supporting Information for details, Figures S19–S21) [18]. The corresponding free *pro*-ligands **1a–c** were also included in the plots for reference. According to these data (Figure S19, Supporting Information), for **3a** a diffusion coefficient of $D = 5.53 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ was observed, corresponding to a found molecular weight ($M_{w\text{found}} = 1463 \text{ Da}$), which is approximately twice the calculated value for the monomer ($M_{w\text{calc}} = 687 \text{ Da}$). This indicates that **3a** exists as a dimer in solution. For comparison, the free ligand **1a** showed $D = 7.54 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ ($M_{w\text{found}} = 740 \text{ Da}$ vs. $M_{w\text{calc}} = 488 \text{ Da}$). For **3b**, a diffusion coefficient of $D = 5.50 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ was obtained ($M_{w\text{found}} = 1481 \text{ Da}$), again approximately twice the calculated monomer mass ($M_{w\text{calc}} = 720 \text{ Da}$), confirming a dimeric structure. The free ligand **1b** exhibited $D = 7.06 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ ($M_{w\text{found}} = 852 \text{ Da}$ vs. $M_{w\text{calc}} = 520 \text{ Da}$). In contrast, complex **3c** showed a diffusion coefficient of $D = 6.15 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ ($M_{w\text{found}} = 1153 \text{ Da}$), which is in good agreement with the calculated monomer mass ($M_{w\text{calc}} = 1092 \text{ Da}$). The free ligand **1c** displayed $D = 6.36 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ ($M_{w\text{found}} = 1071 \text{ Da}$ vs. $M_{w\text{calc}} = 892 \text{ Da}$). These data demonstrate that **3a** and **3b** are dimeric in solution, whereas the bulkier **3c** remains monomeric. The dimerization of **3a** and **3b** is attributed to the formation of phenolate bridges, where each indium center coordinates to a phenolate oxygen atom from the adjacent monomeric

unit, resulting in a five-coordinate indium center in the dimeric species (Figure 7). The monomeric nature of **3c** is rationalized by the increased steric bulk of the SiPh₃ groups, which prevents dimerization and maintains a four-coordinate environment around indium.

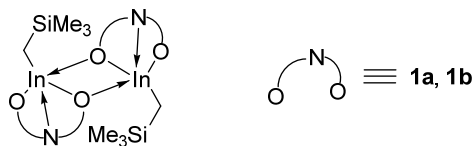


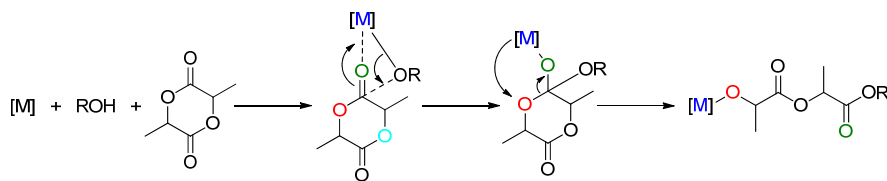
Figure 7. Proposed dimeric structure of indium complexes **3a** (R = ^tBu) and **3b** (R = SiMe₃) in solution.

2.3. Catalytic Activity of the Synthesized Compounds

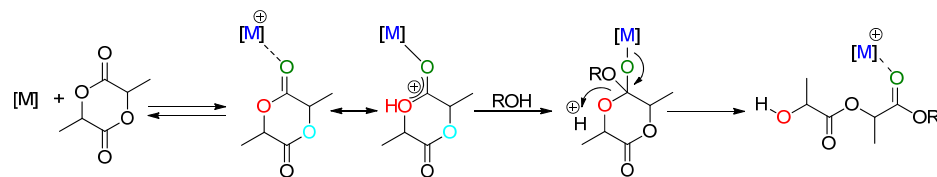
The synthesized O,N,O-type gallium complexes (**2a–c**) and indium complexes (**3a–c**) were tested as initiators in ring-opening polymerization (ROP). Their catalytic activity was investigated under various conditions using ϵ -caprolactone (ϵ -CL), L-lactide (L-LA), and racemic lactide (*rac*-LA). In all experiments, benzyl alcohol (BnOH) was used as a co-initiator in an equimolar amount relative to the complex.

It is important to note that the Ga-CH₂SiMe₃ and In-CH₂SiMe₃ moieties are inert toward alcohols under the reaction conditions, as confirmed by independent NMR experiments (no formation of Ga-OBn or In-OBn species was detected). Also, no migration of ligand from metal atom to polymer due to M–O_{ligand} bond rupture was observed. Consequently, the classical coordination-insertion mechanism, which requires a metal-alkoxide bond as the initiating species, does not operate here. Instead, the polymerization proceeds via an activated monomer mechanism (Scheme 2) [2]. In this mechanism, the Lewis acidic metal center coordinates to and activates the cyclic ester monomer, while the external alcohol (BnOH) acts as the actual nucleophile that attacks the activated monomer. The polymer chain thus grows on the alcohol, and the metal complex serves as a Lewis acid activator throughout the process. This mechanistic picture is fully consistent with literature reports on related indium and gallium alkyl complexes [2].

