Review

Synthesis of Biodegradable Polymers: A Review on the Use of Schiff-Base Metal Complexes as Catalysts for the Ring Opening Polymerization (ROP) of Cyclic Esters

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Abstract: This review describes the recent advances (from 2008 onwards) in the use of Schiff-base metal complexes as catalysts for the ring opening polymerization (ROP) of cyclic esters. The synthesis and structure of the metal complexes, as well as all aspects concerning the polymerization process and the characteristics of the polymers formed, will be discussed.

1. Introduction

Over the past two decades, increasing attention has been dedicated to the development of sustainable polymers that, while retaining all the positive features associated with polyolefins, do not require centuries to biodegrade in the natural environment. In this scenario, polylactones have emerged as suitable candidates, and currently find applications in several fields, spanning from the food and packaging industries to medicinal and pharmaceutical applications [1–5]. Generally, these polymers are synthesized via the metal-catalyzed ring opening polymerization (ROP) of cyclic esters (lactones), with the most common monomers being ε-caprolactone (ε-CL), δ-valerolactone (δ-VL) and lactide (LA) (Figure 1a) [6–8]. In the case of LA, *D*- and *L*-isomers, as well as their racemic mixture (*rac*-lactide, *r*-LA) can be employed; depending on the stereosequence distribution along the PLA chain, different microstructures are possible (Figure 1b) [9]. Currently, the industrial process for the production of *poly*-lactones employs tin octoate as a catalyst [10]. Although this complex is known to be toxic, the leaching of tin does not compromise the biocompatibility of the final material, as the metal tends to be used in amounts below the toxicity level. On the other hand, undesired transesterification reactions are promoted by tin octoate, resulting in broad molecular weight distributions. Hence, alternative systems based on different metal/ligand combinations, capable of better control over the polymerization process, have been explored [11–16]. Complexes derived from Schiff-base ligands emerged as efficient catalysts for the polymerization of α-olefins [17–21], and their use in the production of biodegradable polymers has been receiving growing interest. The success of Schiff-base ligands resides in their high tune-ability and availability. In fact, these species are normally synthesized in quantitative yields from (often) commercially available amines/anilines and carbonyl compounds using simple condensation chemistry. In this review, we describe the recent outputs concerning the use of Schiff-base metal complexes as catalysts for the ROP of cyclic esters. The material covered in this contribution is post-2008 and it is categorized via the metal center employed. Most of the research has focused on the development of catalysts based on earth abundant and non-toxic metals such as Al and Zn (Chart 1). This is not surprising, considering the need for cost-effective and more sustainable processes. Aside

from the synthesis and structure of the complexes, all aspects concerning the polymerization process and the characteristics of the polymer forms will be discussed.
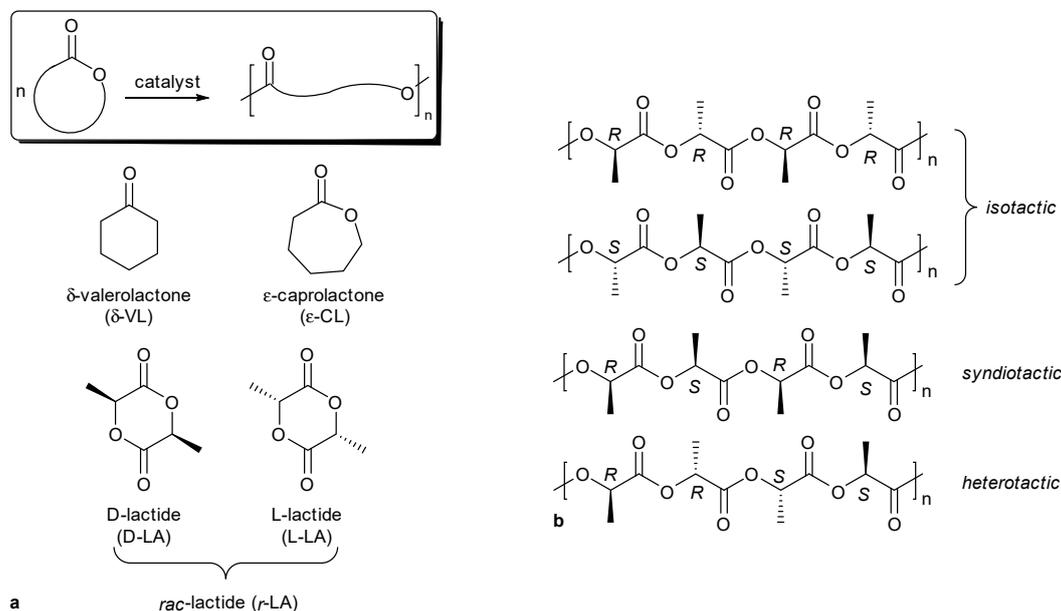
Figure 1. General scheme for the Ring Opening Polymerization (ROP) of common cyclic esters (**a**); possible microstructures of *poly*-lactide (**b**).
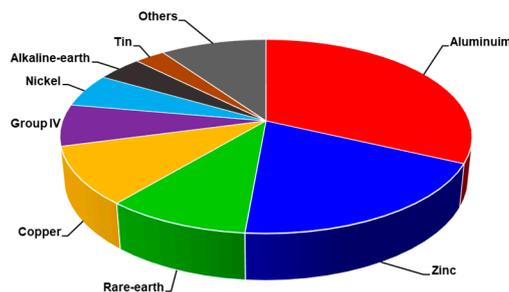

Chart 1. Breakdown of the metal centers employed in the ROP of cyclic esters described in this review.

2. Alkaline Metals

In 2012, Chen et al. prepared 12 novel tetrametallic Li- and Na- complexes (six each) by treating pro-ligands **1–6** with LiO^{t}Bu or NaH in THF (Scheme 1) [22]. All compounds were tested as catalysts in the ROP of *L*-lactide in the presence of benzyl alcohol (BnOH) as co-activator in THF (Table 1). The activity of the Li-based complexes was highly dependent on the structure of the ligand present and followed the trend **6**-Li > **3**-Li > **5**-Li > **1**-Li > **4**-Li > **2**-Li. The polydispersity (M_w/M_n) of the polymers was slightly broad, spanning the range 1.16 to 1.46, while the M_n values were lower than the expected values in all cases. The sodium complexes proved more active than their Li-congeners, allowing for complete conversion in less than 2 min in almost all cases. Nevertheless, poorer control was observed (polydispersities spanning from 1.3 to 1.8). However, narrower M_w/M_n values were obtained by decreasing the catalyst loading, in spite of longer reaction times. Interestingly, the reactivity trend was found to be **3**-Na > **1**-Na ≥ **6**-Na > **5**-Na > **2**-Na > **4**-Na, which was different from that of the Li systems. NMR spectroscopic analysis of the polymer prepared with **4**-Li showed the presence of the diagnostic signals of the BnO- end group, suggesting that the initiation occurs with the insertion of the co-activator into the monomer. Overall, all complexes proved to be better catalysts than previously reported Li- and Na systems. In particular, **3**-Na was found to be more active than a sodium compound

bearing a salen-type ligand, previously reported by Wu et al., capable of producing mainly cyclic oligomers [23].
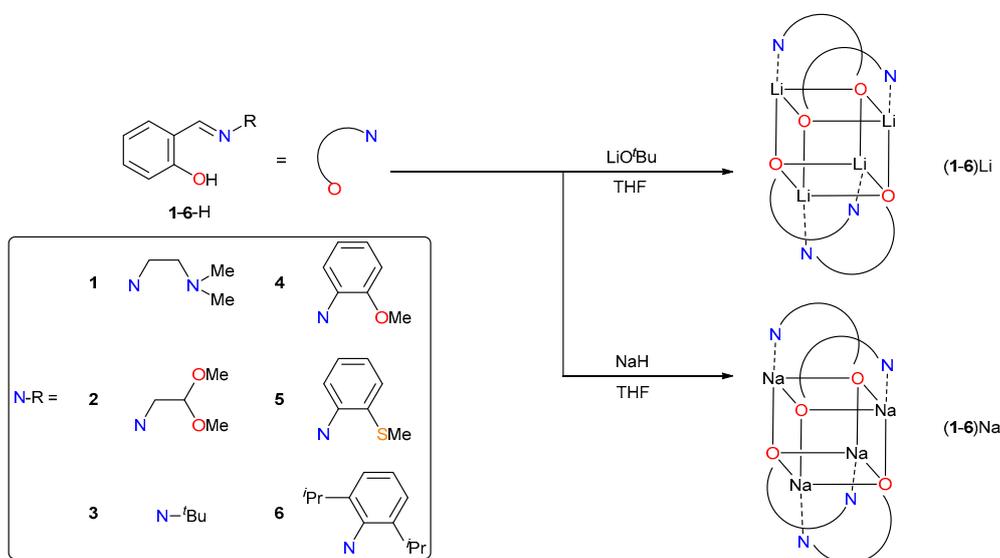
Scheme 1. Synthesis of Li- and Na- complexes of ligands **1–6** [22].

Table 1. ROP of *L*-lactide catalyzed by Li- and Na- complexes of **1–6** [22].

Run	Catalyst	Time (Min)	Conv. (%)[a]	$M_{n(calc.)}$ (Da)[b]	$M_{n(GPC)}$ (Da)[c]	M_w/M_n[c]
1[d]	**1-Li**	90	52	7600	4700	1.16
2[d]	**2-Li**	90	45	3300	6400	1.29
3[d]	**3-Li**	40	88	6500	16,200	1.46
4[d]	**4-Li**	90	10	830	2100	1.14
5[d]	**5-Li**	90	76	5600	10,000	1.33
6[d]	**6-Li**	36	90	6600	15,200	1.31
7[e]	**1-Na**	1	95	13,700	14,200	1.44
8[e]	**2-Na**	1	91	13,200	9000	1.82
9[e]	**3-Na**	0.5	99	14,400	13,400	1.68
10[e]	**4-Na**	40	93	13,500	9000	1.21
11[e]	**5-Na**	2	94	13,700	12,000	1.48
12[e]	**6-Na**	1	99	14,400	13,100	1.58
13[f]	**1-Na**	15	92	26,500	16,000	1.50
14[f]	**2-Na**	130	86	25,000	13,400	1.37
15[f]	**3-Na**	2	99	28,600	23,200	1.36
16[f]	**4-Na**	27.5 h	70	20,300	11,800	1.18
17[f]	**5-Na**	90	82	23,900	14,400	1.38
18[f]	**6-Na**	15	88	25,400	15,500	1.51

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA × [LA]$_0$/[BnOH]$_0$× conversion yield + $M_{w(BnOH)}$. [c] Obtained from Gel Permeation Chromatography (GPC) analysis and calibrated using the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. [d] Reaction condition: toluene (10 mL), [LA] = 0.5 M, [LA]:[BnOH]:[Cat] = 100:1:0.25. [e] Reaction condition: THF (10 mL), [LA] = 0.5 M, [LA]: [BnOH]: [Cat] = 100:1:0.25. [f] Reaction condition: THF (10 mL), [LA] = 1 M, [LA]:[BnOH]:[Cat] = 200:1:0.125.

Lately, a series of Li-, Na, and K phenoxo-imine complexes were disclosed by Tabarnero, Cano et al. [24]. In the presence of BnOH as co-activator, all species proved to be very active in the ROP of *r*-LA, with activity increasing with the size of the metal (K > Na > Li) present. In terms of selectivity, moderate-to high hetero-enrichment was achieved in the presence of the Li-based species (Pr ~ 80). With respect to tridentate ligation, Chen, Lin et al. reported a family of Li- [25] and Na [26] complexes based on [*N*,*N*,*O*]-type Schiff-bases which were active in the ROP of *L*-LA. Under similar

reaction conditions, the Na species proved better performing that the Li analogues; indeed, while full conversion was achieved within minutes in the presence of the former, the latter required up to 21 h. In all cases, good control and polymer M_n matching the expected values were observed. Finally, Wu et al. has recently disclosed six novel Na-Salen complexes [27]. Unlike the previous examples, these species were found to be mononuclear, as observed by Diffusion Ordered Spectroscopy (DOSY). When tested as catalysts in the ROP of *r*-LA, such compounds proved active even in the absence of exogenous alcohol, albeit with poor control and selectivity. However, undesired side-reactions, including monomer epimerization, were suppressed upon addition of excess BnOH (5 equiv.). For tests performed at low temperature (70 °C), good isoselective bias ($P_m = 0.82$) was observed.

3. Alkaline-Earth Metals

Complexes of alkaline-earth metal (in particular Mg- and Ca) have emerged as a promising class of catalysts for the ROP of cyclic esters. Indeed, these metals are not only earth abundant but also relatively non-toxic, and hence potentially biocompatible [28]. The use of Schiff-base alkaline-earth metal complexes in the ROP of cyclic esters will be only briefly discussed, since these systems (along with many others) have been recently reviewed by Zhang, Solan and Sun et al. [29]

3.1. Magnesium

Omondi et al. recently studied the ROP of several lactones initiated by imino-phenolate Mg complexes [30] For ε-CL, full monomer conversion was achieved within 14–55 h at 110 °C under *solvent-free* conditions. In all cases, an induction period of 3 h was observed, and M_n lower than expected were achieved. *L*- and *r*-LA were also efficiently converted, affording polymers with rather broad polydispersities (ca. 2). However, control was improved ($M_w/M_n \sim 1.4$) upon addition of exogenous alcohol as a co-activator. Furthermore, homoleptic Mg complexes bearing β-ketiminato ligands developed by Wang et al. proved capable of promoting the ROP of δ-VL under living and immortal conditions [31]. The process occurred at 35 °C with monomer:Mg ratios as high as 1000:1 and in the presence of an excess (up to 50 equiv.) of BnOH. Extensive NMR spectroscopy and mass spectrometry studies confirmed that only linear *poly*-valerolactones (PVLs) were obtained, excluding the formation of cyclic side-products derived from back-biting. With respect to tridentate ligands, a pyrrolyl-pyridylimine complex active in the ROP of ε-CL and *L*-LA has been reported by Pellecchia et al. in 2017 [32]. In the absence of a co-activator, 200 equiv. of ε-CL were converted within 5 min at 100 °C in toluene. However, the observed M_n values were much higher than the theoretical values, which suggested that only a small fraction of the Mg was active. Indeed, upon introducing BnOH (2 equiv.), higher activity and better control was achieved. Mechanistic investigations proposed the occurrence of an "activated monomer" mechanism. Outstanding performances in the ROP of *L*- and *r*-LA were exhibited by the [*N,N,O*]-based complexes reported by Jones [33]. In particular, they proved active even under industrial relevant conditions, allowing for turnover frequencies up to 10^4 h^{-1}. Interesting activity was observed with analogues systems bearing bulkier substituents [34]. Finally, tridentate ketoimine-magnesium complexes featuring electron donating groups were disclosed by Fritsch et al. and proved particularly active in the homo- and copolymerization of *L*-LA and ε-CL [35].

3.2. Calcium

Calcium complexes of tridentate Schiff-base ligands have been extensively employed as catalysts in the homo- and copolymerization of several cyclic esters (Figure 2) [36–38]. In this scenario, Darensbourgh et al. studied the ROP of *L*-lactide under *solvent-free* conditions catalyzed by complexes **7** and **8** [36]. In terms of activity, the former proved better performing than the latter (80% and 64% conversion for **7** and **8**, respectively). Moreover, high M_n (up to 110 kDa) and narrow polydispersities were achieved. Kinetic investigations performed with **7** suggested the occurrence of a *quasi*-living polymerization process. The microstructure of the polymers was also studied. Interestingly, heterotactic PLAs were isolated with **7**, while essentially atactic materials were obtained in the presence of **8**. Such

different selectivity was thought to be dependent on the steric bulk of the *ortho* substituent on the ligand framework (^{t}Bu and H for **7** and **8**, respectively). The catalysts also proved efficient in the ROP of trimethylene carbonate and in its co-polymerization with *L*-lactide. Lately, Shaver et al. investigated the behavior of **7**, **9** and **10** in the ROP of *ε*-CL and *r*-LA in toluene at room temperature or 70 °C (Table 2) [37]. Such mild reaction conditions were selected in order to limit undesired transesterification processes. Although good catalyst activity was observed for both monomers, control was poor in the case of *ε*-CL, with multimodal distribution and broad polydispersities being obtained. Reactions involving *r*-LA were rather slow, albeit with good control.
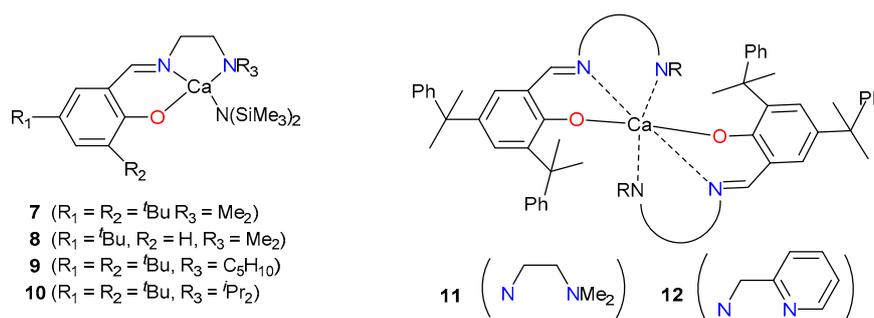

7 (R$_1$ = R$_2$ = ^{t}Bu R$_3$ = Me$_2$)
8 (R$_1$ = ^{t}Bu, R$_2$ = H, R$_3$ = Me$_2$)
9 (R$_1$ = R$_2$ = ^{t}Bu, R$_3$ = C$_5$H$_{10}$)
10 (R$_1$ = R$_2$ = ^{t}Bu, R$_3$ = ^{i}Pr$_2$)

11 (N   NMe$_2$)   **12** (N   N)

Figure 2. Calcium complexes bearing tridentate Schiff-base ligands [36–38].

Table 2. ROP of *ε*-CL and *r*-LA catalyzed by **7**, **9** and **10** [37].

Run	Monomer	Catalyst	Time (Min)	Conv. (%)	M_n (Da)	$M_{n(calc.)}$[a] (Da)	M_w/M_n
1		**7**	15	68	32,841	7922	1.73
2	*ε*-CL	**9**	15	81	21,544	9406	1.80
3		**10**	15	72	32,583	8218	1.72
4		**7**	240	54	8321	7943	1.20
5	*r*-LA	**9**	240	47	5987	6934	1.20
6		**10**	240	58	8986	8520	1.12

For *ε*-CL: Reaction carried out at 25 °C in 3 mL of toluene with monomer:catalyst ratios of 100:1. For *rac*-lactide: Reaction carried at 70 °C in 3 mL of toluene with monomer:catalyst ratios of 100:1. Molecular weights corrected for changes in relative retention times versus styrene standards. M_n, number average molecular weight; $M_{n(calc.)}$, theoretical molecular weight; M_w/M_n polydispersity index. [a] $M_{n(calc.)}$ = Conv.(%) × M_W[*ε*-CL] × 100 + M_W [N(SiMe$_3$)$_2$] for PCL or Conv.(%) × M_W[*r*-LA] × 200 + M_W [N(SiMe$_3$)$_2$] for PLA.

Finally, homoleptic complexes **11** and **12** were recently employed by Lin et al. in the ROP of *L*-LA [38]. The activity of both complexes was quite low in the absence of a co-activator, but it dramatically increased upon addition of 80 equiv. of BnOH, allowing for complete monomer conversion within 30 min at room temperature. The M_n values determined by GPC and NMR spectroscopy were found to be close to the calculated values with narrow polydispersities, which is compatible with a *living* and *immortal* process. Interestingly, **12** was slightly less efficient than its dimethylimino-derivative **11**, suggesting that the more donating pyridyl group has a detrimental effect on the catalyst activity.

