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Mononuclear Salen-gallium complexes for *iso*-selective ring-opening polymerization (ROP) of *rac*-lactide ‡

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‡ Electronic Supplementary Information (ESI) available: Crystallographic and experimental details (Tables S1-S2) and ORTEP with complete labelling (Figures S1-S17) for all the structures, NMR spectra of all complexes (Figures S6-S22), ^{1}H NMR of an isolated PLA sample (Figures S23), SEC traces of all ROP runs (Figures S24-S35), ROP data for complexes **3a**, **3c** and **2f** (Figures S35-S38), homonuclear decoupled ^{1}H NMR spectra of the methine region of the PLA samples (Figures S39) and MALDI-TOF spectra of isolated PLA samples (Figures S40-S41). The crystallographic information files (CIF) of **3a**, **3d**·0.5CH_2Cl_2, **3e**·1.5BnOH, **4d**·$CHCl_3$ and **5b**·2C_6H_6 have been deposited to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1540077-1540081. See DOI: 10.1039/x0xx00000x.

ABSTRACT. A series of mononuclear Salen-supported gallium amido/alkoxide derivatives were prepared and structurally characterized and subsequently used as initiators in *rac*-lactide ring-opening polymerisation (ROP). The reaction of variously substituted salen ligands (**1a-1f**) with 0.5 equiv of $Ga_2(NMe_2)_6$ allowed the isolation of the corresponding (salen)Ga-NMe_2 chelates (**2b-2d**, **2f**) *via* an amine elimination route, as poorly soluble compounds in common solvents. The (salen)Ga-OBn derivatives (**3a-3e**) may be readily accessed by an amine-elimination/alcoholysis sequence and the molecular structures of **3a**, **3d** and **3e** were confirmed through X-ray crystallography diffraction analysis. The present (salen)Ga–X species may effectively mediate the *iso*-selective ROP of *rac*-LA in a controlled manner (P_m up to 0.77 using a 1/1 **2f**/BnOH mixture as ROP initiator), with a ROP activity greatly dependent upon steric hindrance and geometrical constraints imposed by the variously substituted salen ligands. Based on the present study, salen ligands with limited steric hindrance and a certain degree of flexibility appear best suited for *iso*-selective ROP by (salen)Ga chelates. The salen-gallium complex **3a** is also effective for the controlled ROP of CL and the production of PCL-*b*-PLA copolymers.

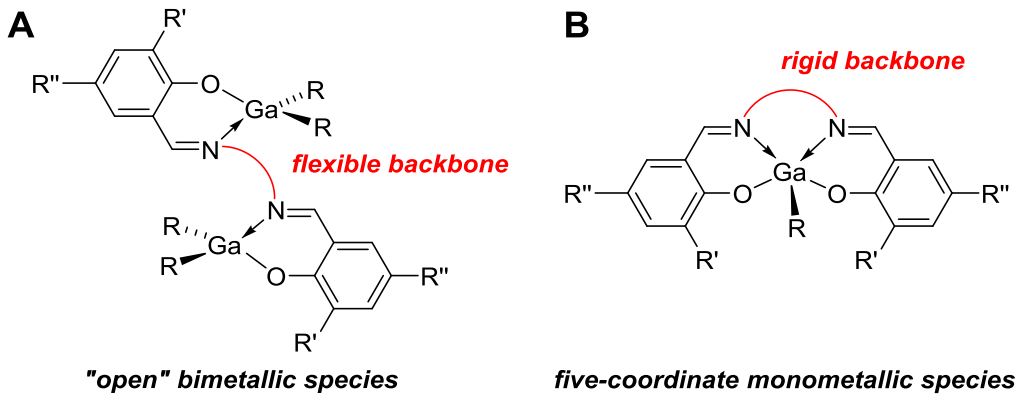
Introduction.

Poly(lactic) acid (PLA), a biodegradable polyester derived from lactic acid, a renewable resource, is currently attracting attention for various applications, ranging from food packaging to biomedical and pharmaceutical applications.[1,2] Its production can be achieved by direct polycondensation from lactic acid or ring-opening polymerization (ROP) of lactide (LA).[1,3] The use of well-defined and ligand-supported complexes of Lewis acidic metal centers stands today as the method of choice to access chain-length controlled and possibly stereo-regular PLA *via* a (stereo)controlled ROP process.[3,4] Several reviews summarize the efforts devoted into the design of such initiators, which are mainly based on Groups 1-2,[5] Group 3 and lanthanides,[6] Group 4,[7] Zn[5b] and Group 13 metals.[4,5a,8] Contrasting with the numerous studies on Al(III)-based initiators and the growing interest in In(III) analogues,[9] Ga(III)-incorporating ROP catalysts remain little explored, despite the well-established better stability of Ga species (vs. Al analogues) in polar/protic medium.[8c] The latter is of particular interest considering that any ROP catalyst should tolerate protic impurities (present in the monomer source) for industrial use. In Ga-mediated lactide ROP, Horeglad and co-workers showed that L-GaR_2(OR') species (L = amine, *N*-heterocyclic carbene, R = Me, R' = alkyl, ester) mediate the low temperature *iso*-selective ROP of PLA.[10] The groups of Williams and Chakraborty reported on the use of Ga species supported by monoanionic *N,O*-chelating ligands for the controlled and isoselective polymerization of *rac*-LA.[11] Our group showed that tetra-coordinate Ga(III) complexes supported by tridentate dianionic *N,O,N* ligands effectively polymerise *rac*-LA and, interestingly, perform better than their Al(III) counter-parts (both in ROP control and activity).[12] The latter prompted us toward further investigations on ligand-supported Ga-based initiators. In that regard, salen-based mononuclear Ga species of the type [(salen)GaX] appeared of interest

given that salen-based Al(III) species are landmark ROP catalysts for the (stereo)controlled ROP of lactide, though typically displaying moderate activity.[13,14,15,16,17,18,19,20,21] Besides, unlike Salen-Al(III) complexes, which are widely used in ROP catalysis of various cyclic polar monomers, (salen)GaX species have been little studied and their preparation remain to be optimized.[19] Recently, the ROP performances of group 13 metal complexes bearing chiral Salen ligands were recently studied and compared.[22] While (salen)AlR derivatives promoted lactide ROP to afford well-defined PLA with high isotacticity ($P_m \approx 0.80$-0.90), the analogous mononuclear (salen)GaR complexes could not be accessed with, instead, the preferred formation of dinuclear gallium species, of general formula [$(GaR_2)_2$(Salen-{κ^2-*N,O*}$_2$)] (R = alkyl; **A**, Scheme 1). The latter dinuclear Ga species only display modest ROP activity/control in lactide ROP.[22,23] While the present study was being finalized, Mehrkhodavandi and co-workers reported on a (salen)Ga–OEt derivative to be poorly active in lactide ROP.[35]

From a structural standpoint, there are only a few structurally characterized five-coordinate Salen-GaX (X = alkyl, halide, azido) complexes containing a flexible salen backbone.[24,25,26] The formation of five-coordinate mononuclear Ga(III) alkyl or halide complexes may however be imposed by using salen ligands with a rigid spacer (such as a phenylene ring) linking the two *N,O*-chelate moieties, as notably demonstrated by Atwood (**B**, Scheme 1).[19,26]

Herein we report on the synthesis and structural characterization of novel mononuclear Ga(III)–amido and –alkoxide species of the type [(salen)GaX] (X = amido, alkoxide), bearing variously substituted salen ligands, and their use as lactide ROP initiators for the controlled and *iso*-selective production of PLA.



Scheme 1. Different coordination modes of Salen ligands towards gallium(III) precursors. **A**: "open" bis-chelate mode dinuclear Ga(III) complexes. **B**: κ^4-N_2,O_2 coordination mode, forming five-coordinate mononuclear Ga(III) complexes, favored with rigid backbone such as *o*-phenylene.