"Coordination-insertion" mechanism:



"Activated monomer" mechanism:



Scheme 2. "Coordination-insertion" and "activated monomer" mechanisms of lactide's ROP.

Furthermore, the use of BnOH as a co-initiator allows the molecular weight of the isolated polymer to be estimated by ¹H NMR spectroscopy. For polymers of moderate molecular weight, the signal of the terminal benzyl group (Ph-CH₂-) can be detected, and

its integral intensity relative to the monomeric unit signals gives the number-average molecular weight (M_n).

2.3.1. Homopolymerization of ϵ -Caprolactone

Polymerizations of ϵ -CL were carried out under identical conditions: in toluene solution (1 M) at 80 °C with BnOH as the external nucleophile. The monomer/initiator/co-initiator ratio was [ϵ -CL]:[I]:[BnOH] = 100:1:1. The results are summarized in Table 1.

Table 1. ROP of ϵ -caprolactone catalyzed by gallium (**2a–c**) and indium (**3a–c**) complexes. Conditions: toluene, 80 °C, [ϵ -CL]:[I]:[BnOH] = 100:1:1.

Entry	Initiator	Time, h	Conversion ^a , [%]	M_n ^b , [kDa]	$M_{n, theo}$ ^c , [kDa]	$\bar{D}$ ^b
1	2a	1	1	-	-	-
2		3	3	-	-	-
3		6	5	-	-	-
4		24	8	-	-	-
5		48	44	7.3	5.1	1.08
6	2b	3	0	-	-	-
7		6	1	-	-	-
8		24	9	-	-	-
9		48	54	-	-	-
10		96	96	13.8	11.1	1.23
11	2c	120	9	0.7	1.1	1.03
12	3a	1	8	-	-	-
13		3	40	-	-	-
14		6	57	-	-	-
15		24	96	-	-	-
16		48	98	10.6	11.3	1.20
17	3b	1	23	-	-	-
18		3	64	-	-	-
19		6	94	-	-	-
20		24	100	11.1	11.5	1.26
21	3c	1	40	-	-	-
22		3	71	-	-	-
23		6	87	-	-	-
24		24	100	7.2	11.5	1.27

^a Determined by ¹H NMR spectroscopy. ^b Determined by GPC (without correction factor). ^c Determined via $M_{n, theo} = [M]/[I] \times M_{monomer} \times \text{conversion} + M_{BnOH}$.

Under these conditions, gallium complexes **2a** and **2b** showed similar activity, but **2b** (SiMe₃) was slightly more active, reaching 54% conversion after 48 h. Complex **2c** (SiPh₃) was much less active, giving only 9% conversion after 120 h. This lower activity is likely due to the increased steric bulk of the triphenylsilyl group, which hinders access of the monomer to the metal center. The slow initiation observed for gallium complexes **2a** and **2b** (entries 1–5 and 6–10, Table 1) is attributed to the steric hindrance imposed by the bulky O,N,O-ligands, which limits monomer access to the metal center at the early stages of the reaction. However, once initiated, the polymerization proceeds in a controlled manner, as demonstrated by the narrow dispersity values ($\bar{D}$ = 1.08–1.23). All three indium complexes exhibited good activity. The molecular weight distributions ($\bar{D}$) of the resulting PCL samples were close to unity (1.08–1.27), indicating a well-controlled, “immortal” polymerization process. The higher activity of the monomeric complex **3c** compared to the dimeric **3a** and **3b** suggests that the dimeric species are likely resting states that require

dissociation to generate the catalytically active species. Thus, the activity of the studied complexes is influenced by two structural factors. The first is the nature of the metal atom. On the one hand, the larger radius of the indium atom should increase the activity of its compounds; on the other hand, the greater Lewis acidity of gallium should also increase the activity of its compounds. In addition, the steric loading of the ligand also affects, to a greater or lesser extent, the accessibility of the metal atom to monomer attack. The observed activity trend (In > Ga) is consistent with recent computational studies on Salen-type catalysts, where increasing the ionic radius of the metal center was shown to enhance catalytic activity by reducing steric congestion around the metal and facilitating monomer coordination [19]. Thus, the higher activity of indium complexes compared to their gallium analogues can be rationalized by the greater steric accessibility of the larger indium center, despite its lower intrinsic Lewis acidity. The smaller gallium atom, in contrast, is more sterically shielded by the bulky O,N,O-ligand, limiting monomer access to the metal center.