4. Early Transition Metals

4.1. Titanium

In 2008, Jones et al. disclosed the synthesis of group IV metal complexes bearing chiral Schiff-base ligands and exhibiting chirality-at-metal [39]. The titanium compounds **13** and **14** (Figure 3) were found to be inactive in the ROP of *rac*-lactide in toluene, while high conversions were obtained in the bulk polymerization with a monomer:Ti ratio of 300 (90% and 95% conversion for **13** and **14**, respectively). High molecular weights (up to 26 kDa) and good control were observed by GPC. Interestingly, the PLAs isolated were essentially atactic, as determined by NMR spectroscopy. Lately,

the same group studied the activity of group IV Salalen species [40]. With respect to the titanium complexes **15** and **16**, good activity was observed both in the presence and in the absence of the solvent. In particular, **15** allowed for complete monomer conversion within 2 h at 80 °C with a LA:Ti ratio of 100:1. On the other hand, **16** required longer reaction times (24 h) to completely convert the monomer under the same reaction conditions. Interestingly, the opposite activity trend was observed under *solvent-free* conditions (89% and 95% conversion for **15** and **16**, respectively). Regardless of the reaction conditions, both catalysts exhibited poor control, with polydispersities spanning from 1.4 to 1.8. In terms of microstructure, all polymers were found to be atactic. NMR spectroscopic analyses highlighted that all macromolecules were isopropoxy-terminated, suggesting that the polymerization was initiated by the insertion of the alkoxy group into a lactide unit.
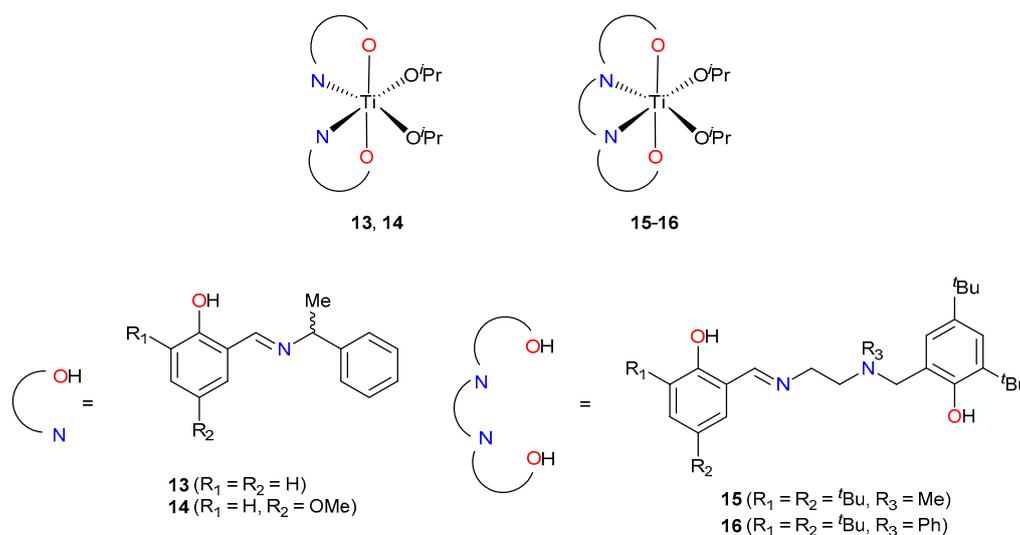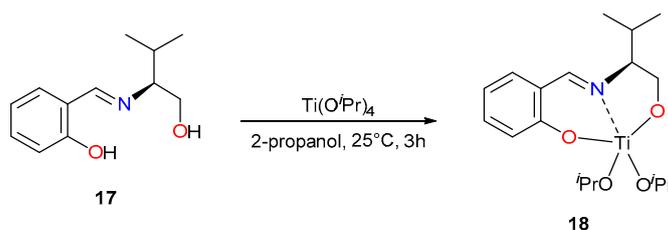

Figure 3. Ti-Schiff-base complexes **13**–**16** [39,40].

In 2015, Muneeswaran, Velmathi et al. developed the novel tridentate Ti complex **18** by reacting an optical active [ONO] ligand (**17**) with the metal precursor in alcoholic medium (Scheme 2) [41].

Scheme 2. Synthesis of complex **18** [41].

The complex was then tested as a catalyst in the ROP of ε-CL under *solvent-free* conditions (Table 3). No reaction was observed after 24 h in a blank test performed at 150 °C in the absence of the catalyst while complete monomer conversion was achieved upon using a CL:Ti ratio of 650:1 under the same reaction conditions. Polymerization also occurred, albeit to a lower extent, when **18** was replaced by either the pro-ligand **17** or the metal precursor Ti(O^{i}Pr)$_4$. Moderate control was observed in all cases and the NMR spectra of the polymer confirmed the presence of both isopropoxy- and –CH$_2$OH chain ends. Finally, the PCLs synthesized with **18** were used in the preparation of novel two-phase polymer nanocomposite with nanocrystalline multiferroic BiFeO$_3$ (BFO NPs).

Table 3. ROP of ε-CL catalyzed by **18** [41].

Run	[M]:[C][a]	Temperature (°C)	Time (h)	$M_n \times 10^3$ (Da)[b]	$M_w \times 10^3$ (Da)[c]	Yield (%)[d]	M_w/M_n
1	-	150	24	-	-	-	-
2	653:1	150	24	31.66	42.12	96	1.33
3	653:1	125	24	22.96	34.55	94	1.52
4	1308:1	150	24	27.38	36.00	95	1.31
5	2612:1	150	24	14.11	22.71	92	1.60
6	3265:1	150	24	9.4	15.15	93	1.61
7	366:1[a*]	150	24	1.46	1.77	74	1.20
8	517:1[a**]	150	24	6.31	9.83	84	1.55

[a] Molar ratio of monomer/catalyst. [a*] Molar ratio of monomer/ligand. [a**] Molar ratio of monomer/Ti(O^{i}Pr)$_4$. [b] M_n is the relative number-average molecular weight. [c] M_w is the relative weight-average molecular weight. [d] Calculated on the basis of the polymer weight.

Interesting activity was also shown by analogue [*O,N,O*]-based complexes recently reported by Lin, Chen et al. [42]. In fact, these systems allowed for the complete conversion of up to 400 equiv. of ε-CL within 12 h at room temperature with good control. The ROP of *L*-LA was also achieved, albeit requiring more forcing reaction conditions.

Titanium complexes of Schiff-base ligands derived from *ortho*-vanillin have been recently synthesized by Williams et al. (Figure 4) [43]. In this species, each metal center is bound to two Schiff-base moieties and two isopropoxy groups derived from the metal precursor. Depending on the steric bulk of the substituent at the N-atom, three coordination types can be adopted. In compounds **19** and **20**, having substituents with rather low steric hindrance, the ligands are bound to the Ti center in a N−O:N−O fashion with the imine nitrogen atom in cis to each other.

Type A-I

19 (R = C$_6$F$_5$)
20 (R = Cy)

Type A-II

21 (R = 2,6-Me$_2$(C$_6$H$_3$))

Type B

22 (R = 2,6-^{i}Pr$_2$(C$_6$H$_3$))
23 (R = 2-Biphenyl)

Type C

24 (R = Adamantyl)
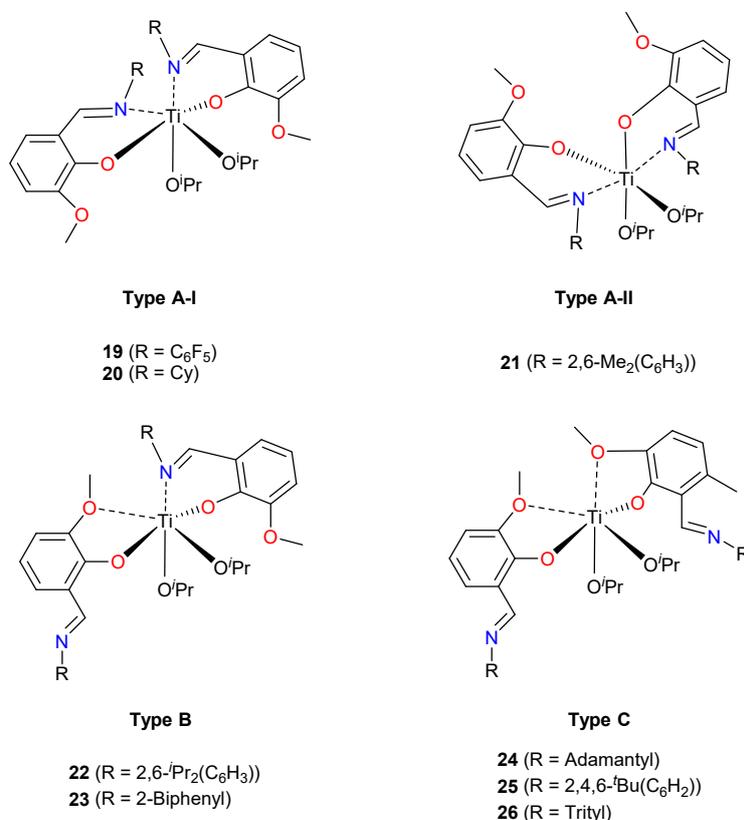**25** (R = 2,4,6-^{t}Bu(C$_6$H$_2$))
26 (R = Trityl)

Figure 4. Binding modes of Ti-based complexes **19–26** [43].

A similar coordination mode is observed in complex **21**, however the N-groups are found in a mutually trans geometry. Upon increasing the steric bulk of the ligands, two more modes were observed. For species **22** and **23**, bearing a 2,6-^{i}Pr$_2$(Phenyl)- and a biphenyl- moiety, respectively, the ligands are bound in an N−O:O−O fashion. Finally, an O−O:O−O coordination was found in **25** and **26**, featuring the bulkiest substituents in the series. The effect of the binding mode on the activity of these complexes in the ROP of ε-CL and ω-pentadecalactone (ω-PDL) was studied. Interestingly, complexes exhibiting O−O chelation by both ligands were found to be the most active. The occurrence of such binding mode was thought to be due to the increased steric hindrance at the imine nitrogen substituent, favoring the formation of five-membered O−O chelation. In turn, this affects the lability of the ligand around the Ti(IV) active site, hence resulting in faster rates.

Very recently, Li et al. synthesized a dinuclear Ti-Salen catalyst able to promote the ROP of 1800 equiv. of *r*-LA at 160 °C in 16 h [44]. The system produced a PLA with very high molecular weight (93 kDa) and narrow polydispersity (1.13). Further mechanical and toxicity tests revealed the biocompatibility of the material and its suitability for tissue engineering applications.

Finally, bimetallic Ti complexes of Schiff-bases derived from the condensation of diaminomaleonitrile with salicylaldehyde derivatives have been disclosed by Chakraborty, Chand et al. (Figure 5) [45].
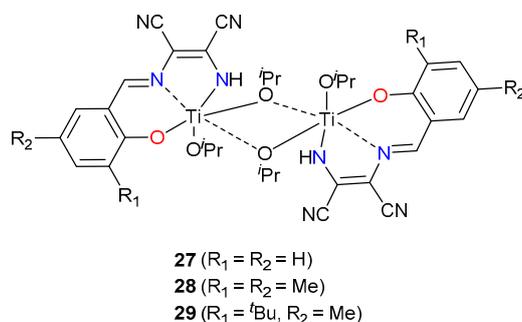

27 (R$_1$ = R$_2$ = H)
28 (R$_1$ = R$_2$ = Me)
29 (R$_1$ = ^{t}Bu, R$_2$ = Me)

Figure 5. Cyano-containing Ti-complexes **27–29** [45].

All complexes were tested as catalysts in the ROP of ε-CL and *r*-LA at 100 and 140 °C, respectively, under *solvent-free* conditions with a monomer:Ti ratio of 200:1 (Table 4). Conversions higher than 90% were achieved within minutes, highlighting the beneficial effect of a strong electron-withdrawing cyano group on the ligand backbone. For both monomers, the activity trend was found to be **29** > **28** > **27**, suggesting that increasing the steric bulk of the substituents on the aromatic ring of the ligand has a positive effect on the polymerization rate.

**Table 4.** ROP of ε-CL and *r*-LA catalyzed by complexes **27–29** [45].

Entry	Catalyst	Monomer^a	Time (Min)	Conv. (%)^b	M_n (kDa)^c	$M_{n(calc.)}$ (kDa)^d	M_w/M_n^{c}	P_r^{e}
1	**27**		10	93	20.45	22.90	1.19	
2	**28**	ε-CL	9	96	20.98	22.90	1.15	-
3	**29**		4	97	21.18	22.90	1.12	
4	**27**		21	92	25.42	28.90	1.17	0.62
5	**28**	*r*-LA	15	96	25.07	28.90	1.15	0.69
6	**29**		8	98	28.15	28.90	1.14	0.68

^{a} Reaction conditions: [M]$_0$/[C]$_0$ = 200:1, 100 °C for ε-CL and 140 °C for *rac*-LA, solvent-free. ^{b} Determined from ^{1}H NMR in CDCl$_3$ at 25 °C. ^{c} Measured by GPC at 27 °C in THF relative to polystyrene standard Mark-Houwink corrections for M_n. ^{d} $M_{n(calc.)}$ = [M]$_0$/[C]$_0$ × M$_{w\,(monomer)}$ + M$_{w(end\text{-}group)}$ at 100% conversion of monomer. ^{e} P_r is the probability for heterotactic enrichment calculated from homonuclear decoupled ^{1}H NMR spectrum in CDCl$_3$ at 25 °C.

The M_n observed by GPC were in good agreement with the calculated values; good control was generally observed, with polydispersities spanning from 1.1 to 1.2. In terms of microstructure, the PLAs were found to be heterotactic (P_r 0.6–0.7), as observed by homonuclear decoupled ^{1}H NMR spectroscopy.

4.2. Zirconium

Jones et al. tested the efficiency of the chiral Schiff-base zirconium complexes **30–35** (Figure 6) as catalysts in the ROP of *rac*-lactide [39]. By performing the reaction in toluene, moderate yields were achieved at 80 °C in two hours or at room temperature after 1 day. Good control was generally observed, and the GPC data were also in agreement with the formation of only one polymer chain per metal center. Interestingly, all samples were heterotactic, with P_r values found in a very narrow range (0.68–0.71), regardless of the configuration of the optical active catalyst employed. Higher reaction rates were observed under *solvent-free* conditions, albeit with less control. In fact, broader molecular weight distributions were generally observed. Furthermore, in this case, heterotactic polymers were isolated. Remarkably, all catalysts proved very robust, allowing for the polymerization of *rac*-lactide even in the presence of water and/or with non-purified monomer.
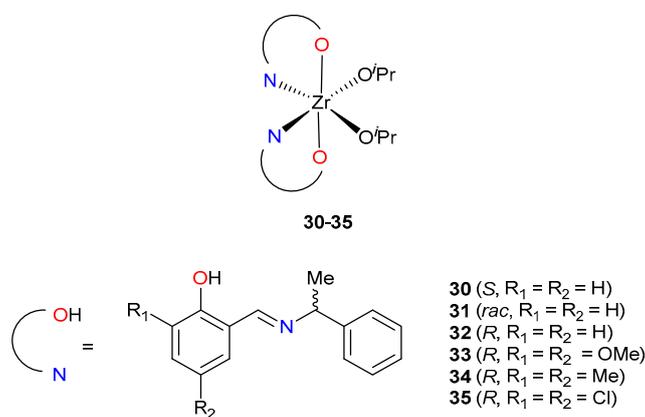
Figure 6. Chiral Zr complexes **30–35** [39].

Zirconium complexes, analogues to the tridentate species **15** and **16**, were lately investigated by the same group [40]. High conversions and good control were achieved both in solution and in bulk. In terms of microstructure, a slight preference towards forming heterotactic polymers was detected (*Pr* ~ 0.69). Finally, bimetallic Zr complexes bearing cyano-containing Schiff-base ligands were considered as catalysts for the ROP of ε-Cl and *r*-LA [45]. Similar to their Ti-analogues **27–29**, high molecular weight and good control were generally observed. Similarly, the reaction rate as well as the heterotactic bias increased with the steric bulk of the ligand. Finally, a redox-switchable Salfen Zr species has been successfully employed in the synthesis of bi- and triblock copolymers of *L*-LA and cyclohexene oxide [46].

4.3. Hafnium

Reports concerning the use of Hf complexes of Schiff base ligands in the ROP of cyclic esters are rather scant. Hf-congeners of the Ti-species **15** and **16** proved to be active in the polymerization of *r*-LA both in solution and in bulk, affording either atactic or isotactic polymers depending on the steric features of the ligand [40]. Finally, the bimetallic complexes **36–38** (Figure 7) proved better performing than their Ti- and Zr- analogues in the ROP of ε-CL and *r*-LA [45]. Furthermore, in this case, both the reaction rate and the syndiotactic bias increased with the steric bulk of the ligand
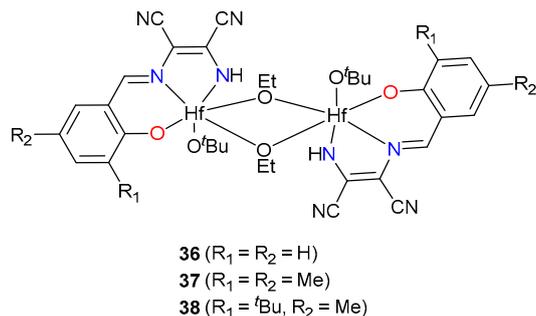
36 (R$_1$ = R$_2$ = H)
37 (R$_1$ = R$_2$ = Me)
38 (R$_1$ = ^{t}Bu, R$_2$ = Me)

Figure 7. Cyano-containing bimetallic Hf complexes **36–38** [45].

4.4. Vanadium

In 2013, our group reported the synthesis of 15 novel V(III) complexes bearing phenoxyimine complexes (Figure 8) [47]. The ability of these species to promote the ROP of ε-CL was investigated (Table 5). In most cases, low to moderate conversions were observed and polymers with M_n much lower than the expected values were obtained. The molecular weight distributions were found in a narrow range (1.2–1.4) in all runs, aside from the test conducted in the presence of the binuclear species **44**.

39 (R = ^{t}Bu)
40 (R = H)

41 (R = ^{t}Bu)
42 (R = H)

43 (R = ^{t}Bu)
44 (R = H)

45 (R = ^{t}Bu)
46 (R = H)

47 (R = ^{t}Bu)
48 (R = H)

49 (R = ^{t}Bu)
50 (R = H)

51

52

53
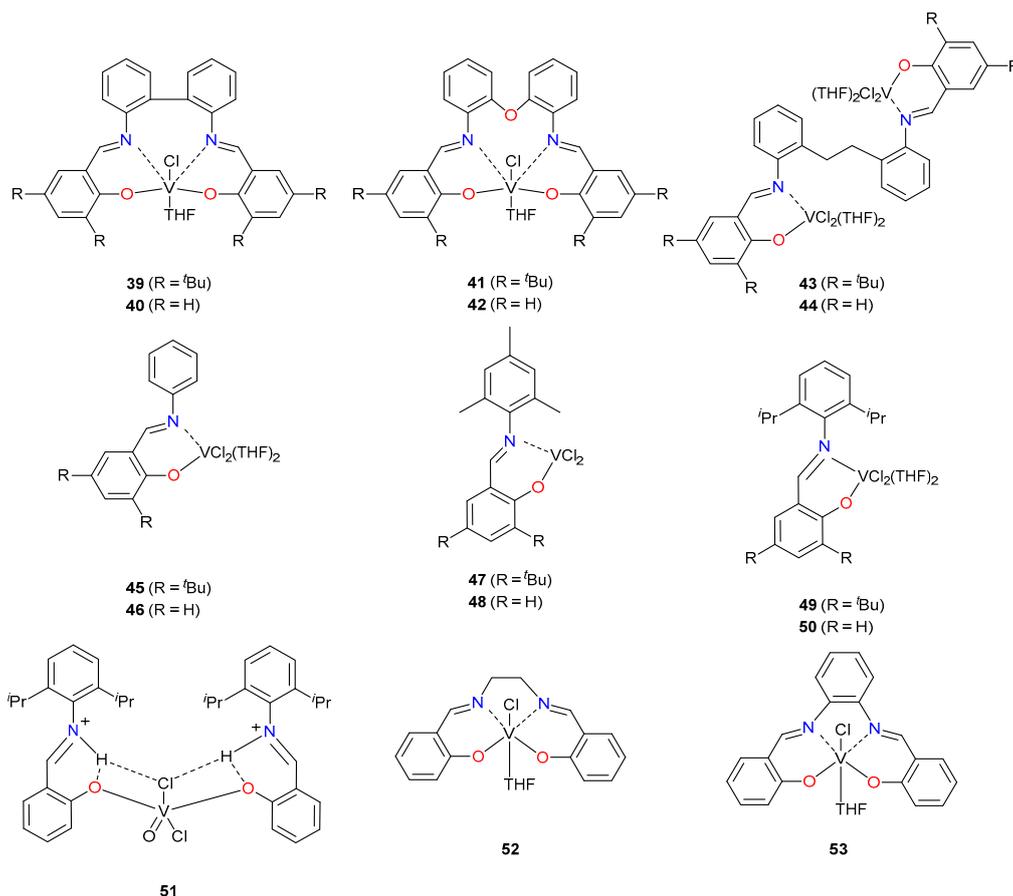
Figure 8. V(III) complexes **39–53** employed in the ROP of ε-caprolactone [47].

Based on the results obtained in the ethylene polymerization [48], we have lately explored the ability of tri- and tetradentate vanadium(V) species as catalysts in the ROP of ε-CL [49]. Conversions lower than 50% were achieved after 24 h at 110 °C in the presence of BnOH as a co-activator. The observed M_n were much lower than the calculated values, suggesting a significant deviation from

a *living* polymerization. Nevertheless, the process was rather controlled, with polydispersities lower than 1.2. Mass Spec and ^{1}H NMR spectroscopy analyses confirmed the presence of the BnO- end group.