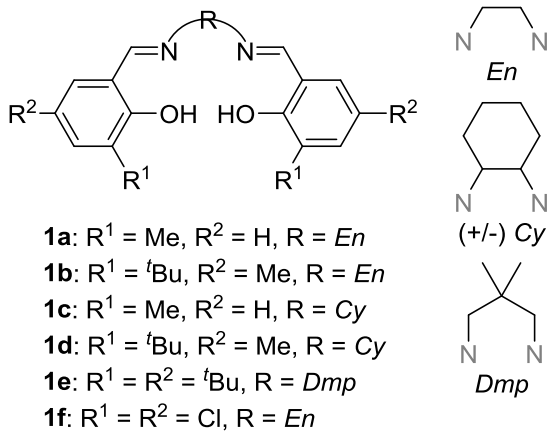
Results and Discussion.

Synthesis and Characterization

A series of five representative salen proteo-ligands (**1a-1f**, Scheme 2), prepared according to published procedures,[27] was selected for the present study based on the reported best ROP performances (excellent control and *iso*-selectivity in LA ROP) of the corresponding (salen)Al–OR chelates.[15,17] Accordingly, several salen backbones [ethylene (*En*), cyclohexyl (*Cy*) and CH_2-CMe_2-CH_2 (*Dmp*)] were selected.

(Salen)Al–OR ROP initiators incorporating ligands **1a-1f** are typically prepared by alcoholysis of the corresponding (salen)Al-alkyl species, compounds readily accessible by an alkane elimination reaction between salen-H_2 and an AlR_3 precursor.[19] In contrast, mononuclear (salen)Ga-alkyl species could not be accessed *via* alkane elimination (between GaR_3 and salen-

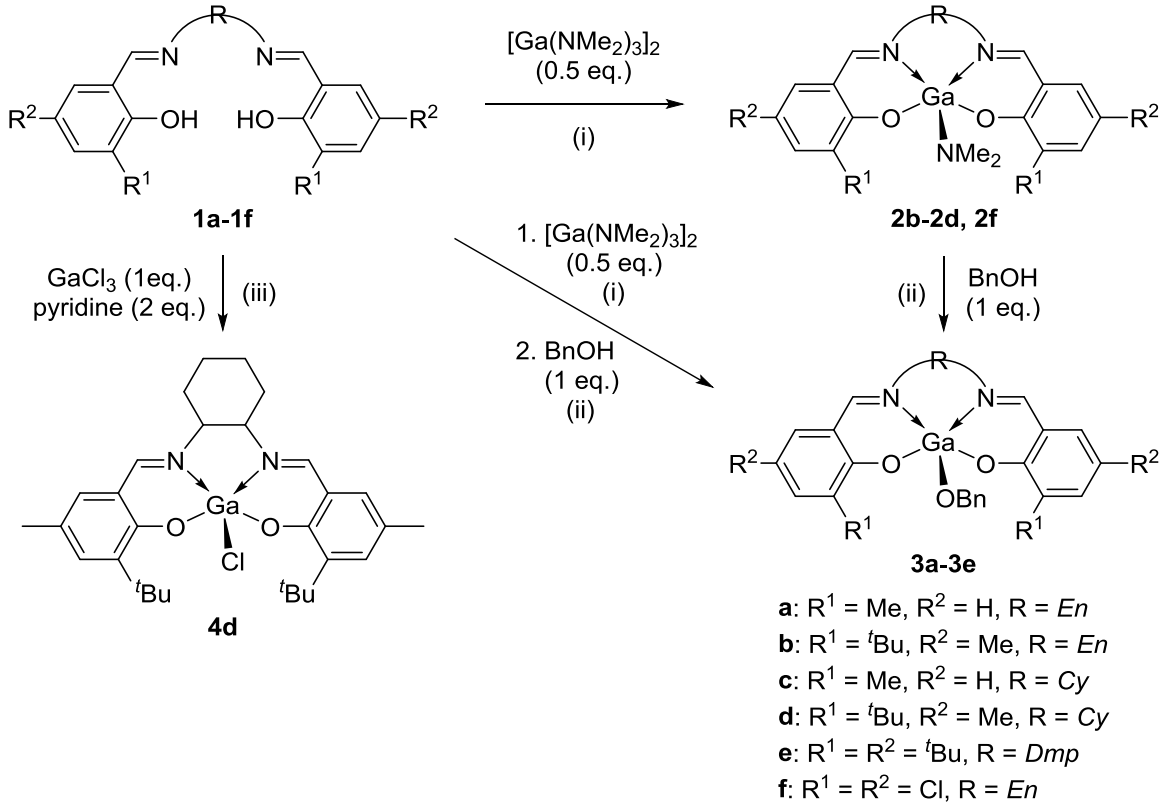
H_2), in line with previous reports.[19] Thus, the reaction of ligands **1a-1f** with a stoichimetric amount of $GaMe_3$ led, in all cases, to a complicated mixture of compounds under various the reactions conditions, precluding further derivatization. Instead, the amine elimination route starting from more nucleophilic $[Ga(NMe_2)_3]_2$ (*vs.* $GaMe_3$) as a Ga(III) precursor,[28] allowed the direct synthesis of the corresponding (salen)Ga–NMe_2 chelates at room temperature (**2b-2d**, **2f**; Scheme 3, i).[29]



Scheme 2. Proteo-ligands **1a-1f**.

Compounds **2b-2d** and **2f** were isolated as yellow powders in excellent yields (> 90%) and display a poor solubility in common organic solvents, preventing the obtainment of ^{13}C NMR data in the case of **2c**, **2d** and **2f**. The formulation and proposed structure for **2b-2d** and **2f** are based on ^{1}H NMR, combustion analysis data and their ready conversion to [Ga(OBn)(Salen)] species (upon alcoholysis), whose molecular structures were unambiguously established by X-ray crystallophy diffraction (*vide infra*). The NMR data for **2b-2d** and **2f** agree with the expected structures, in particular with an effective C_s-symmetry for the ethylene- and CH_2-CMe_2-CH_2-bridged salen derivatives, as reported for related Salen-Ga and Salen-Al compounds.[26,24,30,37,38]

The NMR data also agree with the presence of a Ga–*NMe₂* moiety for **2b-2d** and **2f** (^{1}H NMR singlet resonance ranging from 2.32 to 2.71 ppm).



Scheme 3. Synthesis of the Salen-gallium amido (**2b-2d**, **2f**), alkoxo (**3a-3e**) and chloro (**4d**) complexes. Conditions: (i) toluene, from -35 °C to room temperature, 20 h; (ii) CH_2Cl_2, from -35 °C to room temperature, 20 h; (iii) toluene, from -35 °C to room temperature, 20 h.

The Salen-gallium benzyloxide complexes **3a-3e**·BnOH were readily prepared through an alcoholysis reaction between BnOH and the corresponding Salen-gallium amido complexes (**2a-2e**), and were all isolated in moderate to good yields as analytically pure yellow solids (45-93%; Scheme 3, ii).[31] The NMR data for these chelates agree with the formation of salen-supported Ga–OBn species in all cases. In particular, the ^{1}H NMR spectra for **3a-3e**·BnOH contain

resonances consistent with the presence of a Ga-OCH_2Ph moiety per salen ligand (in the 4.44 – 4.66 ppm region). The reaction of the Ga–NMe_2 species **2f** with BnOH (1equiv) led an unsoluble solid, preventing any further characterization in solution.