For all three ligands, the previously reported aluminum complexes **L**¹ (tBu), **L**² (SiMe₃) and **L**³ (SiPh₃) achieve >99% conversion of ε-CL in bulk at 100 °C within 15–120 min [14,15]. However, these aluminum complexes follow a classical coordination-insertion mechanism after in situ formation of an Al-OBn species, whereas the gallium and indium complexes follow an activated monomer mechanism (M–CH₂SiMe₃ inert toward BnOH). Therefore, direct comparison of turnover frequencies between Al and Ga/In is not straightforward. Nevertheless, among the Ga and In complexes (which share the same mechanism), the indium derivatives are consistently more active than their gallium analogues. For example, the indium complex **3b** (SiMe₃) shows the highest activity (94% conversion in 6 h, entry 19, Table 1), and even the bulky **3c** (SiPh₃) remains active (87% in 6 h, entry 23), benefiting from the larger atomic radius of indium, which reduces steric congestion around the metal center. In contrast, the gallium complex **2c** (SiPh₃) is almost inactive (9% after 120 h, entry 11) due to the combination of smaller atomic radius and steric hindrance from the bulky SiPh₃ groups.

2.3.2. Homopolymerization of L-Lactide

The polymerization of L-LA was carried out in bulk at 100 °C with BnOH as co-initiator ([L-LA]:[I]:[BnOH] = 100:1:1). The results are presented in Table 2.

Table 2. ROP of L-lactide catalyzed by gallium (**2a–c**) and indium (**3a,b**) complexes. Conditions: bulk, 100 °C, [L-LA]:[I]:[BnOH] = 100:1:1.

Entry	Initiator	Time, h	Conversion ^a , [%]	M _n ^b , [kDa]	M _{n, theo} ^c , [kDa]	Đ ^b
1	2a	1	10	-	-	-
2		3	11	-	-	-
3		6	12	-	-	-
4		24	45	-	-	-
5		48	72	-	-	-
6		120	100	4.8	14.5	1.19
7	2b	1	13	-	-	-
8		3	20	-	-	-
9		6	21	-	-	-
10		24	36	-	-	-
11		48	58	-	-	-
12		72	77	3.4	11.2	1.16
13	2c	1	10	-	-	-
14		3	12	-	-	-
15		6	16	-	-	-

16		24	47	-	-	-
17		48	52	-	-	-
18		120	84	3.0	12.2	1.15
19	3a	1	5	-	-	-
20		3	7	-	-	-
21		6	10	-	-	-
22		24	28	-	-	-
23		48	67	-	-	-
24		120	95	4.8	13.8	1.29
25	3b	1	11	-	-	-
26		3	18	-	-	-
27		6	20	-	-	-
28		24	53	-	-	-
29		48	82	-	-	-
30		72	94	3.6	13.6	1.20

^a Determined by ¹H NMR spectroscopy. ^b Determined by GPC (without correction factor). ^c Determined via $M_{n, \text{theo}} = [M]/[I] \times M_{\text{monomer}} \times \text{conversion} + M_{\text{BnOH}}$.

In bulk at 100 °C, complex **2a** (^tBu) was more active than **2b** (SiMe₃), reaching 72% conversion after 48 h versus 58% for **2b**. Complex **2c** (SiPh₃) showed moderate activity (52% after 48 h). Among the indium complexes, **3b** was more active than **3a** (82% vs. 67% conversion at 48 h). The observed molecular weights are low, which is likely due to polymer chain degradation under prolonged thermal exposure—a known issue for polylactide at elevated temperatures. Thus, under these conditions, the rate of degradation competes with or even exceeds the polymerization rate.

The experimental molecular weights ($M_{n, \text{exp}}$) for poly(L-lactide) are consistently lower than the theoretical values ($M_{n, \text{theo}}$). This discrepancy is primarily attributed to transesterification and backbiting reactions that occur at the elevated polymerization temperature (100 °C) over prolonged reaction times (up to 120 h), leading to partial chain degradation and a reduction in M_n .

Additionally, the activated monomer mechanism discussed above may contribute to the observed deviation, as the initiation efficiency in this mechanism can vary depending on the specific complex and reaction conditions [2,12]. The close agreement between $M_{n, \text{exp}}$ and $M_{n, \text{theo}}$ for *rac*-lactide (reaction complete within 1–6 h at 130 °C) supports the conclusion that the primary cause of the lower M_n values for L-LA is thermal degradation over extended reaction times, rather than an inherent lack of control. The narrow dispersity values ($\bar{D} = 1.15$ – 1.29) nevertheless indicate that the polymerization remains well-controlled despite the lower M_n .