Table 5. ROP of ε-CL promoted by **39–53** [47].

| Run[a]	Catalyst	Conv. (%)[b]	$M_{n(calc.)}$ (Da)	$M_{n(GPC)}$ (Da)[c]	M_w/M_n
1	**39**	57	26,024	10,751	1.4
2	**40**	47	21,458	8640	1.4
3	**41**	24	10,960	7977	1.2
4	**42**	33	15,070	9249	1.2
5	**43**	48	21,900	10,080	1.4
6	**44**	70	31,960	11,010	2.3
7	**45**	72	32,870	4973	1.2
8	**46**	100	45,660	4060	1.1
9	**47**	87	39,720	13,670	1.3
10	**48**	93	42,460	14,260	1.1
11	**49**	97	44,290	21,340	1.1
12	**50**	19	8670	-	-
13	**51**	93	42,460	13,290	1.2
14	**52**	94	42,920	4790	1.1
15	**53**	3	1370	4560	1.4

[a] Conditions: toluene (20 mL), [ε-caprolactone] = 2.5 mL, monomer: metal = 400, 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene). 72 h, 80 °C. [b] Obtained from ^{1}H NMR analysis. [c] M_n measured = 0.58 × $M_{n(GPC)}$.

4.5. Chromium

Mononuclear- and dinuclear Cr(III)-salphen complexes **54–57** (Figure 9) have been reported by Rieger et al. in 2010 [50]. Next, their efficiency as catalysts in the ROP of β-butyrolactone (β-BL) was investigated (Table 6).
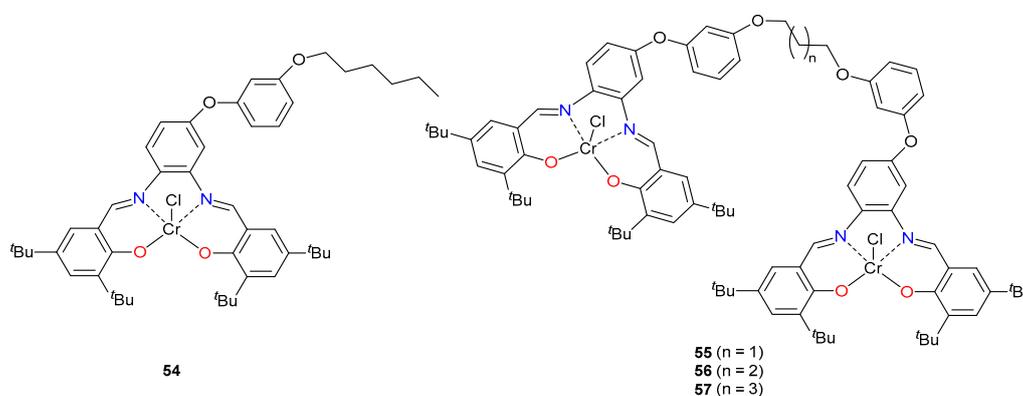
Figure 9. Mono- and dinuclear Cr(III)-salphen complexes **54–57** [50].

The mononuclear species **54** exhibited rather poor activity, allowing for 6% and 30% conversion after 5 and 24 h, respectively, affording polymers with broad dispersity (2.0–2.6). On the other hand, the bimetallic systems proved more active, exhibiting similar behavior regardless the length of the spacer. The use of **55** allowed for complete monomer conversion within 24 h, while moderate conversions were achieved within 5 h in the presence of **56** and **57**. Compared to their mononuclear analogue, **55–57** allowed for higher polymer molecular weights, albeit with broad dispersity.

Table 6. ROP of β-BL catalyzed by **54–57** [50].

Run	Catalyst	Temperature (°C)	Time (h)	Yield (%)[a]	TOF (h^{-1})[b]	M_w (kDa)	M_w/M_n
1	**55**	150	5	6	12	20	2.0
2	**55**	150	24	30	12	25	2.6
3	**56**	125	5	35	70	71	1.9
4	**56**	150	15	86	57	107	1.9
5	**56**	150	24	>99	41	108	1.9
6	**57**	150	5	28	56	68	2.2
7	**58**	150	5	31	62	70	2.1

[a] Determined ^{1}H NMR spectroscopy. [b] Turnover frequency calculated per Cr center.

4.6. Manganese

In 2016, our group developed a series of Mn(II) complexes bearing macrocyclic Schiff-base derived ligands [51]. In spite of their interesting structural features, these species proved to be poorly active as catalysts in the ROP of ε-CL in the presence of BnOH as co-activator. Regardless of the reaction conditions, monomer conversion was generally low (10%–14%) and the reaction products were mainly low molecular weight oligomers.

5. Late Transition Metals

5.1. Iron

Similar to the rare-earth metals, iron-based complexes are attractive catalysts for the synthesis of polylactones, given that the metal precursors are both inexpensive and biocompatible [52]. In spite of that, the Fe-catalyzed ROP of cyclic esters still remains rather underexplored. In this scenario, Garden, Shaver et al. recently studied the behavior of half-salen Fe(III) complexes in the ROP of *r*-LA in the presence of propylene oxide (PO) as co-activator [53]. In most of the cases, low M_n and poor control, accountable to the occurrence of transesterification, were observed. A lack of stereoselectivity was generally observed, with P_i values indicating the formation of atactic PLAs. Nevertheless, these limitations could be overcome upon increasing the amount of co-activator or allowing for the formation of the catalytically active species prior to introduction of the monomer.

Fe(III)-salalen complexes have been recently reported by Jones et al. (Figure 10) [54]. Complex **58** exhibited moderate activity as a catalyst in the ROP of *r*-LA performed in propylene oxide. In this scenario, PO served both as solvent and co-initiator. Good conversion (80%) was achieved at 40 °C after 7 days, affording an isotactic polymer with a high molecular weight and narrow polydispersity. Increase of activity was observed upon increasing the temperature, albeit with a drop of both stereoselectivity and control. In some cases, a bimodal distribution was detected, suggesting the occurrence of two independent processes. Mass spectrometry analysis of such samples showed the presence of two populations differing from the nature of one end-group. The main distribution was assigned to chloropropanol-capped polymers (derived from the ROP of propylene oxide), while the minor population was attributed to PLAs initiated by propane-1,2-diol, an impurity of PO. Upon using a catalytic amount of BnOH as co-activator, a monomodal distribution was observed by GPC, suggesting the formation of only one active species.

This was confirmed by mass spectrometry showing the presence of only one major population corresponding to BnO-capped polymers. In all cases, a small amount of cyclic oligomers was also obtained. Catalysts **59** and **60** bearing the same ethylene bridge, but less bulky aromatic substituents (H and Cl, respectively) than **58**, exhibited higher activity than their *t*Bu-containing analogue. In fact, conversions up to 93% were obtained within 4 to 6 h at 60 °C with good control, albeit with slightly lower stereoselectivity. The methyl analogue **61** proved less performing than **59** and **60**, requiring up

to 2 days to allow complete monomer conversion. Variation of the backbone in complexes **62–64** led to a drop of activity, possibly due to the reduced flexibility of the catalysts.

58 (R = *t*Bu, L = -CH$_2$CH$_2$-)
59 (R = H, L = -CH$_2$CH$_2$-)
60 (R = Cl, L = -CH$_2$CH$_2$-)
61 (R = Me, L = -CH$_2$CH$_2$-)
62 (R = *t*Bu, L = C$_6$H$_4$)
63 (R = *t*Bu, L = CH$_2$C$_5$H$_9$)
64 (R = H, L = C$_6$H$_{10}$)

Figure 10. Salalen complexes **58–64** [54].

Lamberti et al. recently compared the activities of **58** and related Salen- and Salan Fe(III) chloride complexes in the ROP of ε-CL [55]. By performing the reaction in PO as both solvent and co-activator, the activity trend was found to be Salan > Salalen > Salen, which mirrored the order of acidity of the metal center in each complex. Upon introducing bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) as co-activator, no change in the trend was observed, albeit the activity of the catalysts generally improved. Interestingly, **58** proved inactive in the ROP of *L*-LA under similar reaction conditions, possibly due to the formation of stable intermediates inhibiting the process.

Concurrently, Pang, Li et al. disclosed the ROP of *L*- and *rac*-lactide promoted by four novel Fe(III) salen complexes (Figure 11) [56]. Moreover, in this case, propylene oxide served as solvent as well as co-activator. Complexes **65** and **66** exhibited similar catalytic activity, allowing for complete monomer conversion within 10 h at room temperature. Polymerization also occurred with **67** and **68**, albeit with a lower rate. This was attributed to presence of bulky *i*Bu groups reducing the accessibility of the metal center. In spite of their lower activity, a better control was achieved with **67** and **68** compared to the runs involving their less sterically hindered congeners. When the *meso* monomer was employed, all catalysts exhibited moderate isotactic bias, affording polymers with P_m values spanning from 0.68 to 0.77.

65   **66**

67   **68**

Figure 11. Fe(III) salen complexes **65–68** [56].

5.2. Cobalt

Very recently, Sutar et al. described the ROP of *L*-lactide catalyzed by the Co(II) salen complex **69** (Figure 12) [57]. Optimization of the reaction conditions revealed that one equiv./Co of BnOH was

required to enable the polymerization. While moderate activity was observed both in toluene and THF, high conversions (86%) were achieved in CH_2Cl_2 also in the case of monomer:Co ratios as high as 200. The M_n determined by GPC and Vapor Pressure Osmometry were in good agreement with the theoretical values; in addition, narrow polydispersities (between 1.08 and 1.13) were detected. Finally, NMR spectroscopic analysis of the polymers were compatible with α-BnO-ω-CH_2OH terminated PLAs. This data suggested the occurrence a *living* ROP process.
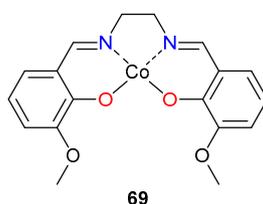
Figure 12. Co(II) salen catalyst for the ROP of *L*-lactide [57].

5.3. Nickel

In 2016, Sutar, Maharana et al. described the ROP of *L*-lactide catalyzed by three novel Ni-salen complexes **70–72** (Figure 13) [58]. During the optimization of the reaction conditions performed at room temperature over 24 h in different solvents, CH_2Cl_2 was found as the most suitable medium. In fact, all catalysts allowed for higher conversions and greater polymer M_n compared to the runs performed in toluene or THF. None of the complexes proved active in the absence of BnOH, while high conversions (90%) were obtained when one equiv./Ni of the co-activator was employed with LA:Ni as high as 200:1, regardless of the catalyst employed. The M_n determined experimentally were in good agreement with the theoretical values and the molecular weight distributions were found in a very narrow range (1.09–1.13). Upon increasing the amount of BnOH (2–4 equiv./Ni), higher reaction rates were observed, albeit with an important decrease of the polymer M_n.
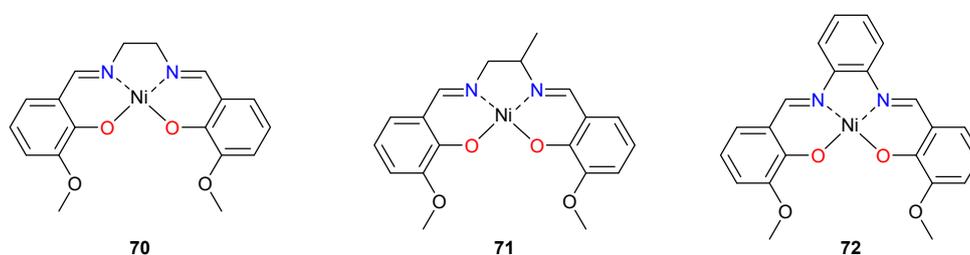
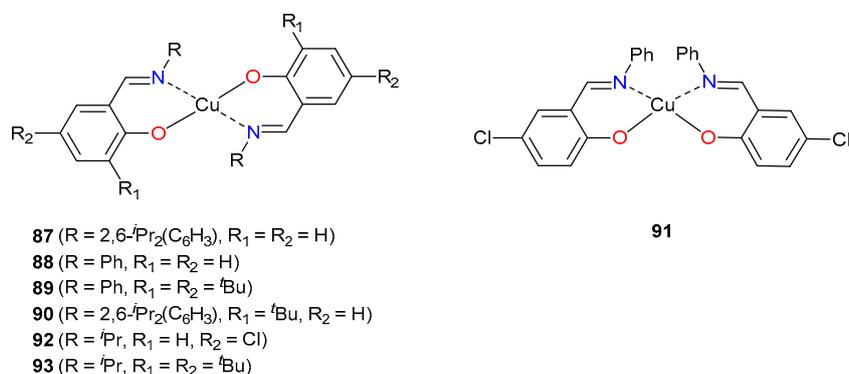**Figure 13.** Ni salen complexes **70–72** [58].

In 2011, a series of heterobimetallic Ni-Ln(III) (Ln = lanthanide) complexes derived from the compounds **70** and **71** were reported by Bao, Lü et al. (Figure 14) [59–61]. In terms of activity, the bimetallic species proved less performing than their monometallic analogues and required higher temperatures and/or longer reaction times to achieve moderate monomer conversions. On the other hand, higher M_n and better control were generally observed, possibly because of cooperative effects between the two metal centers. For complexes **75–77** and **81–84**, the activity trends were **76** > **75** > **77** and **81** > **82** > **83** > **84**, respectively. In both cases, the catalyst efficiency decreased with the lengthening of the Ni⋯Ln intramolecular distance, while the dependency on the lanthanide contraction was observed just for the latter set of complexes.

73 (Ln = Ce)	**74** (Ln = Nd)	**80** (Ln = Ce)	**81** (Ln = Nd)
75 (Ln = Sm)	**76** (Ln = Eu)	**82** (Ln = Sm)	**83** (Ln = Eu)
77 (Ln = Tb)	**78** (Ln = Ho)	**84** (Ln = Tb)	**85** (Ln = Ho)
79 (Ln = Tm)		**86** (Ln = Tm)	
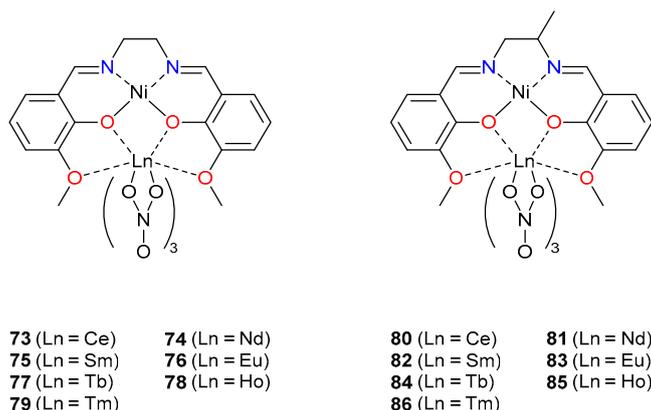
Figure 14. Ni–Ln(III) salen complexes **73**–**86** [59–61].

5.4. Copper

Over the past decade, the ROP of cyclic esters catalyzed by Cu(II) complexes of Schiff-base ligands has obtained increasing attention. Bhaw-Luximon, Mapolie et al. studied the behavior of 7 new copper-phenoxyimino complexes in the ROP of *L*-lactide (Figure 15) [62]. Compounds **87** and **88** were found to be inactive, even under forcing reaction conditions. This was attributed to the deactivation of the catalysts (through the dimerization of the metal centers) due to the absence of bulky substituents at the phenoxy-moiety. Strangely, complex **89** was also poorly active, albeit containing *t*Bu groups both in *ortho*- and *para* positions. Concerning the Cl-containing derivatives, low conversion (18%) was obtained with the cis species **91** while no polymerization was observed in the presence of the trans complex **92**. Finally, complexes **90** and **93**, bearing bulky substituents at both phenoxy- and imino- moieties exhibited moderate to good activity, depending on the solvent employed. The polymers obtained were highly isotactic, as determined by ^{1}H NMR spectroscopy.

87 (R = 2,6-^{i}Pr$_2$(C$_6$H$_3$), R$_1$ = R$_2$ = H)
88 (R = Ph, R$_1$ = R$_2$ = H)
89 (R = Ph, R$_1$ = R$_2$ = ^{t}Bu)
90 (R = 2,6-^{i}Pr$_2$(C$_6$H$_3$), R$_1$ = ^{t}Bu, R$_2$ = H)
92 (R = ^{i}Pr, R$_1$ = H, R$_2$ = Cl)
93 (R = ^{i}Pr, R$_1$ = R$_2$ = ^{t}Bu)

91

**Figure 15.** Cu^{II} complexes **87**–**93** [62].

Lü, Jin et al. developed the salen-based mono- and heterobimetallic species **94** and **95** (Figure 16) [63]. Both complexes proved active in the ROP of *L*-lactide; although higher rates were observed for the monometallic species, the Nd-containing compound allowed for higher polymer M_n and better control. An extensive investigation of the catalytic activity of complex **95** and of its phenyl- and propylene-bridged derivatives **96** and **97** was undertaken by the group of Sutar [64–66]. The compounds exhibited similar catalytic behavior in the ROP of *L*-lactide, allowing for high conversions when activated by one equiv./Cu of BnOH in CH$_2$Cl$_2$ or toluene. A significant drop of conversion was observed upon using THF as reaction medium. This was attributed to catalyst deactivation via the solvent coordination to the metal center. By increasing the amount of co-catalyst, an increase of the reaction rate was observed, albeit with a drop of the polymer M_n. Nevertheless, the process was well controlled, and the molecular weights were in agreement with the calculated

values in all cases, suggesting the occurrence of a *living* process. NMR spectroscopic analysis of the polymer confirmed the presence of both BnO- and –CH$_2$OH end-groups.
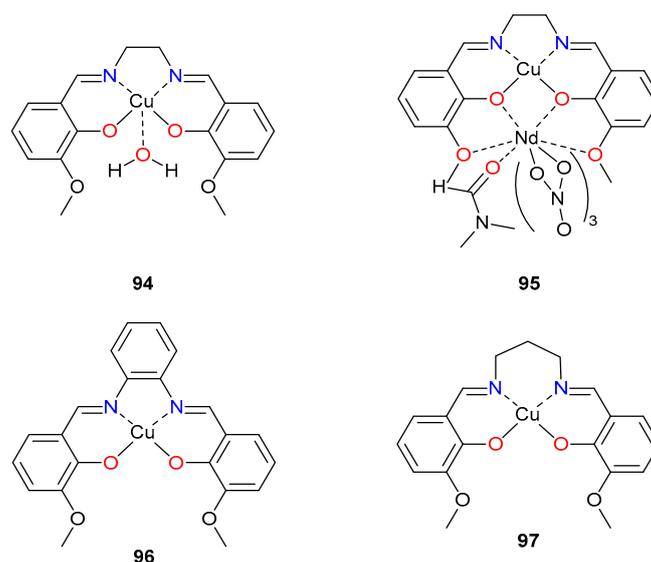
Figure 16. Cu^{II}-[ONNO] complexes active in the ROP of lactide [63–66].

Very recently, Nayab, Lee et al. tested the efficiency of iminomethylpyridine based copper(II) complexes **98–103** (Figure 17) in the ROP of *rac*-lactide [67]. All compounds proved equally performing, allowing for complete monomer conversion at both room temperature and at −25 °C within 2 h with a monomer:Cu ratio of 100:1 in CH$_2$Cl$_2$. The polymer molecular weights were close to the calculated values while the control was highly dependent on the temperature. In fact, polydispersities ranging from 1.5 to 1.8 were achieved at room temperature, while narrower values (1.25–1.54) were observed for the polymers synthesized at −25 °C. This was attributed to the occurrence of undesired transesterification and/or backbiting processes that are less favored at lower temperature. In terms of microstructure, the isolated polymers were mainly hetero-enriched. Furthermore, in this case, higher selectivity was observed at −25 °C compared to the tests at room temperature.
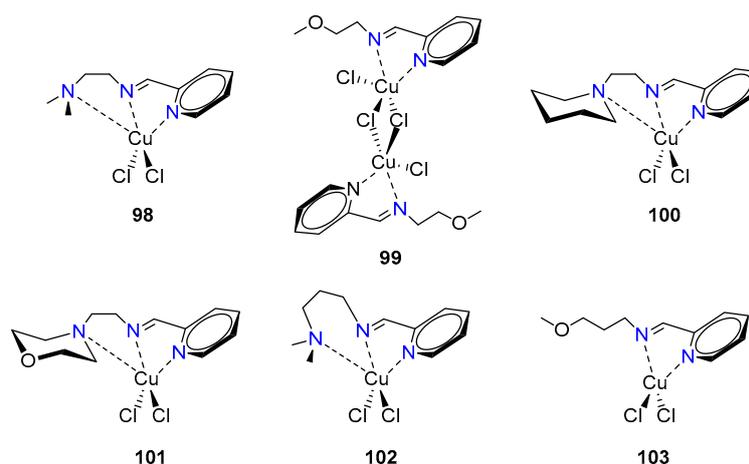

Figure 17. Cu(II)-iminomethylpyridine complexes **98–103** [67].