Compounds **3a**-**3e**·BnOH are rare mononuclear [Ga(OR)(Salen)] complexes.[35] The molecular structures of the [Ga(OBn)(Salen)] complexes **3a**, **3d** and **3e** were confirmed by XRD analysis and are depicted in Figures 1-3 (Figures S1-S3 in ESI). A summary of structural parameters is provided in Table 1. In each complex, the Ga(III) metal center is five-coordinate with a κ^4-N_2,O_2 chelating salen ligand and one benzyl oxide ligand to complete the coordination sphere. In such chelates, the τ (Tau) parameter allows a quantitative measure of the distortion from perfectly square pyramidal (SP) or trigonal bipyramidal (TBP) geometry for five-coordinate metal complexes.[22,32,33,34,35,36,37,38] The broad range of τ values typically encountered in Salen-supported Group 13 metal complexes reflects how the metal coordination geometry may be affected/tuned by the salen backbone and substituents.[22,39,40] Based on literature data, Salen-Group 13 complexes incorporating a flexible and thus less constraining linker, *i.e.* $N(CH_2)_nN$ with n > 2, typically adopt a TBP geometry at the metal center while more rigid Salen bridges (such as ethylene, cyclohexylene and phenylene bridges) favor a SP geometry.[19] The size of the phenolate *ortho*-substituents may also matter, with larger groups typically disfavoring SP geometry to avoid severe steric hindrance. For instance, while the ethylene-bridged and (unsubstituted) phenolate [(Salen)(O^{i}Pr)Al] species adopts a clear-cut SP arrangement (τ = 0.22) the ^{t}Bu-*ortho*-substituted phenolate Al–OEt analogue features a severely distorted SP geometry (τ = 0.44). The values of the τ parameter were calculated for **3a**, **3d** and **3e**·BnOH. In the case of complex **3e**·BnOH (τ = 0.74, Table 1), a geometry closer to a TBP is observed, as expected with a flexible 2,2-dimethyl-1,3-propylene (*Dmp*) linker (Schemes 2-3, Figure 3, Figure S3 in ESI). A

similar arrangement was reported for the Al–Me, Al-Et and Al–OBn analogues of **3e** (τ = 0.72, 0.76 and 0.81).[41,34b] The tendency is opposite for complex **3d** (Figure 2, Figure S2 in ESI), with the Ga(III) center adopting a highly distorted SP geometry (τ = 0.41), in line with a Salen ligand combining a rigid *Cy* backbone and bulky *ortho*-^{t}Bu substituents.[35] The distorted TBP geometry of complex **3a** (τ = 0.70, Figure 1, Figure S1 in ESI) somewhat differ from that in other related ethylene-bridged salen Group 13 metal complexes, which typically adopt distorted SP geometries at the metal center.[19,22] In all three complexes **3a**, **3d** and **3e**, the Ga-*O*Bn, Ga-O_{salen}, Ga-N bond lengths are in the expected ranges [1.830(4)-1.8530(16), 1.830(3)-1.903(3) and 2.007(4)-2.048(4) Å, respectively; Table 1] for such Salen-based chelates. The structural differences between the Salen-Ga alkoxides **3a**, **3d** and **3e** impact their performance as ROP initiators (*vide infra*).

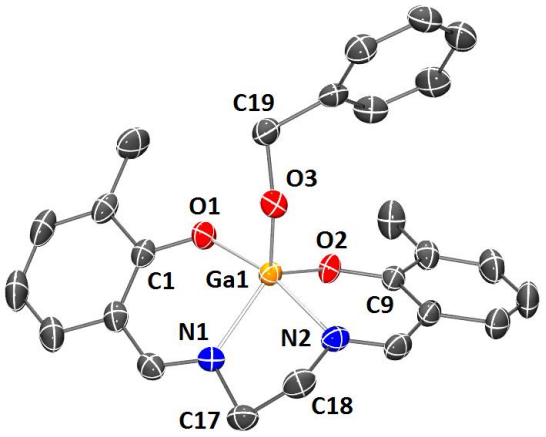


Figure 1. View of the molecular structure of complex **3a**. Hydrogen atoms were omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths and angles are reported in Table 1.

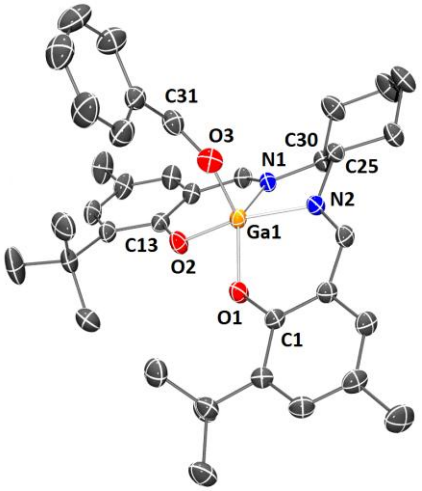


Figure 2. View of the molecular structure of complex **3d**. Hydrogen atoms were omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths and angles are reported in Table 1.

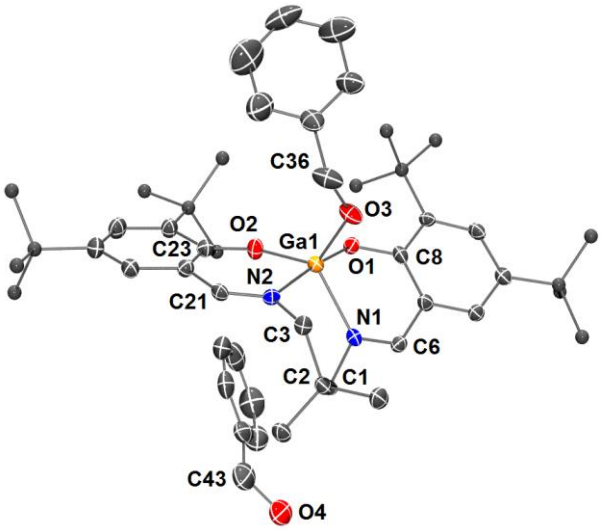


Figure 3. View of the molecular structure of complex **3e**·BnOH. Hydrogen atoms were omitted, and ^{t}Bu groups represented as small spheres for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths and angles are reported in Table 1.

Table 1. Selected bond lengths (Angstroms) and angles (degrees) in the solid-state structures of the [Ga(R)(Salen)] (R = OBn, Cl) complexes (**3a**, **3d**, **3e**·BnOH, **4d**·$CHCl_3$).[a]

	3a	**3d**·0.5CH_2Cl_2	**3e**·1.5BnOH	**4d**·$CHCl_3$
Ga1-O1	1.9019(12)	1.8672(15)	1.903(3)	1.8783(13)
Ga1-O2	1.8764(12)	1.8914(15)	1.830(3)	1.8608(15)
Ga1-N1	2.0360(15)	2.0447(18)	2.007(4)	2.0278(18)
Ga1-N2	2.0388(14)	2.0198(18)	2.048(4)	2.0217(17)
Ga1-O3	1.8509(12)	1.8530(16)	1.830(4)	
Ga1-Cl1				2.2255(6)
d (Ga1-N_2O_2)	0.548	0.499	0.511	0.479
O1-Ga1-O2	91.14(5)	87.90(7)	87.49(15)	88.27(6)
N1-Ga1-N2	78.69(6)	79.81(7)	86.01(16)	79.89(7)
O1-Ga1-N2 (β)	166.49(6)	162.96(7)[b]	170.83(15)	163.84(7)
O2-Ga1-N1 (α)	124.78(6)	137.37(7)[b]	126.58(17)	137.70(7)
τ ; geometry	0.70 ; TBP	0.41 ; SP[c]	0.74 ; TBP	0.44 ; (SP)[c]

[a] Crystallographic data are available in the ESI – Table S1. [b] For **3d**, the O1-Ga1-N2 and O2-Ga1-N1 angles, which are the angles used to calculate the τ parameter, are replaced by O2-Ga1-N2 and O1-Ga1-N1, respectively. [c] The τ parameter calculated for **3d** and **4d** indicates an intermediate geometry between SP and TBP.