Under bulk polymerization conditions at 100 °C with [L-LA]:[M]:[BnOH] = 100:1:1, the aluminum complex (LAIME) required 24 h to reach 63% conversion ($\bar{D} = 1.11$) [14,15]. In comparison, the gallium complex **2a** (^tBu) gave 72% conversion after 48 h ($\bar{D} = 1.19$), and the indium complex **3a** (^tBu) gave 67% conversion after 48 h ($\bar{D} = 1.29$). The activities of **2a** and **3a** are thus broadly comparable to that of (LAIME), although the molecular weights obtained with the Ga and In complexes are lower, likely due to prolonged thermal exposure and partial degradation of the PLA chains. The lower reaction rates for Ga and In under these conditions may reflect the different operating mechanism (activated monomer vs. coordination insertion) as well as the higher steric shielding of the metal center in the Ga/In systems.

2.3.3. Homopolymerization of *rac*-Lactide

Polymerization of *rac*-LA was performed in bulk at 130 °C with BnOH ([*rac*-LA]:[I]:[BnOH] = 100:1:1). The results are given in Table 3.

Table 3. ROP of *rac*-lactide catalyzed by **2a** and **3a**. Conditions: bulk, 130 °C, [*rac*-LA]:[I]:[BnOH] = 100:1:1.

Entry	Initiator	Time, h	Conversion ^a , [%]	M _n ^b , [kDa]	M _{n, theo} ^c , [kDa]	Đ ^b
1	2a	1	0	-	-	-
2		3	41	-	-	-
3		6	96	-	-	-
4		24	98	13.6	14.2	1.74
5	3a	1	93	-	-	-
6		3	97	-	-	-
7		6	98	-	-	-
8		24	100	16.2	14.5	1.87

^a Determined by ¹H NMR spectroscopy. ^b Determined by GPC (without correction factor). ^c Determined via $M_{n, theo} = [M]/[I] \times M_{monomer} \times conversion + M_{BnOH}$.

Complex **2a** reached 96% conversion after 6 h, while **3a** was even more active, giving near-complete conversion in less than 3 h. The molecular weight distributions were relatively broad (Đ = 1.74 for **2a**, 1.87 for **3a**), indicating a less controlled polymerization under these harsh conditions. The lower activity of the gallium complex again reflects the greater steric congestion around the smaller gallium center, which limits monomer accessibility compared to the larger indium atom.

The stereoregularity of the obtained polylactides was examined by homonuclear decoupled ¹H NMR spectroscopy focusing on the methine region. The probability of isotactic enchainment (P_m) was found to be 0.55 for PLA produced with **2a** and 0.59 for PLA produced with **3a**. These values are close to 0.5, indicating that both polymers are essentially atactic with no significant stereoselectivity. This lack of stereo control is consistent with the activated monomer mechanism operating under these conditions, where the chiral information of the lactide is not transferred to the polymer chain.

2.3.4. Copolymerization of ε-Caprolactone and L-Lactide

The copolymerization of ε-CL and L-LA was investigated in bulk at 100 °C with BnOH ([ε-CL]:[L-LA]:[I]:[BnOH] = 100:100:1:1). The results are shown in Table 4.

Table 4. Copolymerization of ε-caprolactone and L-lactide catalyzed by **2a** and **3a**. Conditions: bulk, 100 °C, [ε-CL]:[L-LA]:[I]:[BnOH] = 100:100:1:1.

Entry	Initiator	Time, h	Conversion ^a ε-CL, [%]	Conversion ^a L-LA, [%]	M _n ^b , [kDa]	M _{n, theo} ^c , [kDa]	Đ ^b
1	2a	6	3	0	-	-	-
2		24	20	57	-	-	-
3		48	48	69	-	-	-
4		72	79	78	-	-	-
5		144	100	80	8.8	23.0	1.56
6	3a	6	0	0	-	-	-
7		24	10	69	-	-	-
8		48	33	92	-	-	-
9		72	49	96	-	-	-
10		144	78	100	9.5	23.4	1.32

^a Determined by ¹H NMR spectroscopy. ^b Determined by GPC (without correction factor). ^c Determined via $M_{n, theo} = [M]/[I] \times (M_{CL} \times conversion_{CL} + M_{LA} \times conversion_{LA}) + M_{BnOH}$.

Under these conditions, homopolymerization of L-LA clearly predominates over ϵ -CL incorporation. Unfortunately, neither complex showed efficient copolymerization activity. Although indium complex **3a** is more active in ϵ -CL homopolymerization than in L-LA homopolymerization, in the copolymerization experiment the conversion of ϵ -CL remained low. Previously, our group has shown that L-lactide inhibits the initiation of ϵ -caprolactone under copolymerization conditions, leading to a significant slowdown of ϵ -CL polymerization [15]. Moreover, the polymerization rate of L-LA itself is also reduced.