In 2011, our group reported the synthesis of bimetallic Cu(II) complexes of acyclic Schiff bases ligands derived from amino acids. In spite of their interesting structural features, these compounds proved inactive in the ROP of ε-CL, even at 80 °C and in the presence of BnOH as co-activator [68]. More recently, we have also synthesized mono-and tetra-nuclear Cu species bearing

bis(imino)phenoxide ligands [69]. Furthermore, in this case, the complexes were poorly active in the ROP of ε-CL, affording in the best runs only traces of polymer. In spite of the narrow polydispersities, kinetic investigation excluded the occurrence of a *living* process. NMR spectroscopy and MALDI-TOF analyses performed on these samples highlighted the presence of BnO- end groups.

5.5. Zinc

Over the past couple of decades, increasing attention has been devoted to the development of Zn-based catalysts for the ROP of lactones. Indeed, the use of this metal is very attractive thanks to its earth-abundance (affordability) and to the potential non-toxicity of resultant complexes [70]. Remarkable results have been achieved in the ROP of *L*- and *r*-LA with imino-phenolate Zn species [30,32–34], both in terms of catalyst activity and features (M_n, polydispersity, mechanical properties) of the final materials. More recently, Zn complexes of guanidine-derived Schiff-bases proved to be an outstanding new class of catalysts for the production of PLA under industrially relevant conditions [71]. In this regard, Herres-Pawlis et al. compared the activity of two sets of complexes bearing neutral N-donors, namely imidazolin-2-imine and guanidine, in the ROP or *rac*-lactide (Figure 18) [72]. In terms of monomer conversion, the imidazolin-2-imine derivatives **104** and **105** proved better performing than their guanidine analogues **106** and **107**. Complexes containing Cl ancillary ligands **104** and **106** allowed for higher molecular weights than the acetate congeners, while broad polydispersities (ca. 2.0) were observed in all cases. Atactic PLAs were isolated, regardless of the catalyst employed.


104 (X = Cl)
105 (X = OAc)

106 (X = Cl)
107 (X = OAc)
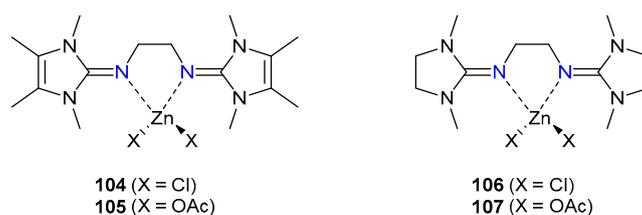
Figure 18. Zn complexes bearing imidalozin-2-imine and guanidine-based ligands [72].

Subsequently, the same group studied the performance of eight Zn complexes derived from the ligands **108–115** (Figure 19) [73]. By performing the ROP of technical grade *r*-LA in bulk at 150 °C, promising results were observed with complexes **111** and **109** after 6 h (80% and 71% conversion). Compound **112** was the least active, allowing for 63% conversion after 7 h, while similar conversions were achieved in the presence of the other systems after 6 h. In all cases, poor control and M_n much lower than the expected values were observed, possibly because of the harsh reaction conditions and/or the presence of traces of water in the monomer promoting undesired chain-transfer reactions. On the other hand, water served as the actual initiator, as confirmed by NMR spectroscopy and MALDI-TOF studies on the isolated PLAs. In terms of microstructure, atactic polymers were obtained, even in the case of chiral complexes. Since the chirality of these species proved to be retained even at high temperature, the poor stereoselectivity was thought to be due to the lack of steric hindrance. Upon employing purified monomer, both M_n and control improved; the same was observed when BnOH was used as co-activator, independently from the purity of the lactide employed. The polymers isolated in the presence of external alcohol featured the BnO- end group, suggesting that BnOH is the actual initiator of the process.

In 2009, Jones et al. reported novel mono- and trinuclear zinc complexes of variously substituted phenoxyimine ligands [74]. All complexes exhibited good catalytic activity in the ROP of *r*-LA in melt conditions at 130 °C. While monozinc species afforded atactic PLAs with moderate control (M_w/M_n spanning from 1.42 to 1.50), broader polydispersities and moderately heterotactic polymers were achieved in the presence of the trinuclear analogues. Promising results were also obtained by using a Si-supported derivative. Lately, the same group furthered explored heterogeneous systems

derived from similar phenoxyimine ligands, which still allowed for good monomer conversions albeit requiring longer reaction times compared to their homogeneous counterparts [75].
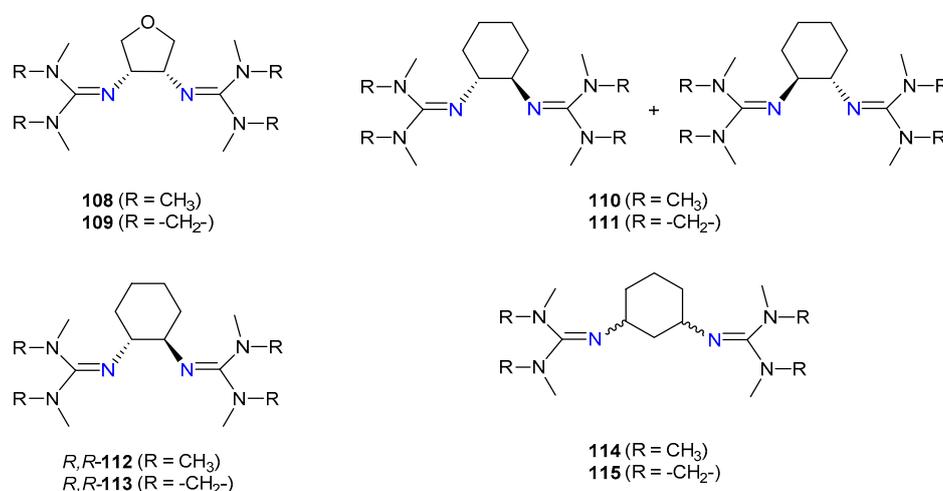
**Figure 19.** Guanidine-derived ligands **108–115** [73].

Very recently, Zn complexes **116–119**, bearing heteroatom-containing [N,O] ligands, were shown to be active in the ROP of *L*-lactide under industrially relevant conditions (Figure 20) [76]. Conversions ranging between 56% and 66% were achieved with all catalysts within 1 h when using purified *L*-LA as monomer. The molecular weights were spanning from 48 and 64 kDa, with polydispersity values found in the range 1.3–1.7. The reaction rate followed the trend **119** >> **116** = **117** > **118**, as determined by in situ IR spectroscopy. Complex **119** was also employed in combination with technical grade *L*-lactide with different monomer:catalyst ratios. While 46% conversion was achieved after ca. 1 h with a LA:Zn ratio of 1000:1, a drastic drop of activity was observed by slightly increasing the amount of monomer. However, the productivity improved when BnOH was introduced as co-activator.
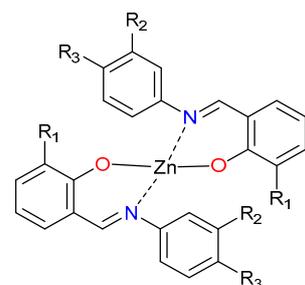
116 ($R_1 = R_2 = H$, $R_3 = SCH_3$)
117 ($R_1 = OCH_3$, $R_2 = H$, $R_3 = SCH_3$)
118 ($R_1 = H$, $R_2 = SCH_3$, $R_3 = H$)
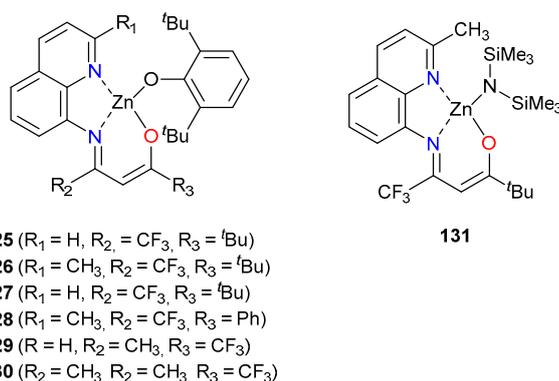**119** ($R_1 = R_2 = H$, $R_3 = F$)

Figure 20. Schiff-base Zn complexes **116–119** [76].

Tridentate ligands have also been widely investigated. Chiral Zn complexes of Schiff-bases derived from natural amino-acid proved extremely active in the ROP of *rac*-lactide (Figure 21) [77]. Complete monomer conversion was achieved after 2 h with LA:Zn ratio as high as 2000:1, affording heterotactic polymers with M_n in agreement with the theoretical values with good control (M_w/M_n ranging between 1.07 and 1.31). By using enantiomerically pure *D*- or *L*-lactide as monomer, highly syndiotactic PLAs were isolated. However, the configuration of the stereogenic centers on the polymer chain was not influenced by the chirality of the complexes, suggesting that the stereoselectivity of the ROP of *r*-LA was controlled via a chain-end mechanism.
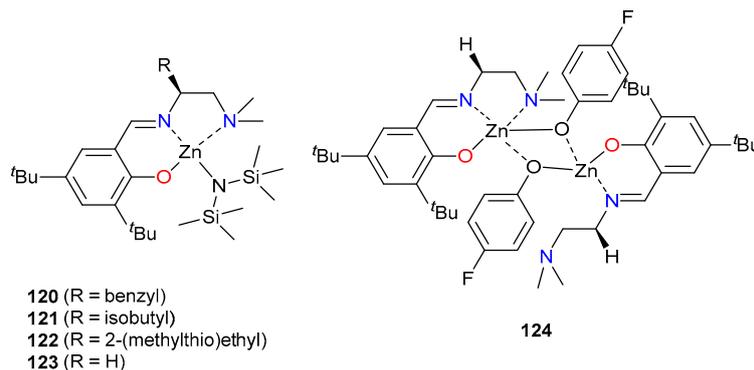
Figure 21. Amino-acid based Zinc Catalysts **120–124** [77].

Zinc complexes of ketoiminate ligands **125–131** (Figure 22) have recently been tested as catalysts in the ROP of *L*-LA (Table 7) [78]. For the zinc phenoxide complexes, complete conversion was achieved after 3 h with complexes **125**, **126**, **129** and **130**. The lower activity exhibited by **127** and **128** was attributed to the presence of the electron withdrawing groups on the ketoiminate moiety, causing a slower propagation rate. Aside from the test performed with **126**, narrow polydispersities and M_n in agreement with the calculated values were achieved. Interestingly, the bis-trimethylsilylamido derivative **131** proved also completely inactive. NMR spectroscopy and MALDI-TOF analyses showed that the polymers prepared with **125–130** and **131** featured 2,6-diisopropylphenoxy- and trimethylsilyl amido- end groups, respectively.

125 (R_1 = H, R_2, = CF_3, R_3 = ^{t}Bu)
126 (R_1 = CH_3, R_2 = CF_3, R_3 = ^{t}Bu)
127 (R_1 = H, R_2 = CF_3, R_3 = ^{t}Bu)
128 (R_1 = CH_3, R_2 = CF_3, R_3 = Ph)
129 (R = H, R_2 = CH_3, R_3 = CF_3)
130 (R_2 = CH_3, R_2 = CH_3, R_3 = CF_3)

Figure 22. Zn ketoiminate complexes bearing trifluoromethyl substituents [78].

**Table 7.** Polymerization of *L*-LA catalyzed by Zn complexes **125–131** [78].

Run[a]	Catalyst	Lactide/Zn	Time (h)	Conv. (%)[b]	$M_{n(calc.)}$ (kDa)[c]	$M_{n(obs)}$ (kDa)[d]	M_w/M_n
1	**125**	500	3	100	72.0	71.7	1.22
2	**126**	500	3	100	72.0	55.8	1.54
3	**127**	500	6	60	43.2	58.7	1.27
4	**128**	500	6	12	8.6	99.9	1.15
5	**129**	500	3	100	72	73.4	1.08
6	**130**	500	3	100	72	105.8	1.14
7	**131**	500	24	5	3.6	191.4	1.08

[a] All reactions were conducted in CH_2Cl_2 at ambient temperature. [b] Obtained from ^{1}H NMR analysis. [c] $M_{n(calc)}$ = $(M/I) \times (\%_{conv.}) \times (M_{w(lactide)})$. [d] $M_{n,obs}$ values were determined by GPC in THF vs. polystyrene standards and were corrected with a Mark-Houwink = 0.58.

Interesting activity was also exhibited by zinc complexes of diaminocyclohexane-derived ligands (Figure 23) [79]. Compounds **135** and **136** proved the most active of the series, allowing for complete monomer conversion within 1 h, in the presence of BnOH as co-activator. Polymerization was also
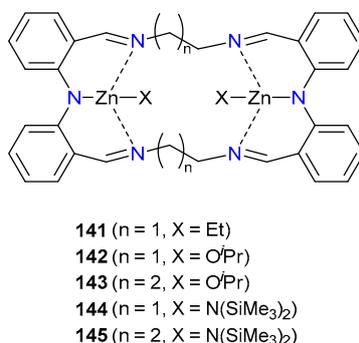
observed with the Boc-derivatives **132–134**, albeit to a lower extent. MALDI-TOF studies showed the presence of the BnO- end group, as well as a minor population accountable to transesterification-derived chains. All catalysts showed a moderate heterotactic bias, with P_r values spanning 0.56–0.67.

132   **133** (R = H)   **135** (R = H)
         134 (R = Cl)   **136** (R = Cl)

Figure 23. Zn complexes based on diaminocyclohexane-derived ligands [79].

Zn complexes bearing half-salphen ligands generated by template synthesis from a metal precursor, N1,N1-dimethylbenzene-1,2-diamine and substituted salicylaldehyde have been recently disclosed by Zhu et al. [80]. Different zinc precursors, namely $Zn(OAc)_2 \cdot 2H_2O$, $ZnCl_2$, $Zn(O_2CCF_3)_2$ and $Zn(O_3SCF_3)_2$, were investigated, and the related complexes were tested in the ROP of ε-CL. In the absence of a co-activator, none of the catalysts proved active, while complete conversion of 400 equiv. of monomer was observed within minutes upon addition a 1:1 mixture of BnOH/LiMe, albeit with poor control.

Multinuclear Zn complexes derived from tridentate [NON]-type ligands have been independently reported by us [68] and Jones et al. [72]. Interestingly, these species were found to be inactive in the ROP of cyclic esters (ε-CL and *r*-LA, respectively).

Very recently, González et al. studied the catalytic behavior of the binuclear tridentate complexes **137–139** in the ROP of *r*-LA (Figure 24) [81]. The only difference between compounds **137** and **138** is the nature of the solvent coordinated to the Zn centers (pyridine and DMF, respectively); compared to the **138**, the fluorine atom is replaced by a *para*-methoxy substituent in **139**. In the absence of an external co-activator, all complexes allowed for complete monomer conversion after 18 h at 130 °C (melt conditions) with LA:Zn ratios as high at 800:1. With respect to the polymer molecular weight, the complexes followed the trend **139** > **137** > **138** (8.5, 4.6 and 3.9 kDa, respectively). The use of BnOH as a co-activator (20 equiv./Zn) allowed for higher reaction rates but determined a drop of M_n. The ^{1}H NMR spectra of the polymers prepared in the presence of the alcohol showed the diagnostic resonances of the benzyloxy- terminal group, suggesting that the co-activator is responsible for the ring-opening of the first monomer unit.

137 (R = F, X = Py)
138 (R = F, X = DMF)
139 (R = OCH$_3$, X = DMF)

Figure 24. [ONO]-type Schiff-base zinc complexes **137–139** [81].

The ROP of *L*-lactide promoted by the tetradentate salen-type zinc complex **140** has been recently disclosed by Sutar et al. (Figure 25) [82]. Similar to its Ni- [58] and Cu- [66] analogues reported by

the same group, the complex proved to be inactive in the absence of a co-activator. Upon using one equiv./Zn of BnOH, good activity was observed in CH$_2$Cl$_2$ (78% conversion) at room temperature after 24 h, while lower conversions were achieved in toluene and THF (60% and 48%, respectively). Further studies conducted in dichloromethane proved **140** was able to efficiently convert the monomer at LA:Zn ratios as high as 200:1, affording polymers with M_n in accordance with the calculated values with good control ($M_w/M_n \sim 1.1$). By increasing the amount of alcohol to 2 and 4 equiv./Zn, faster rates were observed, albeit with a drop of M_n. Finally, kinetic studies suggested that the ROP takes place according to a *living* mechanism.
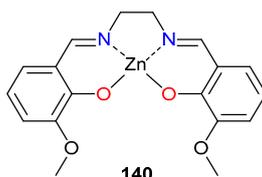
Figure 25. Zn-salen complex **140** active in the ROP of *L*-LA [82].

The use of zinc complexes of macrocyclic Schiff-bases has also been studied. In 2015, Williams, Brooker et al. reported a dinuclear complex based on a bis(anilido)tetraimine macrocycle exhibiting good activity in the ROP of *r*-LA in the presence of 1 equiv./Zn of ^{i}PrOH in THF (Figure 26, **141**) [83]. The M_n of the atactic polymer was in agreement with the calculated value with very narrow polydispersity. NMR spectroscopy and mass spectrometry studies confirmed the presence of the *iso*-propoxy end-group and confirmed the absence of significant transesterification. Moreover, kinetic investigations proved that an induction time is required, while a linear trend was observed for conversions > 20%. Based on these data, it was postulated that the formation of a catalytically active species featuring a Zn-O^{i}Pr bond, generated by the alcoholysis of the parental complex **141**, takes place during the early stages of the reaction. Lately, the same group further investigated this type of systems, synthesizing the well-defined *iso*-propoxy- and hexamethyldisilazane (HMDS)-analogues of **141** (**142–143** and **144–145**, respectively) [84]. All compounds proved extremely active, allowing for complete lactide conversion within 2 min at room temperature. The highest rates were observed for the HMDS-species that showed to be ca. 600 times faster than the alkoxy congeners. The efficiency of these dinuclear compounds was also 6 times per metal center higher than that of their corresponding monometallic analogues, suggesting cooperative effects between the two metal centers. Interestingly, a zero-order rate dependence of lactide was found for the HMDS compounds, while **142** and **143** followed the more common pseudo first-order substrate dependence.

141 (n = 1, X = Et)
142 (n = 1, X = O^{i}Pr)
143 (n = 2, X = O^{i}Pr)
144 (n = 1, X = N(SiMe$_3$)$_2$)
145 (n = 2, X = N(SiMe$_3$)$_2$)

Figure 26. Dizinc(II) complexes of macrocycle Schiff-base ligands [83,84].

Very recently, our group developed mixed Zn/Co heterobimetallic complexes supported by [2+2] Schiff-base macrocycles (**146** and **147**, Figure 27) [85]. These complexes proved efficient activity in the ROP of ε-CL and δ-VL at 130 °C in the presence of BnOH as co-activator. The ^{t}Bu derivative **147** outperformed the Me-congener, possibly because of the higher solubility of the former in the reaction

medium. Kinetic investigations showed a first-order monomer dependence and, interestingly, the ROP of δ-VL proceeded faster than that of ε-CL, with rate constants of 6.10 and 2.12 × 10⁻³ h⁻¹, respectively. Remarkably, the corresponding homo-dinuclear complexes were found to be inactive or poorly active in the ROP of ε-CL and δ-VL, respectively, suggesting the occurrence of cooperative effects between the Co- and Zn centers in the mixed complexes **146** and **147**. Preliminary tests proved that the ROP of *rac*-lactide as well as CL-VL and CL-LA co-polymerization are also possible in the presence of these catalysts.

146 (R = Me)
147 (R = *t*Bu)
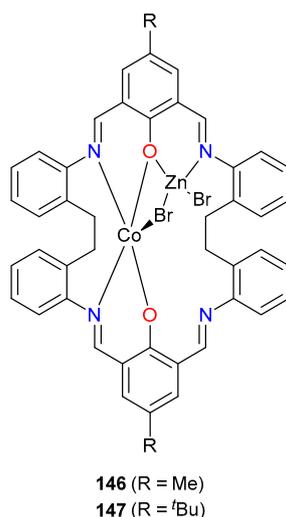
Figure 27. Heterobimetallic macrocyclic complexes **146** and **147** [85].