Attempted crystallization of analytically pure Ga–amido analogue **2d** from $CHCl_3$ (2 days at room temperature) led instead to crystals of the Ga–Cl complex [Ga(Cl)(**1d**)] (**4d**), as confirmed by XRD analysis (Figure 4, Figure S4 in ESI), likely resulting from a protonolysis reaction between **2d** and traces HCl (in $CHCl_3$).[42] In the solid state, complex **4d** contains a central Ga(III)

center in an intermediate geometry between TBP and SP (τ = 0.44), similar to that in the Ga-OBn analogue **3d** (τ = 0.41), but clearly different from the related [Ga(Cl)(Salen)] complex (τ = 0.19, (+/-) *Cy* backbone, *ortho*- and *para*-^{t}Bu substituents) reported by Darensbourg *et al*.[25] Further indicating the limited protolytic stability of Ga–amido derivatives, a left-to-crystallize saturated benzene solution of **2b** afforded crystals of the bridged dinuclear complex [Ga(μ^2-O)(Salen)]$_2$ (**5b**) (Figure 5, Figure S5 in ESI), as deduced from XRD analysis. Complex **5b**, whose formation results from the adventitious presence of water, is a rare μ-oxo Ga–O–Ga dinuclear species.[43] In the solid-state, it is composed of two [Ga(Salen-κ^4-N_2,O_2)] moieties connected through a μ-oxo bridge resulting in five-coordinate gallium centers, which are both in a distorted square pyramidal environment [τ(Ga1) = 0.35 and τ(Ga2) = 0.37]. The Ga2-O5-Ga1 angle [140.23(11)°] in **5b** is much smaller than the Al-O-Al angle [152.0(3)–173.1(1)°] found in previously reported μ-oxo dinuclear Salen-Al structures.[37,38,44,45] The hydrolysis of the Ga–amido **2d** to yield **5d** likely proceeds *via* a similar mechanism to that thoroughly studied by Atwood and Rutherford for (Salen)Al–amido analogues.[37]

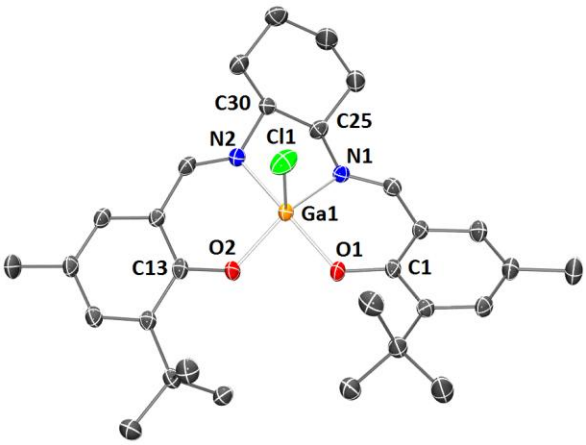


Figure 4. View of the molecular structure of complex **4d** in **4d**·$CHCl_3$. Solvent molecule and hydrogen atoms were omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths and angles are reported in Table 1.

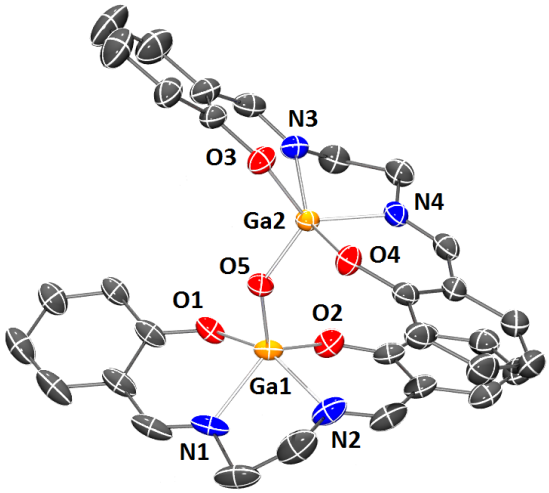


Figure 5. View of the molecular structure of complex **5b** in **5b**·2(C_6H_6). Solvent molecules, hydrogen atoms and the *ortho* (^{t}Bu) and *para* (Me) groups were omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths (Å): Ga1-N1 2.045(2), Ga1-N2 2.046(2), Ga2-N3 2.053(2), Ga2-N4 2.052(2), Ga1-O1 1.8987(19), Ga1-O2 1.9025(19), Ga2-O3 1.8980(19), Ga2-O4 1.9169(17), Ga1-O5 1.7849(18), Ga2-O5 1.7818(18), and angles (deg): O1-Ga1-O2 87.47(8), O3-Ga2-O4 86.74(8), N2-Ga1-N1 78.06(11), N4-Ga2-N3 78.28(9), O1-Ga1-N2 155.21(10), O2-Ga1-N1 133.89(9), O3-Ga2-N4 132.16(9), O4-Ga2-N3 154.30(9), Ga2-O5-Ga1 140.23(11).

Ring-Opening Polymerization (ROP) of cyclic esters

ROP of *rac*-Lactide. The catalytic performances of the salen-Ga alkoxide complexes (**3a** – **3e**) and the Ga–amido species **2f** were evaluated in the ROP of *rac*-LA.[46] The results are compiled in

Table 2. In toluene at 90 °C, complexes **3a** – **3c**, **3e**·BnOH and **2f** initiated the controlled ROP of *rac*-lactide (100 equiv, 40 to 95% conversion within 2.5 to 65 h) to afford isotactically-enriched PLA (P_m = 0.68-0.77) with narrow PDIs (1.10-1.16), as deduced from ^{1}H NMR and SEC data (entries 1, 3, 4, 8, 9, Table 2 and Figures S23-S24, S26-S27, S31-S32 and S38 in ESI). In contrast, the ROP of lactide initiated by species **3d** led to heterotactic-enriched PLA (P_m = 0.38; entry 6, Table 2 and Figures S29 and S38 in ESI). The ROP of *rac*-LA by **3a**, **3c** and **3d** may be performed with a greater efficiency under bulk conditions (100 equiv. lactide, 79-93% conv. to PLA, entries 2, 5 and 7, Table 2 and Figures S25, S28, S30 in ESI). Carrying out the ROP of lactide (100 equiv lactide, toluene, 90 °C) using a 1/1 **3a**/BnOH initiating mixture led to a similar ROP activity to that with **3a** alone, indicating that the presence of an alcohol source little influences catalytic activity. All kinetic data in solution (toluene, 90 °C) for these catalysts are consistent with controlled ROP processes, including a first-order dependence on lactide concentration and a linear correlation between the PLA chain length (M_n) and monomer conversion (Figures 6-7 and Figures S35-S37 in ESI). For the PLA produced with initiators **3a** and **3c**, the observed M_n values are higher than the expected M_n values, which may reflect a rather slow initiation (*vs.* chain propagation) of the ROP process. For PLA produced with catalysts **3b** and **3e**·BnOH, MALDI-TOF spectrometric data agree with a BnO-ester-ended linear PLA with little transesterification, in line with a ROP catalysis proceeding *via* a coordination-insertion mechanism (Figures S39-S40 in ESI).

Regarding the activity for the present Ga systems, the trend is the following: **2f**/BnOH ≈ **3a** > **3e**·BnOH > **3c** > **3d** > **3b**. Thus, the Ga complexes bearing a salen ligand with a somewhat flexible linker such as *En* linker combined with less steric bulky phenolate moieties (*i.e.* **3a** and **2f**/BnOH) perform best. The similar ROP activity of **3a** and **2f**/BnOH parallels the similar size of

the Cl and Me groups and suggest little electronic effect of the Cl groups on ROP activity. In any case, regardless of the phenolates steric bulk, the use of less flexible *Cy* backbone appears detrimental to ROP performance (*i.e.* **3c** and **3d**). In terms to stereoselectivity, the system **2f**/BnOH, which bears an electron-withdrawing salen ligand and an *En* linker (**1f**), is most *iso*-selective ($P_m = 0.77$).[47] Lower and similar isotacticities were observed for **3a** – **3c** and **3e** ($0.68 < P_m < 0.71$), reflecting the little influence of steric hindrance and geometrical constraints on *iso*-selectivity in these systems under the studied conditions. However, interestingly, combining steric hindrance and geometrical constraint at Ga(III), as in initiator **3d**, switches stereoselectivity to an hetero-selective ROP system ($P_m = 0.38$).[48] As a comparison, analogue **3c**, which only differs from **3d** by the smaller size of the phenol *ortho*-substituents (Me in **3c** *vs.* ^{t}Bu in **3d**), is an *iso*-selective ROP catalyst ($P_m = 0.71$). Such an observation agrees with the known tendency of severely crowded ROP initiators for heteroselectivity.[4,5,6,7,49] The present Salen-Ga compounds **3a** – **3e**·BnOH overall perform better in the ROP of LA than the few examples reported to date.