3. Materials and Methods

All experimental manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. The solvents were dried using standard methods and distilled prior to use: toluene was refluxed under Na and distilled; diethyl ether was stored under KOH, refluxed under Na/benzophenone and then distilled; and hexane was refluxed under Na and then distilled. L-LA (98%, Sigma–Aldrich, St. Louis, MO, USA) and rac-LA (98%, Sigma–Aldrich, St. Louis, MO, USA) were recrystallized from toluene and sublimed in vacuo; ϵ -CL (97%, Sigma–Aldrich, St. Louis, MO, USA) was distilled over CaH₂. BnOH was distilled under vacuum and kept over activated 4 Å molecular sieves. CDCl₃ (dried with CaH₂ and kept over activated 4 Å molecular sieves) and C₆D₆ (dried over sodium) were obtained from Deutero GmbH (Kastellaun, Germany). The starting material, ligand **1a** [16], ligands **1b–1c** [15], Me₃SiCH₂MgCl [20], Ga(CH₂SiMe₃)₃ [21] and In(CH₂SiMe₃)₃ [17] were synthesized according to the procedures described in the literature. ¹H (400.13 MHz) and ¹³C (100.61 MHz) NMR spectra were recorded using a Bruker Avance 400 (Bruker Corporation, Billerica, MA, USA) or an Agilent 400-MR spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA) at room temperature (unless otherwise stated). ¹H and ¹³C chemical shifts were reported in ppm relative to Me₄Si as the external standard. Diffusion-ordered spectroscopy (DOSY) experiments were performed at 298 K on a Bruker Avance 400 spectrometer using the stimulated echo sequence with bipolar gradient pulses. Molecular weights (M_w) were estimated from the diffusion coefficients (*D*) using the method of Evans et al. [18], which employs the Stokes–Einstein equation and an empirical power-law relationship between *D* and M_w. High-resolution mass spectra (HRMS) were recorded with a G3 QToF, a quadrupole-time-of-flight mass spectrometer (Waters Corp., Milford, MA, USA) equipped with electrospray ionization (ESI) operated under the positive- and negative-ion modes. The conditions were as follows: an ion source temperature of 550 °C; a drying gas (nitrogen) pressure of 40 psi; a nebulizing gas pressure of 40 psi; a curtain gas pressure of 25 psi; a capillary voltage of 5500 V; and acetonitrile as the solvent.

Single crystals of **2a–c** were investigated on a Bruker D8 QUEST single-crystal X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a PHOTONII detector, charge-integrating pixel array detector (CPAD), laterally graded multilayer (Goebel) mirror, and microfocus Mo-target X-ray tube ($\lambda = 0.73071$ Å). Data reduction and integration were performed with the Bruker software package SAINT (Version 8.40B). The data were corrected for Lorentz and polarization effects. The absorption correction was performed using a multi-scan routine as implemented in SADABS (Version 2016/2) [22]. Crystal structure solution and refinement were performed using the SHELX-2018 package [23]. Atomic positions were located using dual methods and refined using a combination of Fourier synthesis and least-square refinement in isotropic and anisotropic approximations. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C–H hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as *U*_{iso}(H)=1.5*U*_{eq}(C) for methyl H atoms and *U*_{iso}(H)=1.2*U*_{eq}(C) otherwise. Upon the refinement of the disordered structure, the EADP and SADI constraints were employed.

The contribution of strongly disordered solvate molecules to the structural amplitudes in Ga-SiPh₃-CH₂SiMe₃ was excluded by the SQUEEZE method in the PLATON program (version 20260620) [24], which substantially improved the model.

Crystallographic parameters and final residuals for the single-crystal XRD experiments are given in Supporting Information (Table S1).

General procedure for **2a–2c**: Under a stream of argon, a toluene solution of ligand was added dropwise with stirring to a solution of tris(trimethylsilyl)methylgallium Ga(CH₂SiMe₃)₃ in absolute toluene (−95 °C) in a Schlenk flask. The reaction mixture was warmed to room temperature and stirred for 2 days. The mixture was then concentrated in vacuo to remove toluene. The resulting compound was recrystallized from a mixture of absolute toluene and *n*-hexane.

For **2a**: 0.30 g 0.6 mmol **1a**, 0.20 g 0.06 mmol Ga(CH₂SiMe₃)₃, 6 mL toluene. **2a** (0.30 g, 75%) was obtained as a yellowish powder.

NMR ¹H (C₆D₆, δ, ppm): −0.41 (s, 9H, Si(CH₃)₃), −0.14 (s, 2H, CH₂Si(CH₃)₃), 1.33 (s, 18H, C(CH₃)₃), 1.70 (s, 18H, C(CH₃)₃), 7.00–7.02 (d, *J* = 7.8 Hz, 2H, Ar), 7.09–7.11 (m, 1H, Ar), 7.36–7.37 (d, *J* = 2.7 Hz, 2H, Ar), 7.66–7.67 (d, *J* = 2.7 Hz, 2H, Ar).