5.6. Cadmium

Cadmium complexes bearing tridentate Schiff-bases of the type [NN'X] (where X = O, N) have been recently shown to promote the ROP of *rac*-LA (Figure 28) [86]. The tests were performed in dichloromethane at low temperature (−50 or 0 °C) in the presence of MeLi as co-activator. Indeed, the active species was thought to be a Cd-Me containing complexes generated in situ from the interaction of the parental Br-compound with MeLi. All complexes exhibited moderate-to good activity, affording heterotactic PLAs with good control. Although no straightforward structure/activity correlation could be drawn, the activity trend was found to be **151** ~ **153** > **148** > **150** > **149** > **152**.

148 (X = NMe₂)   **150** (X = NMe₂)
149 (X = OMe)   **151** (X = OMe)

152   **153**
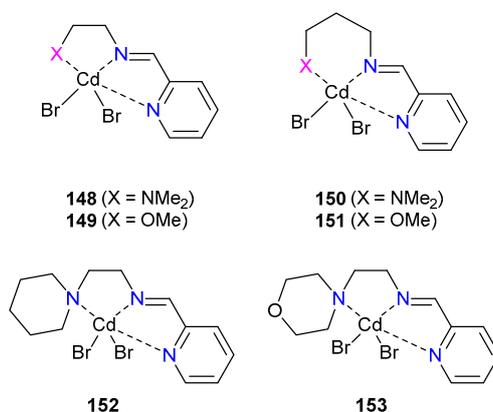
Figure 28. Cadmium complexes of tridentate Schiff-base ligands [86].

6. Rare Earth Metals

The use of rare-earth (Ln) metal complexes of Schiff-bases as catalysts for the ROP of cyclic esters has been widely investigated. In 2010, Shen et al. tested phenoxyimino complexes **154–158** in

the polymerization of ε-CL (Figure 29) [87]. At 50 °C with a monomer:Ln ratio of 100:1, the Y- and Nd-based complexes allowed for complete monomer conversion with good control, while the La- and Gd-analogues proved less performing, affording PCLs in moderate yields. On the other hand, no reaction was observed in the presence of the Sc compound **154** [88]. Upon increasing the CL:Ln ratio to 200:1, **155** outperformed its Nd-congener. Moreover, the latter exhibited good activity even at lower temperature, albeit with less control. NMR spectroscopic investigations performed on oligomeric species suggested that the ROP of the first monomer unit occurs with the cleavage of the acyl-oxygen bond. Lately, the same group extended the scope of ligands synthesizing La- and Gd-compounds having various substituents and at the imine moiety (**159–170**, Figure 29) [89].
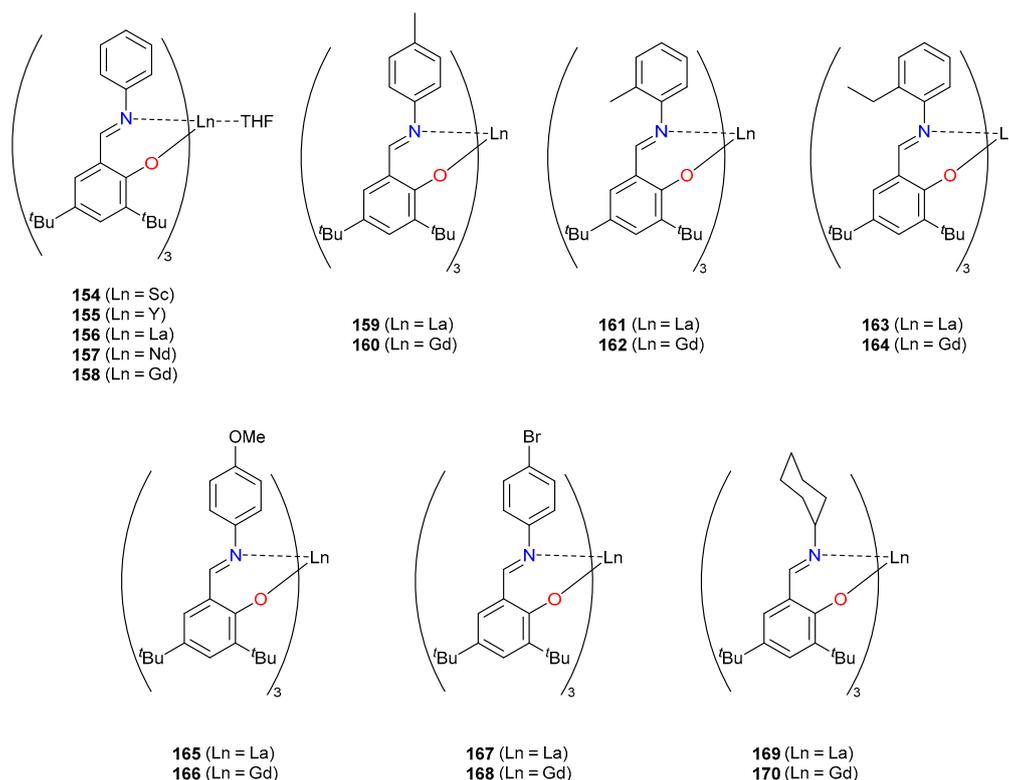
Figure 29. Rare-earth metal complexes bearing phenoxyimine ligands [87,89].

All complexes proved efficient catalysts for the ROP of ε-CL in toluene at room temperature, with monomer:Ln ratios as high as 300:1. Gd-species outperformed the La-analogues, in terms of both polymer M_n and polymerization control. Amongst the series, complexes bearing electron-donating groups at the *para* position (**165–166** and **167–168**) allowed for higher M_n and narrower polydispersities compared to the other systems. Analysis of the polymers by NMR spectroscopy suggested that the reaction is initiated by one phenoxy-group of the catalysts' Schiff-base moiety. Interesting activity in the ROP of ε-CL was observed also in the case of the dinuclear complex **171–173**, bearing a Salen-type ligand (Figure 30) [90]. Good to moderate conversions were achieved in all cases at 70 or 100 °C with CL:Ln ratios as high as 500:1, affording polymers with high M_n (50–90 kDa) and moderate control. The observed reactivity trend was **171** > **172** > **173**, which is in agreement with the sequence of the ionic radii of the metal centers involved in the complexes. Kinetic investigations showed a first-order dependence on the substrate concentration and a linear increase of the M_n with the monomer conversion. The ^{1}H NMR spectra of oligomers isolated after a short reaction time showed resonances corresponding to the Schiff-base scaffold, suggesting that the ligand could serve as the actual initiator of the polymerization.

171 (Ln = La)
172 (Ln = Nd)
173 (Ln = Sm)
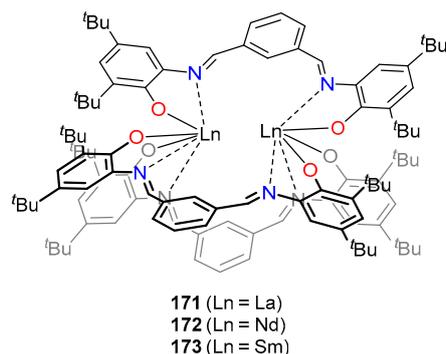
Figure 30. Dinuclear Ln-complexes bearing a tetradentate Schiff-base ligand [90].
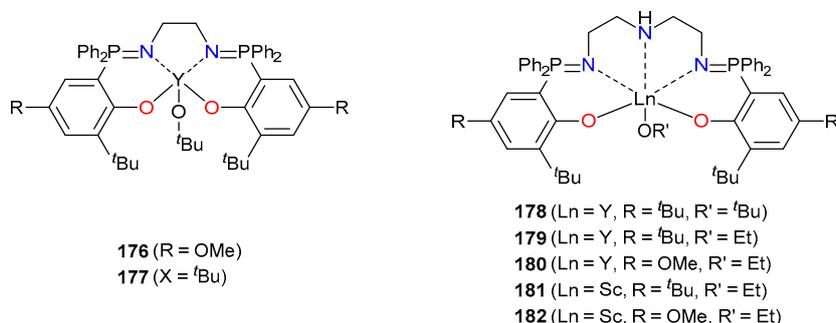
The effect of the oxidation state of the metal center on the activity of the catalyst was studied by Cantat, Diaconescu et al. by using the cerium complexes **174** and **175** bearing a salen- and phosphasalen ligand, respectively (Figure 31) [91]. The Ce(III) center could be reversibly oxidized to Ce(IV) upon addition of a suitable reactant; ferrocenium tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate (FcBAr^F) proved efficient for both catalysts, while I$_2$ only allowed for the oxidation of **175**. In this regard, X-Ray absorption near-edge structure (XANES) and Mössbauer spectroscopic studies confirmed that only the lanthanide was involved in the redox process, while the Fe center retained its +2 oxidation state. When tested in the ROP of *L*-lactide, the Ce(III) complexes were shown to be more active than their oxidized forms; indeed, the addition of FcBAr^F completely passivated the catalysts, while oxidation of **175** with iodine led to a drastic reduction of the reaction rate. However, the polymerization could be re-enabled by adding a reducing agent (Cp$_2$Co) to the reaction mixture, confirming the reversibility of the process. The Ce(III) species were also shown to polymerize 100 equiv. of ε-CL within minutes at room temperature as well as *rac*-lactide at 0 °C with moderate heterotactic bias. The higher activity of the Ce(III) species over their oxidized analogues was thought to be due to electronic factors (i.e., lower electrophilicity of the metal center) that increase the nucleophilicity of the alkoxide ligand of the growing polymer chain. This hypothesis was confirmed by DFT calculations.

174

175
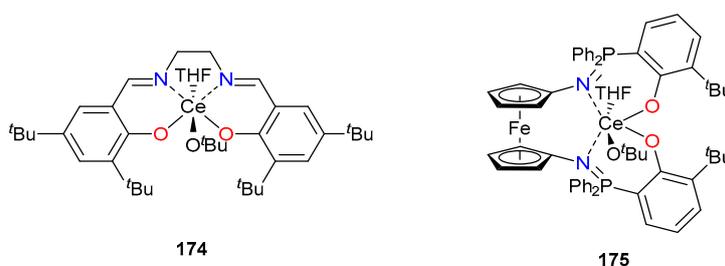
Figure 31. Redox switchable Ce-based catalysts [91].

Tetra- and pentadentate phosphasalen complexes have also been considered (Figure 32) [92,93]. The yttrium complexes **176–177** were found extremely active in the ROP of *rac*-LA at ambient temperature in THF, allowing for complete monomer conversion within seconds, even at very low catalyst loading (0.1 mol%). The pentadentate analogues **178–180** were also highly performing, albeit requiring longer reaction times (20–30 min) to achieve high yields. Interestingly, tetradentate compounds led to heterotactic PLAs while isotactic polymers were isolated in the presence of their pentadentate congeners. In all cases, M_n higher than the expected values were achieved; the control was generally good and dependent on the steric bulk of the alkoxide ancillary ligand. In fact, while the polydispersity was 1.34 in the case of complex **178**, the value observed with its ethoxy-analogues was narrower. Interestingly, no lactide conversion was obtained upon using Sc-complexes **181** and **182**, regardless of the reaction conditions employed. ^{1}H NMR spectroscopic experiments suggested the formation of a chelate Sc-LA species inactive towards polymerization. However, the catalysts

were active in the ROP of ε-CL in toluene at ambient temperature; in this case, **182** allowed for higher conversions that its ^{t}Bu-analogue after 48 h (98% and 84%, respectively). M_n observed were in good agreement with the calculated values and the control was generally good (M_w/M_n ~ 1.05).

176 (R = OMe)
177 (X = ^{t}Bu)

178 (Ln = Y, R = ^{t}Bu, R' = ^{t}Bu)
179 (Ln = Y, R = ^{t}Bu, R' = Et)
180 (Ln = Y, R = OMe, R' = Et)
181 (Ln = Sc, R = ^{t}Bu, R' = Et)
182 (Ln = Sc, R = OMe, R' = Et)

Figure 32. Tetra- and pentadentate phosphasalen Y and Sc complexes [92,93].

Rare-earth complexes bearing pentadentate [ONONO]-type salen ligands have also shown notable activity in the ROP of *r*-LA (Figure 33) [94]. All catalysts completely converted the monomer within 15–20 min at room temperature with LA:Ln ratios as high as 1000:1, proved more active than previously reported tetradentate Y-salen compounds [95]. Heterotactic PLAs were isolated in all cases, with generally high stereoselectivity (P_r spanning from 0.7 to 0.9). The observed polymer M_n were close to the calculated values with moderate to good control. The catalytic activity (**187** ~ **186** > **185** > **184** >> **183**) increased with the ionic radii of the metal center featured in the complexes, while the stereoselectivity followed the reverse trend. A first-order substrate dependence was found in the kinetic investigation while mass-spectrometry on the isolated polymers revealed the presence of the ArO- end group, indicating that the ancillary ligand is responsible for the ring-opening of the first monomer unit.

183 (Ln = Sc, n = 0)
184 (Ln = Yb, n = 0)
185 (Ln = Y, n = 1)
186 (Ln = Sm, n = 1)
187 (Ln = Nd, n = 1)
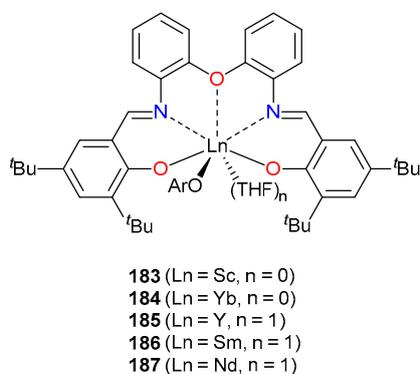
Figure 33. Rare-earth metal complexes of [ONONO]-type Salen ligands active in the ROP of *r*-LA [94].

7. Main Group Metals

7.1. Aluminum

Aluminum complexes have been extensively employed as catalysts for the ROP of cyclic esters. This topic has been described in depth in recent reviews, not only from the catalyst design point of view, but also with respect to scope of monomer [96,97]. Early reports mainly concerned chiral- [98–100] and achiral [101–104] Salen complexes, while Salalen [105,106] or related systems [107] have been subsequently introduced. Very recently, a set of Al catalysts bearing a novel Catalen scaffold has been reported by the group of Jones [108]. One of these systems exhibited the highest activity known to date for an Al complex in the melt ROP of *r*-LA.

Over the past 2 decades, our group have been contributing to the development of the field. Simple arylimino compound **188** (Figure 34) proved inactive in the ROP of ε-CL [109], while the

2,4-*t*Bu-salicylaldehyde derivatives **189–196** exhibited interesting activity towards the polymerization of different monomers [110]. In the presence of BnOH as co-activator, complexes **189** and **195** were the most performing catalysts in the ROP of ε-CL, leading to complete monomer conversion at 80 °C within 3 and 1 h for the former and the latter, respectively. In spite of the higher reaction rate, **195** afforded polymers with lower M_n and broader polydispersitities compared to that isolated in the presence of **189**. Under the same reaction conditions all other complexes showed moderate to good activity. While increasing the temperature (from 80 to 110 °C) was beneficial, the use of an additional equivalent of BnOH led to a significant drop of polymer molecular weight as well as to a broadening of the molecular weight distribution. Complexes **189–196** proved also capable of promoting the ROP of δ-VL and *r*-LA, although the conversions were somewhat lower than that of ε-caprolactone. In the case of the ε-CL/*r*-LA copolymerization, a good lactide incorporation (up to 63%) was observed. NMR spectroscopy and MALDI-TOF mass spectrometry confirmed the presence of the BnO-end group.
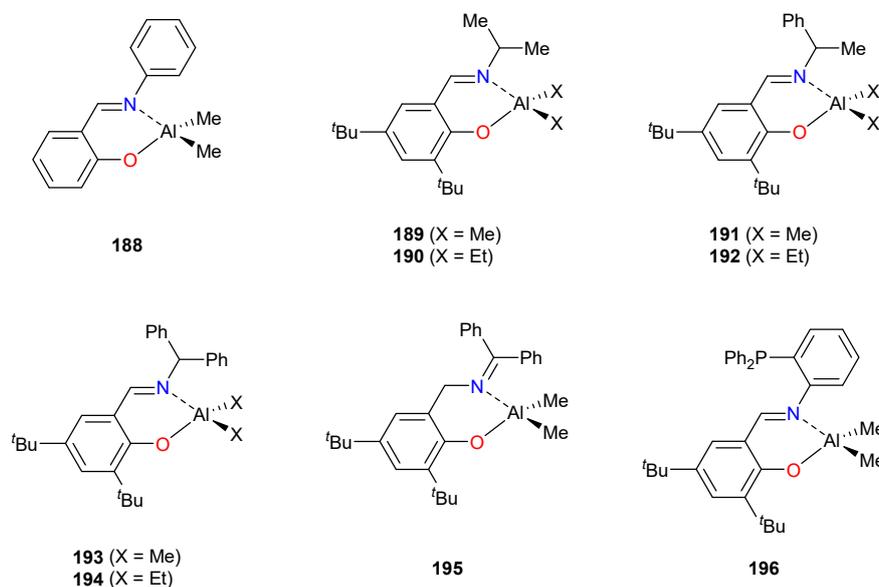
Figure 34. Al-complexes of bidentate Schiff-bases tested in the ROP of cyclic esters [109,110].

The effect of different substituents at both the phenoxy- and the imino-moiety on the catalytic activity of complexes **197–208** in the ROP of lactides was also studied (Figure 35) [111]. In the case of *L*-lactide, conversions spanning from 70% to 99% were obtained after 48 h at 100 °C in toluene, with a LA:Al of 250 by using one equiv./Al of BnOH as co-activator. Higher temperatures and/or greater amount of alcohol led to higher reaction rates, albeit with lower M_n and less control. The polydispersities ranged between 1.20 and 1.25 with unimodal distributions, suggesting single site behavior of the catalysts. No clear structure/activity trend was found, although complexes bearing electron-donating groups were found to be more active; moreover, compounds having more soluble alkyl groups displayed enhanced reactivity. Interestingly, all catalysts proved more active upon replacing *L*-LA with its *D*-isomer. In addition, higher molecular weights and narrower polydispersities were achieved. Such improved behavior was thought to be dependent on the different coordination modes of the monomers at the catalytically active sites. Finally, poorer control and lower polymer molecular weights were observed upon using *r*-LA as the monomer. The ^{13}C NMR spectra of the isolated PLAs suggested that BnOH is also involved both in the initiation and in the termination of the polymer chains.

Figure 35. Al-aldiminophenolates complexes active in the ROP of lactides [111].
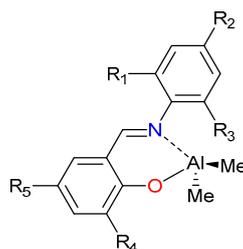
197 ($R_1 = R_3 = Ph_2CH$, $R_2 = {}^iPr$, $R_4 = R_5 = {}^tBu$)
198 ($R_1 = R_3 = Ph_2CH$, $R_2 = Cl$, $R_4 = R_5 = {}^tBu$)
199 ($R_1 = Me$, $R_2 = R_3 = Ph_2CH$, $R_4 = R_5 = {}^tBu$)
200 ($R_1 = {}^iPr$, $R_2 = R_3 = Ph_2CH$, $R_4 = R_5 = {}^tBu$)
201 ($R_1 = R_3 = Ph_2CH$, $R_2 = {}^iPr$, $R_4 = {}^tBu$, $R_5 = Me$)
202 ($R_1 = R_3 = Ph_2CH$, $R_2 = Me$, $R_4 = {}^tBu$, $R_5 = Me$)
203 ($R_1 = Me$ $R_2 = R_3 = Ph_2CH$, $R_4 = {}^tBu$, $R_5 = Me$)
204 ($R_1 = R_2 = Me$, $R_3 = Ph_2CH$, $R_4 = {}^tBu$, $R_5 = Me$)
205 ($R_1 = Me$, $R_2 = H$, $R_3 = Me$, $R_4 = Ph_2CH$, $R_5 = Me$)
206 ($R_1 = R_3 = {}^iPr$, $R_2 = H$, $R_4 = R_5 = I$)
207 ($R_1 = R_3 = {}^iPr$, $R_2 = H$, $R_4 = R_5 = {}^tBu$)
208 ($R_1 = R_3 = {}^iPr$, $R_2 = R_4 = R_5 = H$)

In 2008, Nomura et al. also reported a series of Al-based catalysts for the ROP of several cyclic esters, namely ε-CL, δ-VL and *r*-LA, (Figure 36) [112]. In each catalyst, the 2-*tert*-butylsalicylaldehyde scaffold is retained while different substituents at the N-atom are featured. Regardless of the monomer, catalysts bearing alkyl groups were found to be poorly active while complexes with aromatic substituents proved more efficient, with catalytic activity increasing with the steric bulk of the N-group. Notably, the C_6F_5-derivative was the most active species in all cases, suggesting that also electronic effects influence the catalyst behavior. Narrow polydispersities and M_n in agreement with the calculated values, along with kinetic investigations, confirmed the *living* nature of the polymerization process. In the case of *r*-LA, atactic polymers were isolated. Attempts towards polymerizing smaller lactones such as β-BL and γ-BL were unsuccessful. Lately, the same group investigated the effect of the steric hindrance of the N-substituent on the catalytic activity of binuclear Al-Schiff-base complexes [113].