Table 2. ROP of *rac*-LA initiated by the [Ga(Salen)(OBn)] (**3a** – **3d**), [Ga(Salen)(OBn)(BnOH)] (**3e**·BnOH) and [Ga(Salen)(NMe_2)] complexes (**2f**).[a]

Entry	Init.	Solvent	Temp. (°C)	Time (h)	Conv.[b] (%)	M_n(corr.)[c] (g.mol^{-1})	M_n(theo.)[d] (g.mol^{-1})	M_w/M_n[e]	P_m[f]
1	**3a**	Toluene	90	3.75	75	18 000	10 900	1.15	0.68
2[g]	**3a**	-	130	1	93	25 400	13 500	1.22	0.50
3	**3b**	Toluene	90	65	40	4 000	5 800	1.09	0.71
4	**3c**	Toluene	90	20	95	27 100	13 800	1.16	0.71
5[g]	**3c**	-	130	2	90	21 500	13 100	1.18	0.50

6	**3d**	Toluene	90	20	78	10 500	11 300	1.13	0.38
7[g]	**3d**	-	130	2	79	11 500	11 500	1.22	0.50
8	**3e**•BnOH	Toluene	80	20	94	5 500	6 800[h]	1.10	0.70
9	**2f**	Toluene	90	2.5	66	22 800	9 600	1.11	0.77

[a] Reaction conditions: Ga/LA molar ratio = 1:100, $[LA]_0$ = 1 M for reactions in solution (see Figures S24–S32 in ESI for SEC traces). [b] Determined from ^{1}H NMR analysis. [c] Determined from GPC analysis by using polystyrene standards and applying a correction factor of 0.58.[50] [d] Calculated according to the conversion (M_{LA} = 144.13 g.mol^{-1}). [e] Determined from GPC analysis. [f] Determined by decoupled ^{1}H NMR in the methine region (see Figures S38 in ESI). [g] Under bulk conditions. [h] The $M_{n(theo)}$ value takes into account the involvement of 1 equiv. BnOH (**3e**•BnOH) as a chain transfer agent.

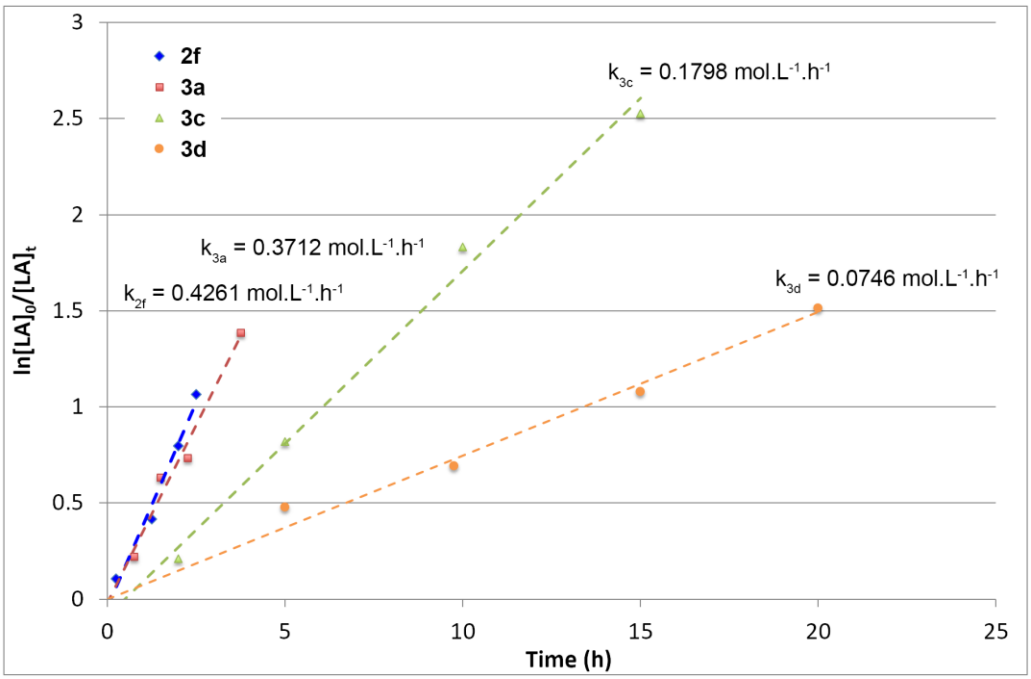


Figure 6. Pseudo-first-order kinetic plot for the ROP of *rac*-LA mediated by catalysts **2f**, **3a**, **3c** and **3d**. Conditions: Ga/[*rac*-LA]$_0$ = 1/100, [*rac*-LA]$_0$ = 1M, toluene, 90 °C.

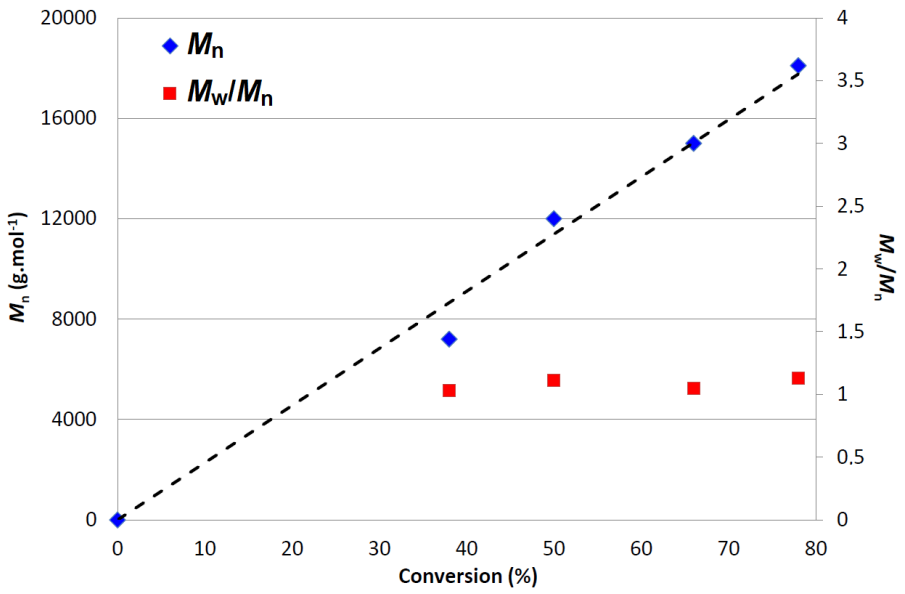


Figure 7. Dependence of M_n and dispersity (M_w/M_n) of the produced PLA on monomer (*rac*-LA) conversion using **3d** as catalyst. Conditions: Ga/[*rac*-LA]$_0$ = 1/100, [*rac*-LA]$_0$ = 1M, toluene, 90 °C.

ROP of ε-Caprolactone (CL) and LA/CL co-polymerization. Complex **3a**, the most active LA ROP system among (salen)Ga–OR species, also readily polymerizes *ε*-CL (93% of 100 equiv., [*ε*-CL]$_0$ = 1 M, toluene, 90 °C, 2 h) to afford narrow-disperse PCL (M_w/M_n = 1.19), though with higher than expected PCL chain length [M_n(corr.) = 23 600 *vs*. M_n(theo.) = 10 600 g.mol^{-1}] (see Figure S33 in ESI).[51] Sequential polymerization of *rac*-LA and *ε*-CL (100 equiv. of each monomer *vs*. Ga, toluene, 90 °C, 13 h) afforded the quantitative formation of the corresponding diblock PLA$_{99}$-*b*-PCL$_{92}$ copolymer [M_n(corr.) = 28 500 g.mol^{-1}, $Đ$ = 1.20, M_n(theo.) = 24 800 g.mol^{-1}, Figure S34 in ESI].[52] This shows that Salen-gallium complexes may be effective for the controlled ROP of CL and the production of PCL-*b*-PLA copolymers.[35] A random LA/CL co-polymerisation test with initiator **3a** (100/100/1 CL/LA/**3a** mixture, toluene, 90 °C, 22 h) led to

the preferential ROP of LA (97% conv. of LA, 19% conv. CL), and thus the production of blocky-type PLA-PCL copolymers (NMR data in ESI, Figure S41).