NMR ¹³C (C₆D₆, δ, ppm): −5.34 (CH₂Si(CH₃)₃), 1.15 (CH₂Si(CH₃)₃), 30.53 (C(CH₃)₃), 32.08 (C(CH₃)₃), 34.75 (C(CH₃)₃), 36.39 (C(CH₃)₃), 122.03, 123.60, 124.35, 131.98, 140.93, 141.83, 142.59, 156.13, 158.87 (Ar).

HRMS (ESI, *m/z*): calculated for C₃₇H₅₄GaNO₂Si: [M+H]⁺ *m/z* 642.3252, founded [M+H]⁺ *m/z* 642.3253.

For **2b**: 0.31 g, 0.6 mmol **1b**, 0.2g 0.06 mmol Ga(CH₂SiMe₃)₃, 6 mL toluene. **2b** (0.31 g, 78%) was obtained as a yellowish powder.

NMR ¹H (CDCl₃, δ, ppm): −0.58 (s, 9H, CH₂Si(CH₃)₃), −0.47 (s, 2H, CH₂Si(CH₃)₃), 0.33 (s, 18H, Si(CH₃)₃), 1.34 (s, 18H, C(CH₃)₃), 7.48–7.50 (m, 4H, Ar), 7.54–7.56 (d, *J* = 8.1 Hz, 2H, Ar), 7.99–8.03 (t, *J* = 8.1 Hz, 1H, Ar).

NMR ¹³C (CDCl₃, δ, ppm): −5.94 (CH₂Si(CH₃)₃), −0.58 (CH₂Si(CH₃)₃), 0.50 (CH₂Si(CH₃)₃), 31.54 (C(CH₃)₃), 34.11 (C(CH₃)₃), 120.85, 121.20, 126.98, 132.49, 136.11, 140.97, 141.42, 155.43, 163.20 (Ar).

HRMS (ESI, *m/z*): calculated for C₃₅H₅₄GaNO₂Si: [M+H]⁺ *m/z* 674.2791, founded [M+H]⁺ *m/z* 674.2785.

For **2c**: 0.33 g 0.4 mmol **1c**, 0.12 g 0.04 mmol Ga(CH₂SiMe₃)₃, 5 mL toluene. **2c** (0.28 g, 72%) was obtained as a yellowish powder.

NMR ¹H (CDCl₃, δ, ppm): −1.72 (s, 2H, CH₂Si(CH₃)₃), −0.67 (s, 9H, CH₂Si(CH₃)₃), 1.19 (s, 18H, C(CH₃)₃), 7.18–7.22 (m, 13H, Ar), 7.30–7.34 (m, 6H, Ar), 7.46–7.48 (m, 4H, Ar), 7.53–7.54 (d, *J* = 2.5 Hz, 2H, Ar), 7.61–7.63 (d, *J* = 6.9 Hz, 13H, Ar), 7.86–7.90 (t, *J* = 8.1 Hz, 1H, Ar).

NMR ¹³C (CDCl₃, δ, ppm): 0.46 (CH₂Si(CH₃)₃), 31.36 (C(CH₃)₃), 34.08 (C(CH₃)₃), 120.55, 121.09, 127.24, 127.42, 127.64, 128.91, 135.21, 136.69, 139.72, 140.63, 141.12, 154.90, 164.11 (Ar); no signal for the GaCH₂Si(CH₃)₃ was observed.

HRMS (ESI, *m/z*): calculated for C₆₅H₆₆GaNO₂Si: [M+H]⁺ *m/z* 1046.3730, founded [M+H]⁺ *m/z* 1046.3725.

General procedure for **3a–3c**: Under a stream of argon, a toluene solution of ligand was added dropwise with stirring to a solution of tris(trimethylsilyl)methylindium In(CH₂SiMe₃)₃ in absolute toluene (−78 °C) in a Schlenk flask. The reaction mixture was warmed to room temperature and stirred for 2 days. The mixture was then concentrated in vacuo to remove toluene. The resulting compound was recrystallized from a mixture of absolute toluene and *n*-hexane.

For **3a**: 0.40 g 0.8 mmol **1a**, 0.32 g 0.09 mmol In(CH₂SiMe₃)₃, 8 mL toluene. **3a** (0.40 g, 71%) was obtained as a yellowish powder.