209 (R = ${}^tBu$)
210 (R = cyclohexyl)
211 (R = adamantyl)
212 (R = Ph)
213 (R = 2,6-$Me_2C_6H_3$)
214 (R = 2,6-${}^iPr_2C_6H_3$)
215 (R = 2,4,6-$Me_3C_6H_3$)
216 (R = 2,4,6-${}^tBu_3C_6H_3$)
217 (R = C_6F_5)

218 (R = Ph)
219 (R = 2,6-${}^iPr_2C_6H_3$)
220 (R = 2,6-$Ph_2C_6H_3$)
221 (R = adamantyl)
222 (R = ${}^tBu$)
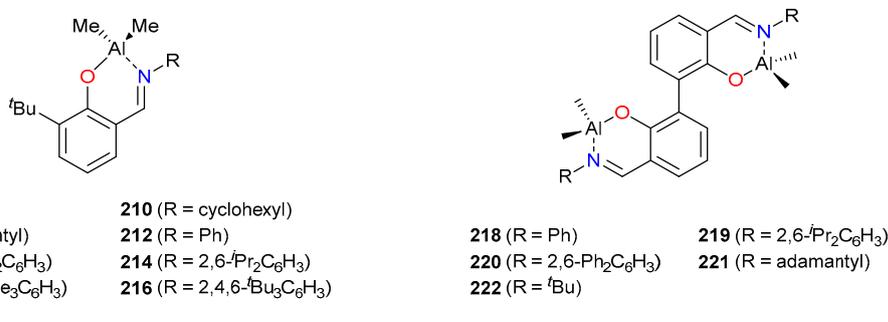
**Figure 36.** Al-Phenoxy-imine catalysts developed by Namura et al. [112,113].

All complexes, activated by BnOH, were tested in the ROP of ε-CL at 70 °C (Table 8). Under the optimized reaction conditions, compound **218** was completely inactive, possibly because of its poor solubility in the reaction medium. Complete monomer conversion was obtained in the presence of **219** after 10 min. Polymer M_n in agreement with the calculated and the narrow polydispersity suggested the occurrence of a *living* process; such a hypothesis was confirmed upon performing a two-step polymerization in which an excess of monomer was added after the initial 10-min polymerization. Good activity was also displayed by **220**, albeit that a longer reaction time (20 min) was required to completely convert the monomer. The adamantyl-congener **221** was less performing, allowing for 75% conversion after 30 min with less control (M_w/M_n = 1.67). Finally, complete conversion was obtained with **222** after the same reaction time, although with a rather broad distribution (1.80). The ${}^1H$ NMR spectra of the isolated polymers displayed the diagnostic resonances of both benzyloxy- and –CH_2OH end groups.

Table 8. ROP of ε-CL catalyzed by dinuclear complexes **218–222** [113].

Run	Catalyst	Al:BnOH:Cl/[a]	Time (Min)	Conv. (%)	$M_{n(calc.)}$[b] × 10^{-4}	$M_{n'}$[c] × 10^{-4}	M_w/M_n[c]
1	**218**	1:1:250	30	Trace	-	-	-
2	**219**	1:1:250	10	100	2.86	3.06	1.16
6[d]	**219**	1:1:250	10 + 10	100		5.91	1.24
7	**220**	1:1:250	10	70	2.01	2.37	1.25
8	**220**	1:1:250	20	100	2.86	3.42	1.28
9	**221**	1:1:250	30	75	2.15	2.72	1.67
10	**222**	1:1:250	30	100	2.86	3.74	1.80

[a] Conditions: V_{total} = 3 mL, ε-CL 5 mmol, 70 °C. [b] Calculated using ($[CL]_0/[OH]_0$) × conv. (%) + BnOH. [c] GPC data in THF vs. polystyrene standards, using a correcting factor of 0.56. [d] Polymerization was conducted for 10 min, ε-CL(5 mmol) was again added, and the polymerization was continued for another 10 min.

Recently, Kirillov, Carpentier et al. reported a series of Al complexes stabilized by phenoxyimine ligands featuring an *ortho*-triphenylsilyl group at the aryloxy moiety and various N-substituents (Figure 37) [114]. When used in combination with an external alcohol (either *i*PrOH or BnOH) all complexes were active in the ROP of *r*-LA at 100 °C, over a period of time ranging between 2 and 20 h, exhibiting *living* character. The experimental polymer molecular weights were in good agreement with the expected values with narrow and unimodal polydispersities. Amongst the series, complex **228** bearing a N-benzyl substituent, exhibited the highest activity. Similarly to the previously encountered Zn-macrocycles **144** and **145** [84], kinetic studies highlighted a zero-order dependence on the lactide concentration. The NMR spectra of the isolated PLAs showed signals accountable to alkoxy- (BnO- or *i*PrO-) terminal groups derived from the insertion of the first monomer unit into the Al-OR bond generated by the reaction of **223–228** with the alcohol employed as co-activator. In terms of polymer microstructure, either iso- or heterotactic PLAs were obtained, depending on the catalyst employed. Indeed, while **225**, **228**, **230** and **232** exhibited isotactic bias, heterotactic enrichment was observed with **223**, **233** and **235**. On the other hand, no selectivity was displayed by **224**, **227** and **229**. The isoselectivity trend was partially rationalized in terms of the bulkiness of the aryl moiety of the N-benzyl substituent; however, the steric hindrance was thought to be only one of the factors influencing the stereoselectivity of the catalysts. In fact, no straightforward correlation could be found in the series of species exhibiting heterotactic bias.
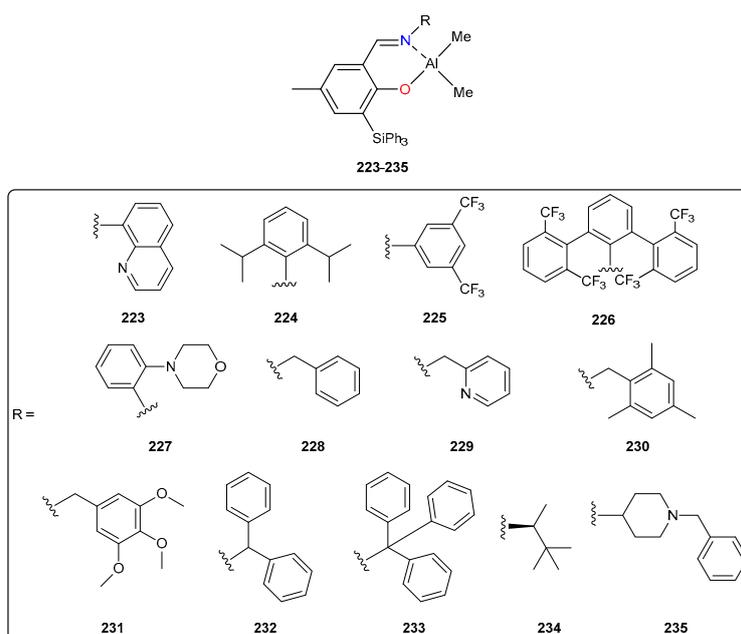
Figure 37. *Ortho*-triphenylsilyl substituted complexes **223–235** [114].

In 2014, Liu et al. disclosed β-ketiminato aluminum complexes active in the homo- and copolymerization of ε-CL and *L*-LA (Figure 38) [115]. Complex **236**, in combination with an equimolar amount of ^{i}PrOH, allowed for complete conversion of 100 equiv. of ε-CL within 5 min at 80 °C, while slightly longer reaction times (10 min) were required by its congeners **237** and **238**. However, the latter proved to be the best catalyst for the ROP of *L*-LA, reaching 96% and 99% conversion after 3 and 4 h, respectively. Molecular weights close to the theoretical values and narrow distributions were observed in all cases; in addition, kinetic investigations suggested the occurrence of a *living* process. This allowed for the synthesis of well-defined block PCL-PLA co-polymers by sequential addition of the two co-monomers. Based on the results obtained in the homo-polymerization tests, species **236** and **238** were employed for the sequential CL-LA and LA-CL co-polymerizations, respectively.
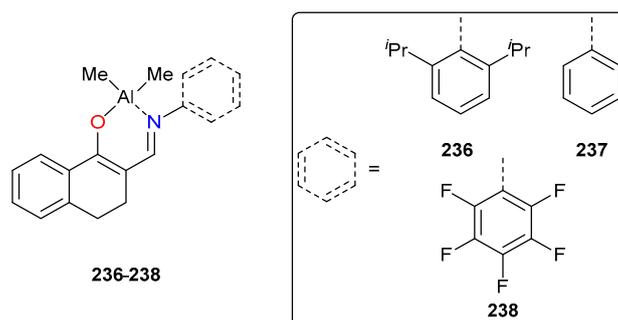
Figure 38. Cyclic β-ketiminato aluminum complexes **236–238** [115].

Very recently, Nie, Han et al. disclosed diarylhydrazone-based Al complexes displaying good activity in the ROP of ε-CL and *r*-LA [116]. The four novel complexes proved to be able to completely convert the monomer under mild conditions (70 °C) with good control and M_n in accordance with the calculated values. However, poor stereoselectivity was observed in the case of *r*-LA, as atactic PLAs (P_r ~ 0.5) were obtained in all cases. Interestingly, these complexes were found to be more active than related [N,O]-supported Al complexes. It was suggested that the presence of an extra N-atom at the ligand framework increases the acidity of the metal center, hence enhancing the catalytic activity.

Aluminum complexes of bidentate thiol Schiff bases have shown interesting activity as catalysts in the ROP of ε-CL (Figure 39, Table 9) [117]. In particular, when complex **239** was activated by two equiv./Al of BnOH, almost complete conversion of 100 equiv. of monomer was achieved in 12 min at room temperature, affording a polymer with narrow dispersity and M_n close to the calculated value.
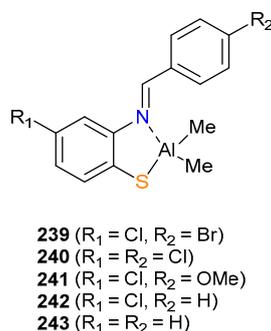

239 (R₁ = Cl, R₂ = Br)
240 (R₁ = R₂ = Cl)
241 (R₁ = Cl, R₂ = OMe)
242 (R₁ = Cl, R₂ = H)
243 (R₁ = R₂ = H)

Figure 39. Five-membered ring Al complexes of N,S-Schiff bases **239–243** [117].

Under the same reaction conditions, lower rates were observed in the presence of the other catalysts, albeit the process resulted to be well controlled in all cases. Upon increasing the amount of co-activator, the reaction resulted to be faster, although with an expected drop of molecular weight and loss of control. Notably, **239** proved efficient even at higher monomer concentrations (up to

350 equiv./Al), allowing for 87% conversion after 3 h at ambient temperature; furthermore, in this case, the polymerization proceeded in a *living* fashion.

Table 9. ROP of ε-CL catalyzed by **239–243** [117].

Entry	Catalyst	Time (Min)	Conv. (%)[a]	$M_{n(calc.)}$ (Da)[b]	$M_{n(NMR)}$ (Da)[a]	$M_{n(gpc)}$ (Da)[c]	M_w/M_n[c]	$k_{obs(error)}$ (min^{-1})[d]	Induction Period (Min)
1	**239**	12	96	5600	4800	5900	1.26	0.284(12)	0.8
2	**240**	12	92	5400	5600	7800	1.19	0.260(17)	1.8
3	**242**	20	92	5400	5200	6400	1.23	0.136(4)	0.9
4	**243**	25	95	5500	7900	8100	1.23	0.115(8)	0.8
5	**241**	25	90	5200	5500	5200	1.21	0.105(4)	2.6

Reaction conditions: Toluene (5 mL), $[M]_0$:$[Cat]_0$:$[BnOH]_0$ = 100:1:2, [CL] = 2.0 M, at room temperature. [a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of the monomer ×[monomer]$_0$/[BnOH]$_0$ × conversion yield + $M_{w(BnOH)}$. [c] Obtained from GPC analysis and calibration on the basis of the basis of the polystyrene standards. $M_{n(GPC)}$ values are obtained from GPC multiplied by 0.56. [d] The observed k_{obs} value is the slope of the first-order kinetic plot of ε-caprolactone polymerization vs. time. The conversion of ε-caprolactone with time was monitored using ^{1}H NMR.

Recently, dinuclear aluminum complexes supported by bis-iminophenolate ligands have been independently reported by the groups of Wang [118] and Liu [119]. Such systems were highly active in the ROP of *rac*-lactide, affording high molecular weight polymers with narrow polydispersities. The good performances of these catalysts were attributed to cooperative effects of the two Al-centers.
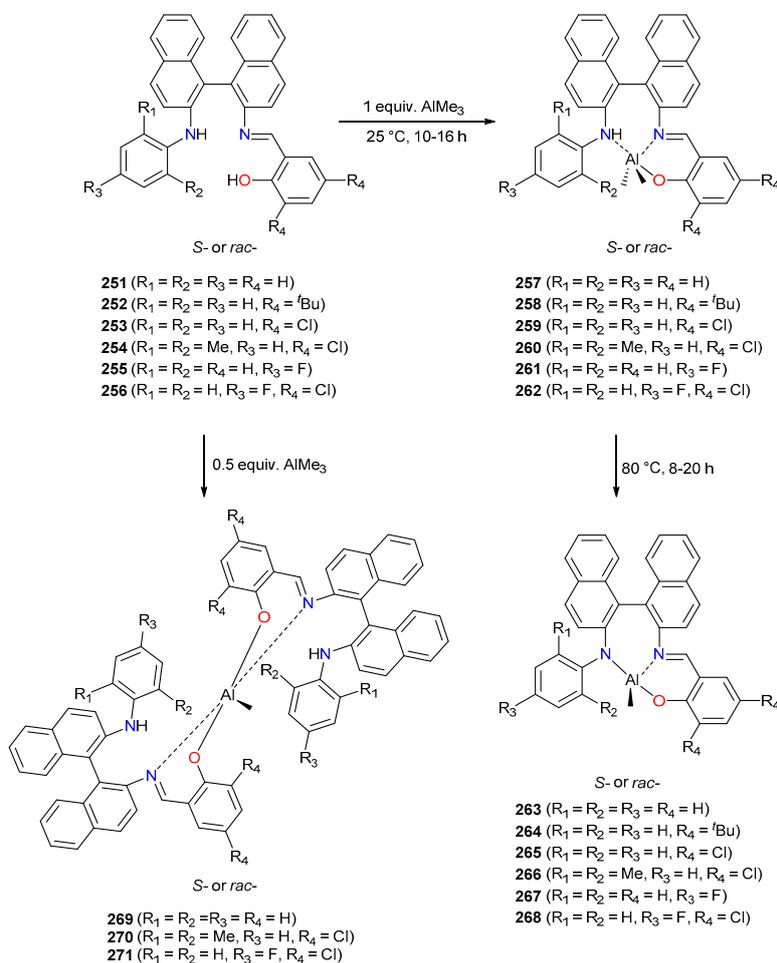
With respect to tridentate systems, our group reported the mono- and dinuclear species **244** and **245** bearing [NON] scaffold and, lately, the 8-quinolinolates [ONN]-based complexes **246–250** (Figure 40) [109,120]. When used in combination with 1 equiv. of BnOH, **244** and **245** allowed for 50% and 37% conversion, respectively, of 500 equiv. of ε-CL after 11 h at room temperature. The process was well controlled, and the polymer molecular weights matched the expected values. The 8-quinolinolates derivatives were found to be more active at higher temperatures (60–90 °C), exhibiting *living* behavior. Although the molecular weight distributions were rather narrow and unimodal, a certain degree of transesterification was observed, especially at higher monomer conversion. Interestingly, the transesterification increased according to the trend **248** < **247** < **246** < **249**, **250**, suggesting that a bulky *ortho*-substituent reduces the occurrence of the undesired side-process.
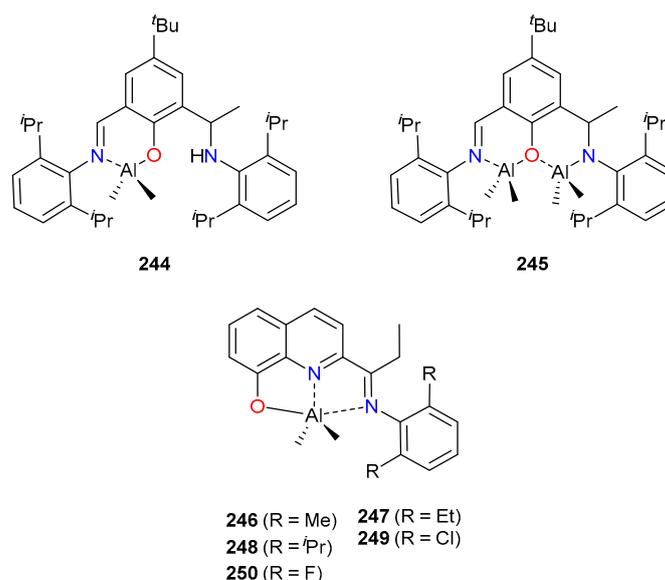
Figure 40. Al complexes of tridentate Schiff-base ligands active in the ROP of ε-CL [109,120].

Aluminum complexes of unsymmetrical dinaphthalene-imine derivatives have been disclosed by Pang et al. in 2015 (Scheme 3) [121]. The reaction of either the *S*- or *rac*-ligands **251–256** with one

equivalent of trimethylaluminum led to the -AlMe$_2$ complexes **257–262** (*S*- or *rac*, depending on the starting ligand). Upon prolonged heating, these compounds released methane and their mono-methyl analogues **263–268** were isolated. Finally, the bis-Schiff-base species **269–271** (*S*- or *rac*) were obtained by treating the corresponding ligands with 0.5 equivalents of the metal precursor.


251 (R$_1$ = R$_2$ = R$_3$ = R$_4$ = H)
252 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = ^{t}Bu)
253 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = Cl)
254 (R$_1$ = R$_2$ = Me, R$_3$ = H, R$_4$ = Cl)
255 (R$_1$ = R$_2$ = R$_4$ = H, R$_3$ = F)
256 (R$_1$ = R$_2$ = H, R$_3$ = F, R$_4$ = Cl)

257 (R$_1$ = R$_2$ = R$_3$ = R$_4$ = H)
258 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = ^{t}Bu)
259 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = Cl)
260 (R$_1$ = R$_2$ = Me, R$_3$ = H, R$_4$ = Cl)
261 (R$_1$ = R$_2$ = R$_4$ = H, R$_3$ = F)
262 (R$_1$ = R$_2$ = H, R$_3$ = F, R$_4$ = Cl)

269 (R$_1$ = R$_2$ = R$_3$ = R$_4$ = H)
270 (R$_1$ = R$_2$ = Me, R$_3$ = H, R$_4$ = Cl)
271 (R$_1$ = R$_2$ = H, R$_3$ = F, R$_4$ = Cl)

263 (R$_1$ = R$_2$ = R$_3$ = R$_4$ = H)
264 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = ^{t}Bu)
265 (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = Cl)
266 (R$_1$ = R$_2$ = Me, R$_3$ = H, R$_4$ = Cl)
267 (R$_1$ = R$_2$ = R$_4$ = H, R$_3$ = F)
268 (R$_1$ = R$_2$ = H, R$_3$ = F, R$_4$ = Cl)

Scheme 3. Synthesis of Al-based complexes of unsymmetrical dinaphthalene-imine derivatives [121].