Conclusion

A series of mononuclear Salen-supported gallium amido/alkoxide derivatives were prepared and structurally characterized *via* a straightforward amine-elimination/alcoholysis sequence, which, unlike the alkane elimination route, provided access to (κ^4-salen)Ga chelates. In addition to their poor solubility, the more basic Ga-amido species clearly display a decreased protolytic stability when compared the Ga-alkoxide analogues, as reflected by the ready formation of protonolysis products **4b** and **5b**. For the most part, the present (salen)Ga–X species effectively mediate the *iso*-selective ROP of *rac*-LA in a controlled manner (P_m up to 0.77), with a ROP activity greatly dependent upon steric hindrance and geometrical constraints imposed by the salen ligands. Based on the present study, salen ligands with limited steric hindrance and a certain degree of flexibility appear best suited for *iso*-selective ROP by (salen)Ga chelates, a trend observed with other metal-based lactide ROP initiators.[53] When compared to their Al analogues, the present (salen)Ga species display comparable ROP activity and control, but (salen)Al species typically exhibit higher *iso*-selectivities under similar reaction conditions.

Experimental Section.

General Procedures. All experiments were carried out under N_2 in an Mbraun Unilab glovebox. Toluene, pentane and dichloromethane were dried using an MBraun SPS system and

stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. Tetrahydrofuran was distilled over Na/benzophenone and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. Anhydrous BnOH (99.8% purity, Aldrich), CD_2Cl_2, $CDCl_3$ and C_6D_6 were stored over activated molecular sieves (4 Å) in a glovebox for 24 h prior to use. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France) or Aldrich. Gallium trichloride was purchased from Strem Chemicals and used as received. *rac*-Lactide (98% purity, Aldrich) was recrystallized and sublimed once before use. ε-Caprolactone (97% purity, Aldrich) was distilled from CaH_2 prior to use. All other chemicals were purchased from Aldrich and were used as received. The NMR spectra were recorded on Bruker AC 300, 400 or 500 MHz NMR spectrometers in Teflon-valved J-Young NMR tubes at ambient temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm *vs*. $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. The coupling constants are reported in Hertz. Elemental analysis for all compounds were performed at the Service de Microanalyse of the Université de Strasbourg (Strasbourg, France). GPC analyses were performed on a system equipped with a Shimadzu RID10A refractive index detector with HPLC grade THF as an eluent (with molecular masses and PDIs calculated using polystyrene standards). These were adjusted with appropriate correction factors for the M_n values. For the X-ray diffraction studies, the intensity data were collected at 173(2) K on a Bruker Apex II diffractometer (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-2013) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-13/14) with anisotropic thermal parameters for all the non-hydrogen atoms.[54] The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-13/14 procedures) and refined riding on the corresponding parent atoms. For compound **3e**·1.5BnOH, the SQUEEZE instruction in PLATON was applied.[55] The

residual electron density was assigned to half a molecule of benzyl alcohol. Crystallographic and experimental details for all structures are summarized in the Supporting Information (Tables S1-S2 in ESI). The Salen ligands[27] and $[Ga(NMe_2)_3]_2$[56] were synthesized according to literature procedures. As often observed in Salen-Group 13 chemistry, several complexes were found poorly soluble in common organic solvents, which prevented the recording of their ^{13}C NMR spectra.

*Synthesis of the Salen-gallium(III) amido complexes (**2b-2d, 2f**)*

[Ga(NMe$_2$)(1b)] (2b)

A precooled toluene solution (-35 °C, 5 mL) of $Ga(NMe_2)_3$ (99 mg, 0.49 mmol) was added slowly to a precooled toluene solution (-35 °C, 10 mL) of **1b** (100 mg, 0.24 mmol) under vigorous stirring. The resulting solution was stirred for 20 h at room temperature. The solution was then evaporated to dryness and the resulting solid washed with pentane (2 x 10 mL) to give **2b** as a light yellow powder (120.0 mg, 95% yield). Anal. Calcd for $C_{28}H_{40}GaN_3O_2$ (434.19): C 64.63; H 7.75; N 8.08; found: C 65.01, H 7.55, N 8.12. ^1H NMR (400 MHz, C_6D_6): δ 1.85 (s, 18H, Ar^t*Bu*), 2.24 (s, 6H, Ar*Me*), 2.53 (m, 2H, NC*H*$_2$C*H*$_2$N), 2.71 (s, 6H, N(C*H*$_3$)$_2$), 3.07 (m, 2H, NC*H*$_2$C*H*$_2$N), 6.57 (d, $^4J_{H,H}$ = 2.0 Hz, 2H, Ar), 7.39 (d, $^4J_{H,H}$ = 2.0 Hz, 2H, Ar), 7.47 (s, 2H, ArC*H*N). ^{13}C NMR (100 MHz, C_6D_6): δ 20.8 (Ar*C*H$_3$), 30.2 (ArC(*C*H$_3$)$_3$), 36.0 (Ar*C*(CH$_3$)$_3$), 43.3 (N(*C*H$_3$)$_2$), 53.8 (N*C*H$_2$*C*H$_2$N), 118.0 (Ar), 123.5 (Ar), 131.5 (Ar), 134.0 (Ar), 142.5 (Ar), 167.5 (Ar), 169.0 (Ar*C*HN).

[Ga(NMe$_2$)(1c)] (2c)

The same procedure as for complex **2b** was used with $Ga(NMe_2)_3$ (68 mg, 0.34 mmol), and **1c** (100 mg, 0.28 mmol) and afforded **2c** as a bright yellow powder (120.1 mg, 91% yield). Anal. Calcd for $C_{24}H_{30}GaN_3O_2$ (462.25): C 62.36; H 6.54; N 9.09; found: C 62.22, H 6.45, N 8.96. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (m, 4H, cyclohexyl), 2.09 (m, 2H, cyclohexyl), 2.35 (s, 3H, N(C*H*$_3$)$_2$), 2.37 (s, 3H, N(C*H*$_3$)$_2$), 2.41 (s, 6H, ArC*H*$_3$), 2.46 (m br, 1H, cyclohexyl), 2.63 (m br, 1H, cyclohexyl), 3.15 (t br, 1H, NC*H*C*H*N), 3.72 (t br, 1H, NC*H*C*H*N), 6.61 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, Ar), 6.67 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, Ar), 6.97 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar), 7.04 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, Ar), 7.27 and 7.31 (2 d overlapping and overlapping the solvent residual peak, $^3J_{H,H}$ = 6.9 Hz, approx.. 2H, Ar), 8.19 (s br, 1H, ArC*H*N), 8.37 (s br, 1H, ArC*H*N).

[Ga(NMe$_2$)(1d)] (2d)

The same procedure as for complex **2b** was used with $Ga(NMe_2)_3$ (44 mg, 0.22 mmol), and **1d** (100 mg, 0.22 mmol) and afforded **2d** as a light yellow powder (123.7 mg, 98% yield). Anal. Calcd for $C_{32}H_{46}GaN_3O_2$ (574.46): C 66.91; H 8.07; N 7.31; found: C 66.72, H 7.97, N 7.55. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (m br, 4H, cyclohexyl), 1.52 (s, 18H, Ar^t*Bu*), 2.10 (m, 2H, cyclohexyl), 2.24 (s, 3H, Ar*Me*), 2.26 (s, 3H, Ar*Me*), 2.41 (s, 6H, N(C*H*$_3$)$_2$), 2.49 (m, 1H, cyclohexyl), 2.62 (m, 1H, cyclohexyl), 3.14 (t br, $^3J_{H,H}$ = 12 Hz, 1H, NC*H*C*H*N), 3.85 (t br, $^3J_{H,H}$ = 12 Hz, 1H, NC*H*C*H*N), 6.83 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, Ar), 6.86 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, Ar), 7.25 (d, $^4J_{H,H}$ = 2.6 Hz, 2H, Ar), 8.21 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N), 8.36 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N).