NMR ^1H (CDCl_3 , δ , ppm): -0.86 (s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.33 – -0.30 (d, $J = 12.5$ Hz, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.14 – -0.11 (d, $J = 12.5$ Hz, 1H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.01 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.19 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.61 (s, 9H, $\text{C}(\text{CH}_3)_3$), 6.67 – 6.69 (m, 2H, Ar), 7.02 – 7.04 (d, $J = 7.8$ Hz, 1H, Ar), 7.06 – 7.08 (d, $J = 7.8$ Hz, 1H, Ar), 7.13 (d, $J = 2.5$ Hz, 1H, Ar), 7.34 (d, $J = 2.5$ Hz, 1H, Ar), 7.58 – 7.62 (t, $J = 7.8$ Hz, 1H, Ar).

NMR ^{13}C (CDCl_3 , δ , ppm): 0.40 ($\text{CH}_2\text{Si}(\text{CH}_3)_3$), 29.85 ($\text{C}(\text{CH}_3)_3$), 31.45 ($\text{C}(\text{CH}_3)_3$), 31.59 ($\text{C}(\text{CH}_3)_3$), 32.17 ($\text{C}(\text{CH}_3)_3$), 33.97 ($\text{C}(\text{CH}_3)_3$), 34.30 ($\text{C}(\text{CH}_3)_3$), 35.02 ($\text{C}(\text{CH}_3)_3$), 35.58 ($\text{C}(\text{CH}_3)_3$), 123.83 , 124.40 , 125.23 , 125.69 , 126.45 , 127.37 , 127.99 , 128.22 , 131.24 , 139.77 , 139.96 , 140.09 , 160.40 , 160.63 , 161.82 (Ar); no signal for the $\text{InCH}_2\text{SiMe}_3$ was observed.

HRMS (ESI, m/z): calculated for $\text{C}_{37}\text{H}_{54}\text{InNO}_2\text{Si}$: $[\text{M}+\text{H}]^+$ m/z 688.3040, founded $[\text{M}+\text{H}]^+$ m/z 688.3036.

For **3b**: 0.29 g, 0.6 mmol **1b**, 0.21 g, 0.06 mmol $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, 6 mL toluene. **3b** (0.32 g, 80%) was obtained as a yellowish powder.

NMR ^1H (CDCl_3 , δ , ppm): -0.87 (s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.21 – -0.20 (d, $J = 2.4$ Hz, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.13 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.46 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$), 6.78 – 6.79 (d, $J = 2.4$ Hz, 1H, Ar), 6.84 – 6.85 (d, $J = 2.4$ Hz, 1H, Ar), 7.07 – 7.09 (d, $J = 7.8$ Hz, 2H, Ar), 7.21 (d, $J = 2.4$ Hz, 1H, Ar), 7.39 – 7.40 (d, $J = 2.4$ Hz, 1H, Ar), 7.60 – 7.64 (t, $J = 7.8$ Hz, 1H, Ar).

NMR ^{13}C (C_6D_6 , δ , ppm): 0.49 ($\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.75 (CH_2SiMe_3), 2.46 ($\text{Si}(\text{CH}_3)_3$), 31.97 ($\text{C}(\text{CH}_3)_3$), 32.23 ($\text{C}(\text{CH}_3)_3$), 34.44 ($\text{C}(\text{CH}_3)_3$), 34.55 ($\text{C}(\text{CH}_3)_3$), 123.06 , 124.13 , 124.43 , 130.72 , 130.92 , 131.06 , 131.79 , 132.58 , 134.98 , 135.35 , 138.90 , 140.93 , 143.28 , 160.02 , 160.76 , 162.41 , 166.51 (Ar).

HRMS (ESI, m/z): calculated for $\text{C}_{35}\text{H}_{54}\text{InNO}_2\text{Si}_3$: $[\text{M}+\text{H}]^+$ m/z 720.2574, founded $[\text{M}+\text{H}]^+$ m/z 720.2553.

For **3c**: 0.26 g 0.3 mmol **1c**, 0.12 g 0.03 mmol $\text{In}(\text{CH}_2\text{SiMe}_3)_3$, 5 mL toluene. **3c** (0.25 g, 78%) was obtained as a yellowish powder.

NMR ^1H (CDCl_3 , δ , ppm): -1.16 (s, 2H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), -0.57 (s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$), 1.13 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.16 – 7.17 (d, $J = 2.4$ Hz, 2H, Ar), 7.24 – 7.27 (m, 11H, Ar), 7.31 – 7.38 (m, 9H, Ar), 7.45 – 7.47 (d, $J = 8.1$ Hz, 2H, Ar), 7.55 – 7.58 (m, 12H, Ar), 7.96 – 8.00 (t, $J = 8.1$ Hz, 1H, Ar).