Next, the ability of these complexes to polymerize *L*- and *rac*-lactide was investigated. Moderate to high activity was displayed at 70 °C in the presence of isopropanol as co-activator. The optical active complexes were found better performing than their racemic analogues, both in terms of activity and stereoselectivity. Noteworthy, is the fact that the conversions improved upon increasing the steric bulk of the substituents on the phenyl moiety. All polymers were isotactic and the isoselectivity increased with the steric hindrance of the groups at the salicylaldehyde part. Kinetic studies showed that the M_n linearly increased with the monomer conversion while the polydispersity remained constant throughout the reaction, proving the occurrence of a *living* polymerization. The presence of the isopropoxy end group was observed in the ^{1}H NMR spectrum of the isolated polymers, suggesting that the active species features an Al-O^{i}Pr bond arising from the reaction of the pre-catalysts with the co-activator. The whole process proceeds according to a coordination–insertion mechanism.
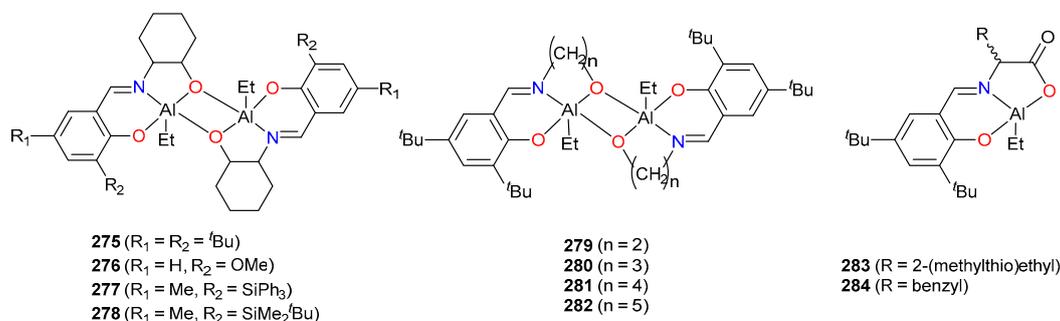
Tridentate complexes with different N-side arms were recently studied by Zhang et al. (Figure 41) [122]. When used as catalysts in the ROP of *ε*-CL and *δ*-VL in the absence of a co-activator, random polymerization and low control was observed, while the addition of 1 equiv./Al of BnOH led the generation of systems displaying moderate to high activity depending on the side-arm of the starting complex. In fact, the reactivity trend was found to be **272** > **273** > **274**. Systems based on **272–273**/BnOH proved efficient also under *immortal* conditions, affording high molecular weight

polymer with narrow polydispersities (as low as 1.2). NMR spectroscopy and mass spectrometry studies confirmed the presence of the benzyloxy-end group as well as showing the formation of cyclic oligomers generated by intramolecular back-biting. Controlled block CL/VL co-polymers were obtained by sequential monomer addition in the presence of the **273**/BnOH system, both at room temperature and at higher temperature. On the other hand, the catalysts based on the other two Al-complexes allowed for good control only at low temperature, while undesired transesterification was observed under more forcing conditions.
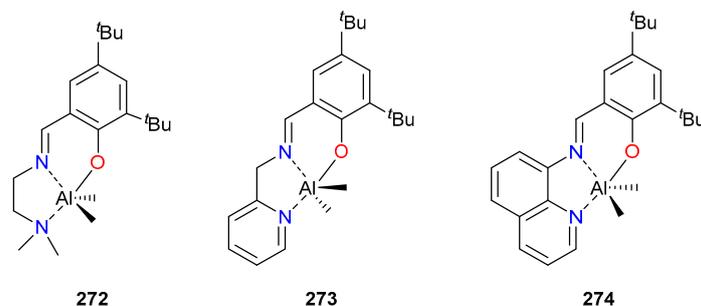
Figure 41. Tridentate Al-based catalysts **272–274** active in the homo- and co-polymerization of ε-CL and δ-VL [122].

Aluminum catalysts supported by half-salen ligands were reported derived from natural products have been reported by Darensbourg and Karroonnirun (Figure 42) [123]. The backbone of the dinuclear complexes **275–278** and **279–282** derived from modified chiral- and aliphatic amino-alcohols, respectively, while the monometallic species **283** and **284** were based on amino-acids. All complexes were tested as catalysts in the ROP of *rac*-LA both in deuterated chloroform and in toluene at 60 °C, with a monomer to Al ratio of 50:1. Compound **275** proved inactive in the chlorinated solvent at room temperature, while moderate conversion was achieved after 66 h in toluene at 70 °C. Within the same set of complexes, bulky or electron-donating substituents had a detrimental effect on the polymerization, both in terms of conversion and iso-selectivity. In fact, while the PLA isolated in the presence of 275 displayed a P_m value of 0.7, lower values (< 0.5) were observed for the polymers obtained with **276** and **277**. The catalysts derived from the aliphatic amino-alcohols, except for **282**, exhibited higher rates than their chiral counterparts, albeit with similar isoselectivity ($P_m > 0.7$). The amino acid-based compounds were found as active as **275–278** although exhibiting higher stereoselectivity. In all cases, the polymer molecular weights were in accordance with the expected values with narrow polydispersites spanning from 1.03 to 1.08. Complexes **274–282** were found capable to promote, to a certain extent, the epimerization of *D*- or *L*-lactide of the racemic mixture of the monomer into its *meso* form prior to polymerization, as observed by ^{1}H NMR spectroscopy (appearance of a diagnostic signal at 1.70 ppm).

275 (R$_1$ = R$_2$ = ^{t}Bu)
276 (R$_1$ = H, R$_2$ = OMe)
277 (R$_1$ = Me, R$_2$ = SiPh$_3$)
278 (R$_1$ = Me, R$_2$ = SiMe$_2$^{t}Bu)

279 (n = 2)
280 (n = 3)
281 (n = 4)
282 (n = 5)

283 (R = 2-(methylthio)ethyl)
284 (R = benzyl)

Figure 42. Half-salen aluminum complexes active in the ROP of *rac*-LA [123].

With respect to tetradentate complexes, an Al-isopropoxy species supported by the racemic CF$_3$/phenoxy-diimino ligand reported by Carpentier et al. exhibited moderate activity in the ROP

of *rac*-LA [95]. The process occurred in a *living* fashion affording isotactic PLAs with good control. The same group also disclosed a series of chiral Salen-Al complexes bearing alkyl- or alkoxy ancillary ligands [124]. When tested in the ROP of *r*-LA, exogenous alcohol was required by the former, while the well-defined isopropoxy-derivatives acted as single-component catalysts. Enhanced reactivity was observed for the complexes bearing either electron-withdrawing (NO_2) or non-sterically demanding (H) substituents. High isoselectivity was generally observed in such systems.

Later, salalen-type complexes active in the ROP of lactide were studied by the group of Jones. (Figure 43) [125,126]. Upon activation with BnOH, the ethylene-bridged species **284**, **286**, **288** and **290** showed a slight isotactic bias, whereas heterotactic PLAs were isolated in the presence of **285**, **287** and **289**. The BnO-derivatives of complexes **291–299** were screened in bulk conditions with a monomer to Al ratio of 300 at 130 °C. While almost complete conversions were achieved with **296** and **298** within 2 h, the other systems required longer reaction time to allow for low- to moderate conversions. The rather broad polydispersities observed in the runs involving **292–293** and **297–298** (spanning from 1.5 to 1.7) suggested the occurrence of undesired transesterification. Concerning the polymer microstructure, **294** and **297** exhibited isotactic bias while slightly hetero-enriched PLAs were isolated in the presence of the other catalysts.

283 (R$_1$ = R$_2$ = ^{t}Bu, R$_3$ = Me)
285 (R$_1$ = Me, R$_2$ = H, R$_3$ = Me)
287 (R$_1$ = R$_2$ = H, R$_3$ = Me)
289 (R$_1$ = R$_2$ = Cl, R$_3$ = Me)

284 (R$_1$ = R$_2$ = ^{t}Bu, R$_3$ = Ph)
286 (R$_1$ = Me, R$_2$ = H, R$_3$ = Ph)
288 (R$_1$ = R$_2$ = H, R$_3$ = Ph)
290 (R$_1$ = R$_2$ = Cl, R$_3$ = Ph)

291 (R$_1$ = R$_2$ = ^{t}Bu)
293 (R$_1$ = Cl, R$_2$ = ^{t}Bu)
295 (R$_1$ = R$_2$ = H)
297 (R$_1$ = ^{t}Bu, R$_2$ = Cl)
299 (R$_1$ = Cl, R$_2$ = Cl)

292 (R$_1$ = H, R$_2$ = ^{t}Bu)
294 (R$_1$ = ^{t}Bu, R$_2$ = H)
296 (R$_1$ = Cl, R$_2$ = H)
298 (R$_1$ = H, R$_2$ = Cl)
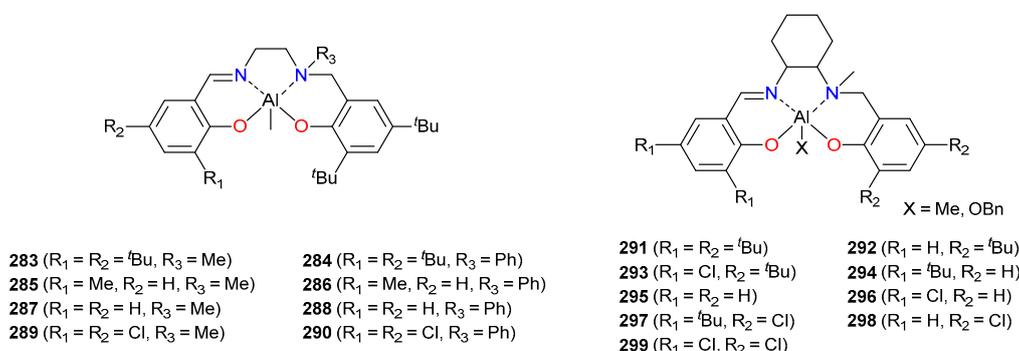
Figure 43. Salalen complexes active in the ROP of *rac*-lactide [125,126].

The polymerization was then performed in solution by employing both the well-defined BnO-derivatives as well as their parental methyl analogues activated in situ with 1 equiv. of BnOH (Table 10). The Al-Me compounds were found to be less active in all cases, aside from **294** and **297**, for which their Al-OBn congeners allowed for much higher conversions. Control was generally better than for the *solvent-free* tests, although broad polydispersity was observed in the run involving **298**-OBn (1.67). Interestingly, the polymer M_n are higher than the expected values, suggesting that in solution not all Al-centers initiate the polymerization.

Al complexes of aminopiperidine-based Salalen and half-Salalen ligands have been recently studied by Mahon, Jones et al. [127]. These species, activated by BnOH, proved active in the ROP of *r*-LA under relatively mild conditions, allowing for moderate- to high conversions and good control ($M_w/M_n < 1.1$). In terms of stereocontrol, heterotactic enrichment was generally observed. The occurrence of transesterification, albeit to a small extent, was confirmed by mass spectrometry.

Methyl- and benzyloxy Al complexes bearing salphen ligands (Figure 44) were also found active in the ROP of *rac*-lactide (Table 11) [128]. In the case of compound **300**, the active species was generated in situ upon addition of an equimolar amount of BnOH; however, the M_n of the isolated polymer was higher than the calculated value, indicating only a partial activation. On the other hand, higher conversions and narrower distributions were obtained with the BnO-derivatives **301–303**. Moreover, the observed polymer M_n were in perfect agreement with the theoretical values. Interestingly, the presence of bulky *ortho* substituents positively affected the reaction rate, albeit playing a detrimental effect on the stereoselectivity.

Table 10. ROP of *rac*-LA catalyzed by **291–299** (Me- and BnO-derivatives) [126].

Run	Catalyst	Time (Days)	Conv. (%)[a]	M_n[b]	M_w/M_n[b]	P_r[c]
1	**291**-Me	4	42	8950	1.06	0.49
2	**291**-OBn	4	26	3750	1.08	0.54
3	**292**-Me	4	71	12,200	1.07	0.65
4	**292**-OBn	4	91	19,550	1.12	0.61
5	**293**-Me	4	97	17,150	1.35	0.60
6	**293**-OBn	4	99	17,000	1.18	0.69
7	**294**-Me	4	83	7700	1.06	0.57
8	**294**-OBn	10	40	6400	1.08	0.42
9	**295**-OBn	4	96	24,600	1.12	0.56
10	**296**-OBn	4	96	19,900	1.27	0.54
11	**297**-Me	4	61	7100	1.07	0.54
12	**297**-OBn	10	49	8300	1.06	0.31
13	**298**-OBn	4	96	14,600	1.67	0.54
14	**299**-OBn	4	99	19,350	1.15	0.73

Reaction conditions: monomer: initiator ratio 100:1 (: 1 BnOH if required) solvent toluene, T = 80 °C. [a] Obtained from ^{1}H NMR analysis. [b] Determined from GPC analysis using THF as the solvent and reference to polystyrene standards. [c] Determined from the analysis of the methane region of the ^{1}H homonuclear decoupled NMR spectrum.

300

301 (R_1 = R_2 = ^tBu, R_3 = Ph, R_4 = H)
302 (R_1 = R_2 = R_3 = R_4 = ^tBu)
303 (R_1 = R_3 = Ph, R_2 = R_4 = H)
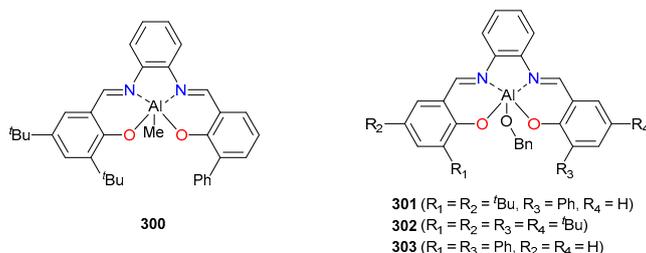
Figure 44. Unsymmetrical- and symmetric Al-salphen complexes [128].

Table 11. ROP of *rac*-lactide catalyzed by **300–303** [128].

Entry[a]	Catalyst	Time (h)	Conv. (%)[a]	M_n[b]	$M_{n(calc.)}$[c]	M_w/M_n[b]	P_i[d]
1	**300**[e]	24	75	9200	5500	1.24	78
2	**301**	12	95	6700	6900	1.12	77
3	**302**	24	85	6800	6200	1.13	79
4	**303**	12	95	6800	6900	1.12	68

Reaction conditions: 20 μmol of Al, LA/Al = 50, 2 mL of toluene solution, 110 °C. [a] Obtained from ^{1}H NMR spectroscopic analysis. [b] GPC data in THF vs. polystyrene standards, using a correcting factor of 0.58. [c] Mn(cal.) = M(LA) × ([LA]/[Al] × conversion + $M_{(BnOH)}$. [d] Determined by homo-decoupled ^{1}H NMR spectroscopy. [e] 20 μmol of BnOH was added.

Similar to phenoxyimine-based compounds, Al complexes of enolic Schiff-bases **304–310** proved interesting activity as catalysts for the isoselective ROP of *rac*-lactide (Figure 45) [129]. Due to their higher flexibility, species bearing a C3 backbone (**307** and **308**) were more active than their ethylene-bridge analogues. In turn, the presence of the germinal methyl groups on **308**, allegedly helping the cleavage of Al-OR bond during the catalysis, proved also beneficial. Compound **306** exhibited higher activity than its Me- and Ph-analogues, possibly because of the presence of the electron-withdrawing group (CF_3). Being all non-chiral catalysts, the isoselectivity was explained considering the polymerization following a chain-end control mechanism.
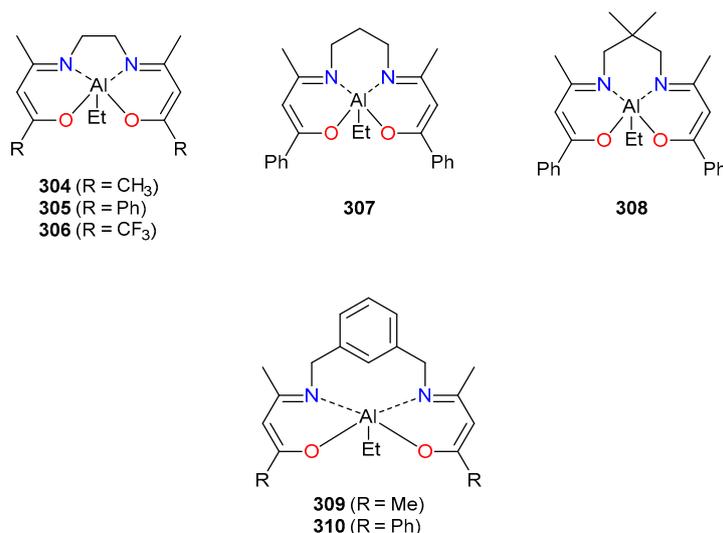
**Figure 45.** Enolic Schiff-base aluminum complexes **304–310** [129].

Recently, salen-aluminum complexes bearing cyclic β-ketoiminato ligands reported by Wang et al. proved promising activity in the ROP of larger lactones, such as ω-pentadecalactone, ambrettolide and ethylene brassylate [130]. The complexes, activated by BnOH, were able to completely convert such monomers within 3 h at 130–150 °C, with a monomer:Al ratio as high as 1000. However, poor control (M_w/M_n spanning from 1.5–1.8) was generally obtained, and the observed M_n were lower than the calculated values. Mass spectrometry analyses indicated the formation of linear macromolecules and, to a lower extent, cyclic oligomers. Finally, the complexes proved extremely active in the ROP of smaller lactones (ε-CL and lactides). Indeed, the monomers were fully converted at room temperature within 1 h, with good control and M_n matching the expected values. High isoselective bias ($P_m = 0.88$) was observed in the case of *r*-LA.

Bimetallic species **311–314**, activated with ^{i}PrOH, proved efficient catalysts in the ROP of ε-CL and *rac*-lactide (Figure 46) [131]. For both monomers, the increase of steric bulk at the *ortho* substituent resulted in a drop of activity. Nevertheless, good control (M_w/M_n ranging between 1.09 and 1.22) and M_n matching the expected values were obtained in all cases, regardless of the monomer. With respect to the polymerization of *r*-LA, all catalysts displayed isotactic bias and the stereoselectivity increased in accordance with the steric hindrance of the *ortho* substituents at the ligand. Kinetic experiments showed a first-order dependence on the monomer concentration and confirmed the occurrence of a *living* polymerization according to a coordination/insertion mechanism.
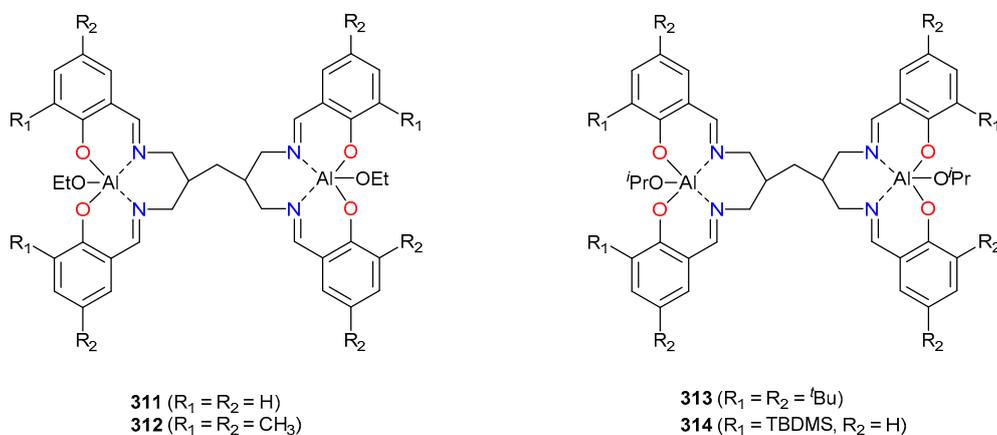
Figure 46. Bimetallic Al-salen complexes **311–314** [131].

Complexes **315–317**, activated by four equivalents of ^{i}PrOH proved capable of polymerizing *r*-LA under relatively mild conditions (Figure 47) [132]. The length of the backbone linker significantly influenced both the activity and the stereoselectivity of these species. In fact, **315** was found to be more active than its larger congeners, allowing for complete monomer conversion within 12 h, affording polymers whose molecular weights were close to the predicted values with good control and high isoselectivity (up to 82%). Longer reaction times were required in the case of **316** and **317** and the observed molecular masses were ca. half of the expected, suggesting that polymerization takes place only at one Al- center. A lower isotactic bias (56%–59%) was also observed, possibly due to the greater flexibility of the catalysts compared to **315**. The highest performances of the latter were attributed to possible cooperative effects between the two metal centers in close proximity due to the shorter backbone. The complex also proved as an efficient catalyst for the homo- and copolymerization of other cyclic esters (*L*-LA, ε-CL and β-BL), epoxides and anhydrides [133].

315 (n = 1)
316 (n = 3)
317 (n = 10)
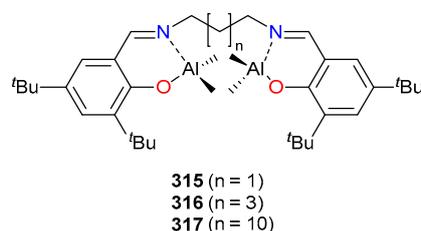
Figure 47. Bimetallic Al-complexes active in the ROP of lactones, epoxides and anhydrides [132,133].