[Ga(NMe$_2$)(1f)] (2f)

The same procedure as for complex **2b** was used with $Ga(NMe_2)_3$ (101 mg, 0.50 mmol), and **1f** (203 mg, 0.50 mmol) and afforded **2f** as a light yellow powder (238.2 mg, 92% yield). Anal. Calcd for $C_{18}H_{16}Cl_4GaN_3O_2$ (517.87): C 41.75; H 3.11; N 8.11; found: C 41.58, H 3.20, N 8.27. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.32 (s, 6H, N(C*H*$_3$)$_2$), 3.85 (m br, 2H, NC*H*$_2$C*H*$_2$N), 4.04 (m br, 2H, NC*H*$_2$C*H*$_2$N), 7.08 (d, $^4J_{H,H}$ = 2.8 Hz, 2H, Ar), 7.25 (m, 2H, Ar), 7.51 (t, $^4J_{H,H}$ = 2.8 Hz, 2H, ArC*H*N).

*Synthesis of the Salen-gallium(III) alkoxide complexes (**3a-3e**)*

[Ga(OBn)(1a)] (3a)

A precooled toluene solution (-35 °C, 5 mL) of $Ga(NMe_2)_3$ (68.1 mg, 0.34 mmol) was added slowly to a precooled toluene solution (-35 °C, 10 mL) of **1a** (100 mg, 0.34 mmol) under vigorous stirring. The resulting suspension was stirred for 20 h at room temperature. The solvent was then evaporated to dryness and the resulting solid washed with pentane (2 x 10 mL) to give a yellow powder (93.0 mg) insoluble in common deuterated solvent and being used directly for the next step.

A precooled CH_2Cl_2 solution (-35 °C, 5 mL) of benzyl alcohol (24 µL, 0.23 mmol) was added slowly to a precooled CH_2Cl_2 suspension of the aforementioned powder (93.0 mg) under vigorous stirring. The resulting solution was stirred for 2 h at room temperature before being evaporated to dryness. The resulting solid was washed with pentane (2 x 10 mL) to afford **3a** as a yellow powder (100.1 mg, 63% yield). Anal. Calcd for $C_{25}H_{25}GaN_2O_3$ (471.21): C 63.72; H 5.35; N 5.95; found: C 63.29, H 5.40, N 6.12. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 6H, Ar*Me*), 3.69 (m br, 2H, NC*H*$_2$C*H*$_2$N), 4.03 (m br, 2H, NC*H*$_2$C*H*$_2$N), 4.66 (s, 2H, C*H*$_2$OBn), 6.62 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ar), 6.97 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H, Ar), 7.04 – 7.13 (m, 5H,

Ar), 7.28 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H, Ar), 8.27 (s, 2H, ArC*H*N). ^{13}C NMR (500 MHz, $CDCl_3$): δ 16.4 (Ar*C*H_3), 53.7 (N*C*H_2*C*H_2N), 66.8 (O*C*H_2Ph), 116.1 (Ar), 116.9 (Ar), 125.9 (Ar), 126.7 (Ar), 127.6 (Ar), 131.5 (Ar), 131.6 (Ar), 135.9 (Ar), 145.5 (Ar), 167.4 (Ar), 170.0 (Ar*C*HN).

[Ga(OBn)(1b)] (3b)

A precooled CH_2Cl_2 solution (-35 °C, 5 mL) of benzyl alcohol (20 µL, 0.19 mmol) is added slowly to a precooled CH_2Cl_2 suspension of **2b** (100 mg, 0.19 mmol) under vigorous stirring. The resulting solution was stirred for 2 h at room temperature before being evaporated to dryness. The resulting solid was washed with pentane (2 x 10 mL) to afford **3b** as a light yellow powder (102.5 mg, 92% yield). Anal. Calcd for $C_{33}H_{41}GaN_2O_3$ (583.43): C 67.94, H 7.08, N 4.80; found: C 68.32, H 6.99, N 4.77. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.75 (s, 18H, Ar^t*Bu*), 2.48 (s, 6H, Ar*Me*), 3.85 (m, 2H, NC*H*$_2$C*H*$_2$N), 4.11 (m, 2H, NC*H*$_2$C*H*$_2$N), 4.84 (s, 2H, C*H*$_2$ OBn), 6.90 (s br, 2H, Ar), 7.25-7.26 (overlapping solvent peak, 3H, Ar), 7.46 (s br, 2H, Ar), 7.48-7.55 (m, 2H, Ar), 8.31 (s br, 2H, ArC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7 (Ar*C*H_3), 29.8 (ArC(*C*H_3)$_3$), 35.6 (Ar*C*(CH_3)$_3$), 53.7 (N*C*H_2*C*H_2N), 66.7 (O*C*H_2Ph), 117.7 (Ar), 124.3 (Ar), 125.8 (Ar), 126.8 (Ar), 127.5 (Ar), 131.7 (Ar), 134.1 (Ar), 142.0 (Ar), 145.6 (Ar), 166.4 (Ar), 170.0 (Ar*C*HN).

[Ga(OBn)(1c)] (3c)

The same procedure as for complex **3b** was used with benzyl alcohol (27 µL, 0.26 mmol), and **2c** (120.1 mg, 0.26 mmol) and afforded **3c** as a light yellow powder (129.3 mg, 95% yield). Anal. Calcd for $C_{29}H_{31}GaN_2O_3$ (525.30): C 66.31; H 5.95; N 5.33; found: C 66.47, H 5.88, N

5.27. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (m, 4H, cyclohexyl), 2.00 (m, 2H, cyclohexyl), 2.25 (s, 3H, ArCH_3), 2.27 (s, 3H, ArCH_3), 2.34 (m br, 1H, cyclohexyl), 2.40 (m br, 1H, cyclohexyl), 2.99 (t br, 1H, NC*H*C*H*N), 3.67 (t br, 1H, NC*H*C*H*N), 4.58 and 4.69 (AB spin system, $^{2}J_{H,H}$ = 15 Hz, 2H, CH_2 OBn), 6.54-6.66 (m, 2H, Ar), 6.86 (d, $^{3}J_{H,H}$ = 8.3, 1H, *Ar* OBn), 6.99-7.04 (m, 4H, *Ar* OBn), 7.26-7.35 (m, 4H, Ar), 8.04 (s br, 1H, ArC*H*N), 8.13 (s br, 1H, ArC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (Ar*C*H_3), 16.4 (Ar*C*H_3), 23.4 (cyclohexyl), 24.2 (cyclohexyl), 26.8 (cyclohexyl), 28.3 (cyclohexyl), 62.4 (N*C*H_2*C*H_2N), 64.5 (N*C*H_2*C*H_2N), 66.8 (O*C*H_2Ph), 115.8 (Ar), 116.2 (Ar), 116.7 (Ar), 117.0 (Ar), 125.9 (Ar), 126.9 (Ar), 127.1 (Ar), 127.6 (Ar), 128.7 (Ar), 131.4 (Ar), 131.6 (Ar), 131.7 (Ar), 132.2 (Ar), 135.4 (Ar), 136.0 (Ar), 145.6 (Ar), 163.8 (Ar*C*HN), 166.4 (Ar), 167.9 (Ar), 168.1 (Ar*C*HN).