NMR ^{13}C (CDCl_3 , δ , ppm): -3.98 ($\text{CH}_2\text{Si}(\text{CH}_3)_3$), 0.96 ($\text{CH}_2\text{Si}(\text{CH}_3)_3$), 31.33 ($\text{C}(\text{CH}_3)_3$), 33.88 ($\text{C}(\text{CH}_3)_3$), 122.95 , 123.21 , 125.00 , 127.55 , 127.78 , 128.03 , 130.49 , 135.93 , 136.44 , 138.89 , 139.45 , 140.19 , 158.58 , 167.01 (Ar).

HRMS (ESI, m/z): calculated for $\text{C}_{65}\text{H}_{66}\text{InNO}_2\text{Si}_3$: $[\text{M}+\text{H}]^+$ m/z 1092.3514, founded $[\text{M}+\text{H}]^+$ m/z 1092.3506.

4. Conclusions

In this work, a family of gallium and indium complexes supported by pyridine-2,6-bis(phenolate) ligands with varying ortho-substituents (^tBu , SiMe_3 , SiPh_3) was successfully synthesized via SiMe_4 elimination from $\text{M}(\text{CH}_2\text{SiMe}_3)_3$ ($\text{M} = \text{Ga}$, In). The gallium complexes **2a–c** are monomeric in the solid state and in solution. DOSY NMR studies of the indium complexes revealed that **3a** (^tBu) and **3b** (SiMe_3) are dimeric in solution, whereas the bulky **3c** (SiPh_3) is monomeric.

The complexes were evaluated as initiators for the ring-opening polymerization of ϵ -caprolactone, L-lactide, and *rac*-lactide in the presence of benzyl alcohol. The $\text{M}-\text{CH}_2\text{SiMe}_3$ bond is inert toward alcohols, which points to an activated monomer mechanism rather than the classical coordination-insertion pathway.

The activity of the studied complexes is influenced by two structural factors. The first is the nature of the metal atom. On the one hand, the larger radius of the indium atom should increase the activity of its compounds; on the other hand, the expected greater Lewis acidity of gallium should also increase the activity of its compounds. In addition, the steric loading of the ligand also affects, to a greater or lesser extent, the accessibility of

the metal atom to monomer attack. The actual activity of the indium and gallium complexes is an interplay between these factors. Indium complexes often showed higher activity than their gallium analogues, which is attributed to the larger ionic radius of indium. The steric bulk of the ligand plays a decisive role: the most hindered SiPh₃-substituted indium complex **3c** exhibited excellent activity (full conversion of ϵ -CL in 24 h at 80 °C), whereas the corresponding gallium complex **2c** was almost inactive.

Comparison with previously reported aluminum analogues reveals that indium complexes are generally more active than both aluminum and gallium congeners, despite the different operating mechanisms. Overall, the indium complexes described here represent efficient, well-defined initiators for the controlled ROP of cyclic esters, and the ligand steric environment can be tuned to balance activity and stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics14090231/s1>. Figure S1: ¹H NMR spectrum of compound **2a** (C₆D₆, 400 MHz); Figure S2: ¹³C NMR spectrum of compound **2a** (C₆D₆, 101 MHz); Figure S3: HRMS (ESI) spectrum of compound **2a**; Figure S4: ¹H NMR spectrum of compound **2b** (CDCl₃, 400 MHz); Figure S5: ¹³C NMR spectrum of compound **2b** (CDCl₃, 101 MHz); Figure S6: HRMS (ESI) spectrum of compound **2b**; Figure S7: ¹H NMR spectrum of compound **2c** (CDCl₃, 400 MHz); Figure S8: ¹³C NMR spectrum of compound **2c** (CDCl₃, 101 MHz); Figure S9: HRMS (ESI) spectrum of compound **2c**; Figure S10: ¹H NMR spectrum of compound **3a** (CDCl₃, 400 MHz); Figure S11: ¹³C NMR spectrum of compound **3a** (CDCl₃, 101 MHz); Figure S12: HRMS (ESI) spectrum of compound **3a**; Figure S13: ¹H NMR spectrum of compound **3b** (CDCl₃, 400 MHz); Figure S14: ¹³C NMR spectrum of compound **3b** (CDCl₃, 101 MHz); Figure S15: HRMS (ESI) spectrum of compound **3b**; Figure S16: ¹H NMR spectrum of compound **3c** (CDCl₃, 400 MHz); Figure S17: ¹³C NMR spectrum of compound **3c** (CDCl₃, 101 MHz); Figure S18: HRMS (ESI) spectrum of compound **3c**; Figure S19: DOSY NMR spectrum of compound **3a** (CDCl₃, 298 K); Figure S20: DOSY NMR spectrum of compound **3b** (CDCl₃, 298 K); Figure S21: DOSY NMR spectrum of compound **3c** (CDCl₃, 298 K); Table S1: Crystallographic parameters and final residuals for the single-crystal X-ray diffraction experiments of compounds **2a–2c**.

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