High activity was also observed upon using compounds **318–320** as catalysts in the ROP of *rac*-lactide (Figure 48) [134]. While long reaction times were required in the absence of a co-activator, faster rates were achieved upon introducing one to four equivalents of ^{i}PrOH. Interestingly, the racemic compound **318** exhibited the same activity as its chiral version **320**; instead, complex **319** proved slightly more active. This was attributed to the effect of the electron-withdrawing Br-substituents. Good control was observed in all runs and atactic PLAs were isolated regardless of the catalyst employed (racemic or chiral). Finally, **318** proved efficient also in the polymerization of ε-CL and β-BL as well as in the copolymerization of phthalic anhydride with cyclohexene oxide and limonene oxide and in the terpolymerization of such monomers with lactide affording di-block polyesters. Moreover, in this case, the high activity of these catalysts was attributed to the cooperative effects of the two metal centers favored by the rigidity of the ligand.


rac-**318** (R = ^{t}Bu)
rac-**319** (R = Br)

R-**320** (R = ^{t}Bu)
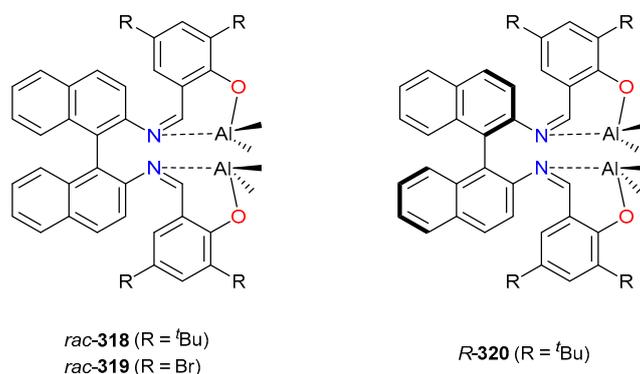
Figure 48. Bimetallic Al complexes supported by binaphthyl- Schiff-base ligands [134].

Functionalized aliphatic polyesters could be directly accessed via the ROP of "alternative" monomers, such as α-X-ε-caprolactones (X = Cl, Br, I) [135–137]. In this scenario, the polymerization of α-Cl-ε-CL, catalyzed by previously reported Al-salen complexes [103,138], has been recently studied by Dagorne et al. [139]. The reaction was tested both in solution and under *solvent-free* conditions; in both case, good conversions were obtained, although thermal degradation was observed in the latter

case. This was thought to be due to the cleavage of C-Cl bonds occurring under the forcing reaction conditions. When an excess of alcohol was introduced in the reaction mixture (*immortal* process), complete conversion and good control were achieved. Furthermore, such an approach was employed for the synthesis of *poly-α*-Cl-CL and PLA diblock co-polymers with interesting thermal features.

Reports concerning the use of macrocyclic Al systems are scant. Our group reported complexes based on the [2 + 2] macrocyclic ligands **321–322** and **323–325**, bearing ethylene- and oxo bridges, respectively (Figure 49) [109,140]. Di- and tetrametallic species were obtained upon treating these ligands with the corresponding amount of AlR$_3$ (R = Me or Et) in either toluene or hexane at reflux. Ethylene-bridged complexes were active in the ROP of ε-CL and beneficial cooperative effects were observed for multimetallic systems not displaying an aluminoxane-type bonding (Al-O-Al). While oxo-bridged complexes outperformed their ethylene-analogues in both the ROP of *r*-LA and ε-CL, no evidence of cooperative effects was observed with these systems.

321 (R = Me)
322 (R = ^{t}Bu)

323 (R = Me)
324 (R = ^{t}Bu)
325 (R = Cl)
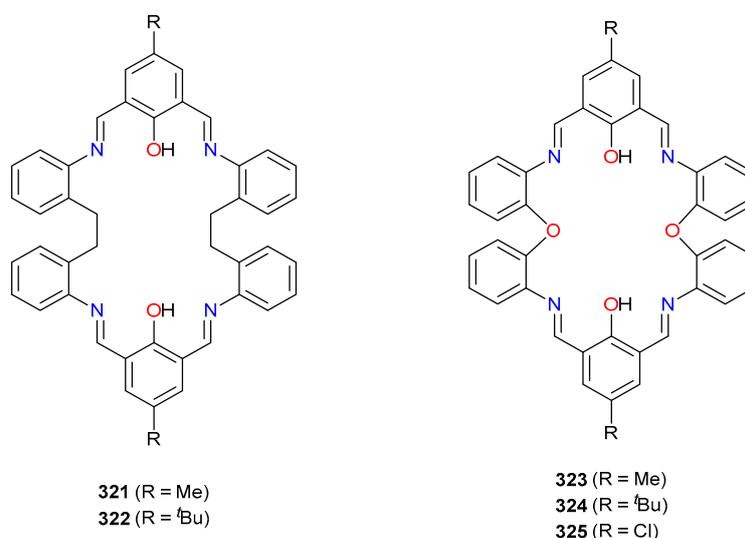
Figure 49. Ethylene- and oxo-bridged [2 + 2] macrocyclic Schiff-base ligands [109,140].

7.2. Gallium

Unlike their Al counterparts, Ga(III) catalysts for the ROP of cyclic esters remain widely unexplored. Mononuclear Salen complexes **326–331** (Figure 50) proved active in the ROP of *r*-LA, both in toluene and in bulk [141]. Regardless of the reaction conditions, the activity trend was found to be **331** ~ **326** > **330** > **328** > **329** > **327**, suggesting that less sterically demanding substituents and flexible linkers are beneficial. In terms of stereoselectivity, while isotactic PLAs were isolated with **326–328** and **330–331**, hetero-enrichment was observed with **329**. In particular, the highest isoselectivity (P_m = 0.77) was achieved with **331**, bearing electron-withdrawing Cl groups. Compound **326** also proved to be efficient in the ROP of ε-CL and in the CL/LA copolymerization. Similar Salen-based complexes exhibiting poor activity were concomitantly reported by Mehrkhodavandi et al. [142]. With respect to bimetallic complexes, species **332–334** proved able to catalyze the ROP of *r*-LA at 70–100 °C, albeit with poor stereocontrol [124].

Finally, compounds **335–338** and the salt **339** (Figure 51) were found to be capable of acting as catalysts in the ROP of 200 equiv. of *r*- or *L*-LA at 140 °C under *solvent-free* conditions [143]. Complex **335** proved the most active, requiring 9 h to fully convert the monomer, while longer reaction times were necessary in the case of **336–338** (14–20 h). In all cases, M_n values in agreement with the theoretical values and good control were achieved. Moreover, high isotactic bias was observed (P_m 0.79–0.84). On the other hand, **339** was the least performing, requiring 50 h to completely convert the monomer and affording atactic PLAs with M_n lower than the expected values, albeit with narrow polydispersities

(1.18–1.19). NMR spectroscopy and mass spectrometry analyses on low molecular weight samples revealed that the ligand is incorporated in the polymers as one of the end-groups.
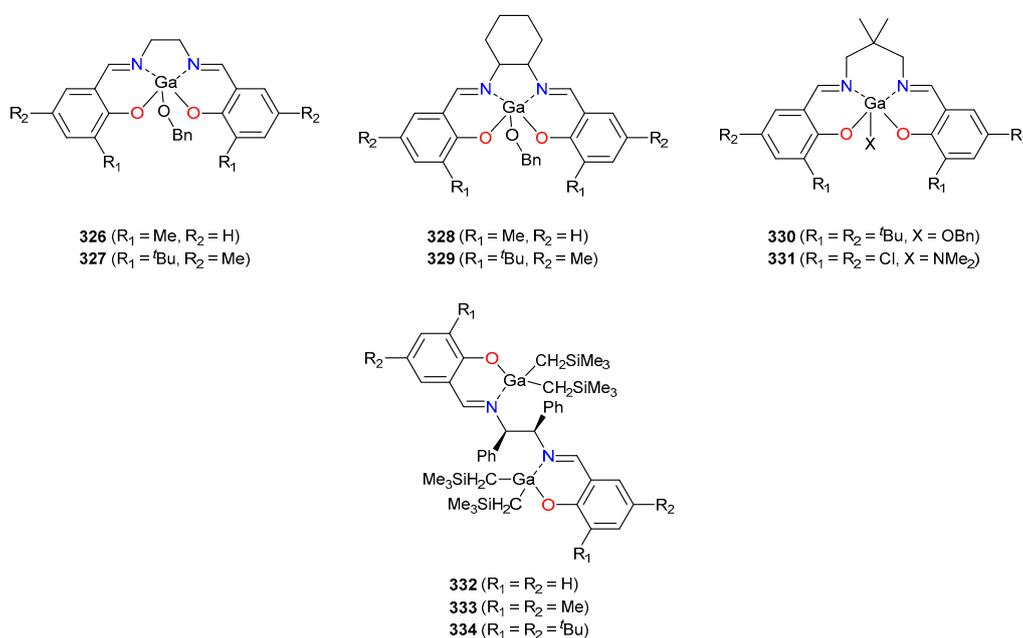

326 (R₁ = Me, R₂ = H)
327 (R₁ = *t*Bu, R₂ = Me)

328 (R₁ = Me, R₂ = H)
329 (R₁ = *t*Bu, R₂ = Me)

330 (R₁ = R₂ = *t*Bu, X = OBn)
331 (R₁ = R₂ = Cl, X = NMe₂)

332 (R₁ = R₂ = H)
333 (R₁ = R₂ = Me)
334 (R₁ = R₂ = *t*Bu)

Figure 50. Ga-based catalyst **326–334** [124,141].

335 (R = 4-MeO(C₆H₄))
336 (2,4,6-Me₃(C₆H₂))
337 (2,6-*i*Pr₂(C₆H₃))
338 (R = *t*Bu)

339
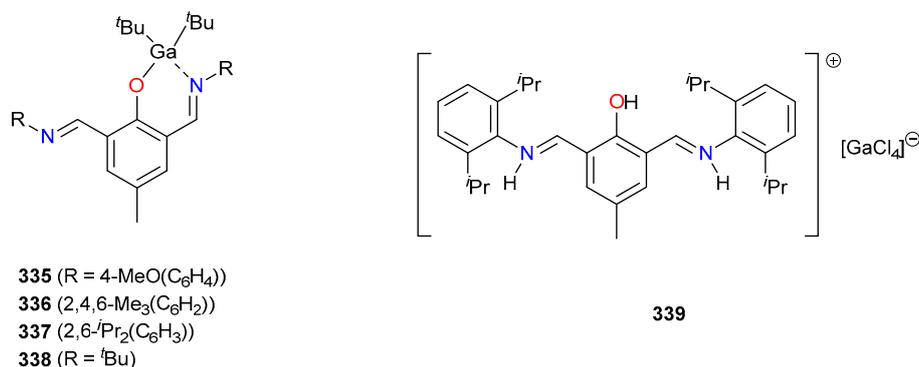
Figure 51. Bis(imino)phenoxide-based Ga complexes [143].

7.3. Indium

Recently, the use of In(III)-based systems for the production of biodegradable polymers has been drawing increasing attention [144]. Carpentier et al. disclosed Salen complexes **340–342** (Figure 52) active in the ROP of *r*-LA at 100 °C in the presence of BnOH as co-activator, affording atactic PLAs [124]. While no reaction was observed in the absence of exogenous alcohol, no significant improvement of the reaction rate was detected under *living* conditions (excess BnOH). It was proposed that the polymerization occurred according to an activated monomer mechanism, as previously observed with analogous phenoxy-imine-In complexes reported by the same group [114]. The catalytic activity followed the trend **342** >> **340** > **341**, indicating that electron-withdrawing and/or less sterically demanding substituents are beneficial. Concerning the diiminophenolate species **343–346**, behavior similar to that of their Ga-analogues was observed [143].
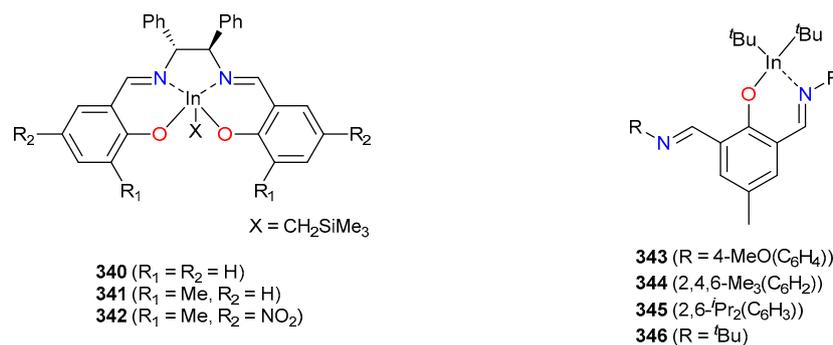
Figure 52. Indium(III) complexes **340**–**346** [124,143].

Highly isoselective Salen-In catalysts have been studied by the group of Mehrkhodavandi (Figure 53). Preliminary tests revealed that *rac*-**347** is capable of converting up to 1000 equiv. of *r*-LA at room temperature within 4 h or under 10 min, in CH_2Cl_2 or bulk, respectively [145]. Upon using the optical active version of the complex, namely (*R,R*)-**347**, high isoselectivity ($P_m = 0.77$) was obtained. The catalysts proved site-selective, exhibiting higher preference towards *L*-LA than *D*-LA; hence, upon feeding the racemic monomer, stereo-block PLLA-*b*-PDLA with high crystallinity was isolated. The effect of the steric encumbrance of the *ortho* substituents was next investigated [146]. All dinuclear complexes **348**–**351** allowed for complete *r*-LA conversion at room temperature; however, catalysts bearing bulky substituents (i.e., **349** and **350**) exhibited lower propagation rates than that of smaller congeners. On the other hand, isoselectivity increased with the steric hindrance of the *ortho* groups. The mononuclear analogues **352**–**354** showed faster rates albeit with lower stereoselectivity. In all cases, M_n values lower than the expected values were observed, suggesting the occurrence of transesterification. Finally, the same group disclosed a set of cationic hemi-Salen indium complexes bearing hemilabile thiophenyl, furfuryl or pyridyl pendant arms [147]. Amongst the series, the pyridyl-derivative proved active in the ROP of *r*-LA in the absence of a co-activator, producing high molecular weight polymers with narrow polydispersity.
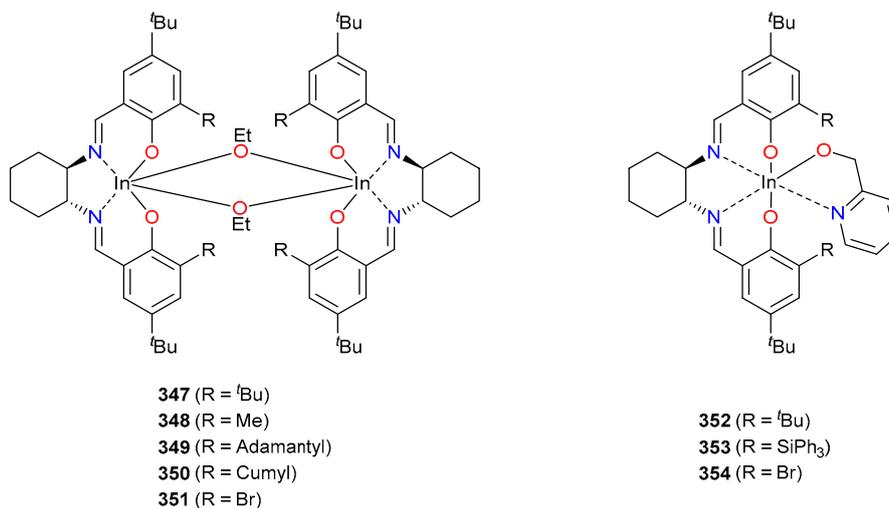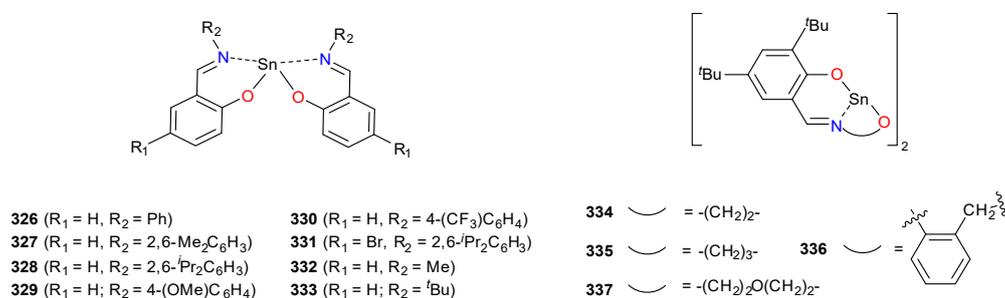

Figure 53. Salen-In catalysts for the isoselective ROP of *rac*-Lactide [145,146].

7.4. Tin

Reports describing the use of Schiff-base tin complexes as catalysts for the ROP of cyclic esters are scant. Sn(II) species bearing bi- and tridentate ligands have been recently disclosed by Phomphrai et al. and tested in the polymerization of lactide and ε-CL (Figure 54) [148,149]. Cyclic PLAs were obtained in the melt polymerization of *L*-LA with **355**–**362** in the absence of a co-activator, while linear polymers were isolated upon introducing BnOH. The activity trend was strongly influenced by the

nature of the *ortho*-substituents. Indeed, while high activity was observed with **358** and **362**, bulky and/or electron-withdrawing groups had a detrimental effect. No racemization of the stereocenter of the poly-(*L*-lactide) was observed in all cases. When *rac*-lactide was used as monomer, atactic PLAs with a slight hetero-enrichment were isolated. The tridentate compounds **363**, **364** and **365** were also found to be active in the melt polymerization of *L*-LA; no monomer conversion was observed with **365**. Cyclic polyesters were isolated in the case of **363**, while its congeners afforded linear macromolecules, albeit with poor control. This indicated that for **364** and **366**, intermolecular transesterification occurs at a faster rate than the intramolecular process that would lead to cyclic species. This was attributed to the longer alkoxy- chains (compared to shorted ethylene bridge of **363**) keeping the ester group of the growing chain away from the metal center, hence suppressing the cyclization. In the case of ε-CL, cyclic polymers were isolated with all catalysts for long reaction time (4 to 48 h) runs, while a mixture of linear- and cyclic products were observed after 2, 10 and 30 min. This suggested that the cyclization competes with the chain propagation during the early stages of the polymerization and becomes the main event throughout the process.

326 (R_1 = H, R_2 = Ph)
327 (R_1 = H, R_2 = 2,6-$Me_2C_6H_3$)
328 (R_1 = H, R_2 = 2,6-$^iPr_2C_6H_3$)
329 (R_1 = H; R_2 = 4-(OMe)C_6H_4)

330 (R_1 = H, R_2 = 4-(CF_3)C_6H_4)
331 (R_1 = Br, R_2 = 2,6-$^iPr_2C_6H_3$)
332 (R_1 = H, R_2 = Me)
333 (R_1 = H; R_2 = ^tBu)

334 = -$(CH_2)_2$-
335 = -$(CH_2)_3$-
336 =
337 = -$(CH_2)_2O(CH_2)_2$-

Figure 54. Schiff-based Sn^{II} complexes active in the ROP of ε-CL and lactides [148,149].

8. Conclusions

Schiff-base metal complexes have emerged as an interesting class of catalysts for the ROP of cyclic esters showing, in many cases, remarkable performances even at low loadings and under mild conditions. The majority of the reports herein described focused on the production of *poly*-lactides, while other monomers (i.e., ε-CL and/or δ-VL) have been considered less. This could be justified considering the extensive use of PLAs in the daily life, compared to the rather limited applications of other biodegradable polyesters. With respect to the type of ligands, the use of bi-, tri- and tetradentate Schiff-bases has been well documented, while contributions concerning multidentate and macrocyclic scaffolds are still scant (Chart 2).
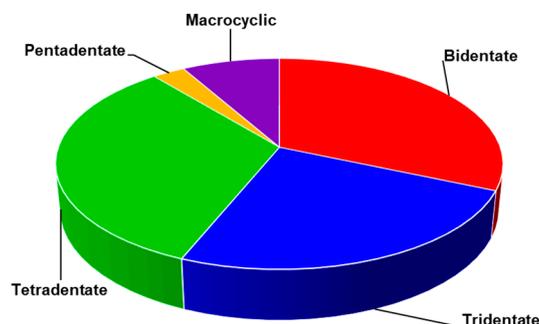
Chart 2. Breakdown of the denticity of the Schiff-base ligands reported in the review.

Given the need for cost-effect and environmentally friendly processes, the development of catalysts based on abundant and non-toxic metals is proposed as a valuable solution. In this regard, systems based on alkaline-earth metals, as well as zinc and iron are highly attractive and, as demonstrated in this review, are drawing increasing attention. Nevertheless, only limited examples [71,78,108] are capable

of affording polymers with sufficiently high M_n to be industrially relevant. The use of such benign metals in combination with multidentate or macrocyclic ligands can access new families of homo- and hetero-multinuclear species showing enhanced performances due to cooperative effects [109,140]. The design of ligand frameworks based on or inspired by biomolecules (i.e., amino acids) could also be envisioned. Indeed, this would lead to optical active catalysts with (potential) high stereoselectivity and, possibly, low toxicity [150].

Overall, the ease of synthesis of this class of ligand set, together with the facile modification, means that Schiff-bases are likely to attract continued interest as ancillary ligands in the metal-based ROP of cyclic esters.

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