[Ga(OBn)(1d)] (3d)

The same procedure as for complex **3b** was used with benzyl alcohol (22 μL, 0.22 mmol), and **2d** (123.7 mg, 0.22 mmol) and afforded **3d** as a light yellow powder (120.8 mg, 95% yield). Anal. Calcd for $C_{37}H_{47}GaN_2O_3$ (637.52): C 69.71; H 7.43; N 4.39; found: C 69.65, H 7.39, N 4.43. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (m, 4H, cyclohexyl), 1.51 (s, 9H, Ar^{t}Bu), 1.53 (s, 9H, Ar^{t}Bu), 2.02 (m, 2H, cyclohexyl), 2.25 (s, 6H, ArCH_3), 2.32 (m br, 1H, cyclohexyl), 2.43 (m br, 1H, cyclohexyl), 3.04 (t br, $^{3}J_{H,H}$ = 9 Hz, 1H, NC*H*C*H*N), 3.61 (t br, $^{3}J_{H,H}$ = 9 Hz, 1H, NC*H*C*H*N), 4.57 and 4.67 (AB spin system, $^{2}J_{H,H}$ = 15 Hz, 2H, CH_2 OBn), 6.74 (d, $^{4}J_{H,H}$ = 2.3 Hz, 1H, Ar), 6.81 (d, $^{4}J_{H,H}$ = 2.3 Hz, 1H, Ar), 6.99-7.02 (m, 4H, *Ar* OBn), 7.21 (d, $^{4}J_{H,H}$ = 2.3 Hz, 1H, Ar), 7.23 (d, $^{4}J_{H,H}$ = 2.3 Hz, 1H, Ar), 7.36 (d, $^{3}J_{H,H}$ = 4.3 Hz, 1H, *Ar* OBn), 8.03 (d, $^{4}J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N), 8.15 (d, $^{4}J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7 (Ar*C*H_3), 23.7 (cyclohexyl), 24.2 (cyclohexyl), 26.9 (cyclohexyl), 27.9 (cyclohexyl), 29.8

(ArC(CH$_3$)$_3$), 29.9 (ArC(CH$_3$)$_3$), 35.5 (ArC(CH$_3$)$_3$), 35.6 (ArC(CH$_3$)$_3$), 62.2 (NCH$_2$$CH_2$N), 64.2 (N$CH_2$$CH_2$N), 66.8 (O$CH_2$Ph), 117.6 (Ar), 117.6 (Ar), 124.1 (Ar), 124.3 (Ar), 125.8 (Ar), 127.0 (Ar), 127.1 (Ar), 127.5 (Ar), 128.7 (Ar), 131.8 (Ar), 132.2 (Ar), 133.4 (Ar), 134.3 (Ar), 141.8 (Ar), 142.1 (Ar), 145.7 (Ar), 163.8 (ArCHN), 165.6 (Ar), 167.1 (Ar), 168.0 (ArCHN).

[Ga(OBn)(1e)] (3e)

A precooled toluene solution (-35 °C, 5 mL) of Ga(NMe$_2$)$_3$ (38 mg, 0.19 mmol) was added to a precooled toluene solution (-35 °C, 5 mL) of **1e** (100 mg, 0.19 mmol) under stirring. The reaction mixture was then heated at 90 °C overnight. The volatiles were subsequently evaporated, to yield a yellow solid, which was used without further purification for the next step.

A precooled CH_2Cl_2 solution (-35 °C, 1 mL) of benzyl alcohol (19 µL, 0.19 mmol) was added to a CH_2Cl_2 suspension of the aforementioned powder and the mixture was stirred at room temperature overnight. The solvent was then removed under vacuum and the yellow residue was washed twice with cold pentane (2 x 10 mL). Complex **3e** was isolated as a yellow powder (60 mg, 0.14 mmol, 45% yield). Anal. Calcd for $C_{49}H_{67}GaN_2O_4$ (**3e**•BnOH) (817.81): C 71.97; H 8.26; N 3.43; found: C 71.54; H 8.20; N 3.56. ^{1}H NMR (C_6D_6, 400 MHz): 0.37 (s, Me, 3H), 0.58 (s, Me, 3H), 1.26 (s, residual BnOH, 1.5H), 1.36 (s, Ar^{t}Bu, 18H), 1.78 (s, Ar^{t}Bu, 18H), 2.65 and 3.31 (AB spin system, $^2J_{H,H}$ = 12.4 Hz, NCH$_2$, 2H + 2H), 4.44 (br, CH_2 OBn + residual BnOH, 5H), 6.88 (d, $^4J_{H,H}$ = 2.6 Hz, Ar, 2H), 7.20-7.06 (m, *Ar* OBn + residual BnOH, 12H), 7.48 (s, ArCHN, 2H), 7.73 (d, $^4J_{H,H}$ = 2.6 Hz, Ar, 2H). ^{13}C NMR (C_6D_6, 125 MHz): 24.9 (Me), 24.9 (Me) 29.9 (tBu), 31.3 (tBu), 33.8 (C_{quat}), 35.3 (C_{quat}), 35.8 (C_{quat}), 67.9 (CH$_2$), 117.3 (C_{quat}), 126.7 (Ar), 127.6 (Ar), 127.8 (C_{quat}), 128.0 (Ar), 128.1 (Ar), 130.2 (Ar), 137.7 (C_{quat}), 141.8 (C_{quat}), 167.1 (C_{quat}), 170.5 (ArCHN).

[Ga(Cl)(1d)] (4d)

A precooled toluene solution (-35 °C, 5 mL) of $GaCl_3$ (38.1 mg, 0.22 mmol) was added slowly to a precooled toluene solution (-35 °C, 10 mL) of **1d** (100 mg, 0.22 mmol) and pyridine (34.2 mg, 0.44 mmol) under vigorous stirring. The resulting suspension was stirred for 20 h at room temperature. The pyridine hydrochloride was then filtered out and the solvent was evaporated to dryness. The resulting solid was washed with pentane (2 x 10 mL) to give **4d** as a yellow powder (118.0 mg, 96% yield). Anal. Calcd for $C_{30}H_{40}ClGaN_2O_2$ (565.84) C 63.68, H 7.13, N 4.95, found: C 63.90, H 7.47, N 4.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (m, 4H, cyclohexyl), 1.52 (s, 9H, Ar^{t}Bu), 1.53 (s, 9H, Ar^{t}Bu), 2.09 (m, 2H, cyclohexyl), 2.26 (s, 3H, ArCH_3), 2.27 (s, 3H, ArCH_3), 2.44 (m br, 1H, cyclohexyl), 2.57 (m br, 1H, cyclohexyl), 3.23 (t br, $^3J_{H,H}$ = 12 Hz, 1H, NC*H*C*H*N), 3.73 (t br, $^3J_{H,H}$ = 12 Hz, 1H, NC*H*C*H*N), 6.85 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, Ar), 6.87 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, Ar), 7.24-7.26 (overlapped with residual solvent peak, 2H, Ar), 8.13 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N), 8.31 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, ArC*H*N).

General procedure for the polymerization experiments

ROP of *rac*-LA or *ε*-CL in solution

In a glovebox, the initiator was charged in a vial equipped with a Teflon™-tight screw-cap and a monomer solution ($[M]_0$ = 1 M in toluene) was added *via* a syringe all at once. The solution was vigorously stirred for the appropriate time and at the chosen temperature conditions. When the desired time was reached, aliquots were taken and analyzed by ^{1}H NMR spectroscopy to estimate the conversion. The reaction mixture was exposed to air and volatiles removed under

vacuum; the resulting solid was then washed several times with MeOH, dried in vacuo until constant weight and subsequently analyzed by ^{1}H NMR and SEC.

Co-polymerization of *rac*-LA and ε-CL in solution

For the sequential co-polymerization run, an identical procedure to that above was used with the addition of the incoming ε-CL monomer solution (1 M in toluene) after (nearly) complete consumption of the *rac*-LA (as monitored by ^{1}H NMR).

ROP of *rac*-LA in bulk conditions

In a glovebox, solid initiator and *rac*-LA were charged in a vial equipped with a Teflon™-tight screw-cap and the mixture was vigorously stirred for the appropriate time at 130 °C. When the desired time was reached, aliquots were taken and analyzed by ^{1}H NMR spectroscopy to estimate the conversion. The reaction mixture was exposed to air and the resulting solid was then washed several times with MeOH, dried in vacuo until constant weight and subsequently analyzed by ^{1}H NMR and SEC.

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