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ARTICLE TYPE

Aluminum alkyl complexes: synthesis, structure, and application in ROP of cyclic esters

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Aluminum alkyl complexes have very useful applications as catalysts or reagents in small molecule transformations and as cocatalysts in olefin polymerization. This short review focuses on some recent development in the design, synthesis and structure of aluminum(III) alkyl complexes supported by various ligands bearing nitrogen, oxygen, sulfur or phosphorus atoms, and therir catalytic applications in ring-opening polymerization (ROP) of cyclic esters. The coordination chemistry of the Al metal centre and the catalytic activity changes of the complexes caused by ligand modifications are also discussed.

1. Introduction

In the earth's crust, aluminum is the most abundant metal element, and researches into the chemistry of this element have resulted in many applications with great impact on the daily life. Organoaluminium chemistry has gained great interest since Ziegler's discovery that the $AlEt_3$/transition metal combination could catalyze olefin polymerization under low pressure. The versatility of organoaluminum have given tremendous boost to the development of aluminum chemistry.[1-3] This perspective deals mainly with the chemistry of trivalent organoaluminium complexes.[4-6] The low valent aluminum chemistry is less explored owing to the low stability of oxidation state of the aluminum atom, but it has progressed significantly in the past decades and interested readers may refer to other reviews.[7-12]

In the past decades a variety of reactions and reagents involving organoaluminum(III) compounds have been developed as selective reagents for a variety of organic transformations.[5,6] In particular aluminum alkoxides and aluminum alkyl complexes have displayed good catalytic activity toward ring-opening polymerization of lactide and cyclic esters.[13-16] Several aluminum alkoxide catalysts have been successfully applied for the stereoselective ROP of *rac*-LA by Spassky et al.[17-21] In most cases, the actual initiators/catalysts in the living polymerization systems are aluminum alkoxides, which can be pre-prepared by the reaction of ligated aluminum alkyl complexes with alcohols or generated in situ by treatment of corresponding ligated aluminum alkyls with alcohols. So, the design and separation of new well-defined aluminum alkyls are crucial.

The synthesis of organoaluminum alkyl complexes can be accomplished from aluminum alkyl or aluminum halide precursors following two general routes, namely ligand exchange with protic ligands (Route I) or salt metathesis (Route II) (Scheme 1).[22-25] The surrounding ancillary ligands affect both the stability and the catalytic performance of the aluminum alkyl complexes, which enables fine-tunings of the reactivity of metal species by altering the electronic and steric properties of ligands.

In search for aluminum alkyl complexes with well-balanced robust catalytic activity and stability, various bidentate or multidentate ligands bearing *N*-, *O*-, *S*-or *P*-donor atoms have been synthesized and examined in this field. In this perspective, recent results in aluminum(III) alkyl chemistry with emphasis on their synthesis, structure, and catalytic performance in ring-opening polymerization (ROP) of cyclic esters supported by various ligands are reviewed since 2000, and related studies on catalytic mechanisms would also be discussed.[26]

Scheme 1. Synthesis of aluminum alkyl complexes

2. Aluminum alkyl complexes supported by *N*, *O* Ligands

2.1 Tetradentate

2.1.1 Aluminum alkyl complexes supported by Salen、Salan and Salalen ligands

The Salen ligands (salen is an abbreviation for N_2O_2 bis(Schiff base)-bis(phenolate)) are easily achieved by condensation of salicyl carbonyl derivatives and diamines, which have widespread utility in the chemical sciences.[27-30] The general term "salan" was introduced by Atwood to refer to saturated Salen ligands and Salalens are {ONNO}-type ligands including an imine- and an amine neutral donors and two phenolate arms. It is easy to adjust the properties of these ligands with varying substituents on the phenyl ring and diamine backbones. This versatility in ligand design enables easy modulation of the steric and electronic effects at the central metal ion. Tetradentate aluminum alkyl complexes can be prepared by treatment of such ligands with trialkyl aluminum, and X-ray structures showed the geometry at aluminum in these complexes is either distorted square pyramidal or trigonal bipyamidal.

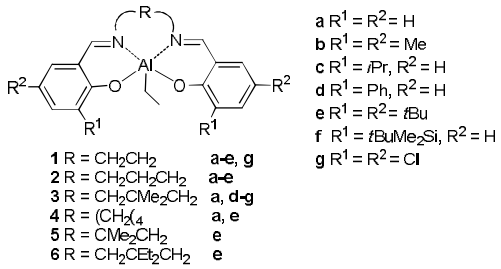


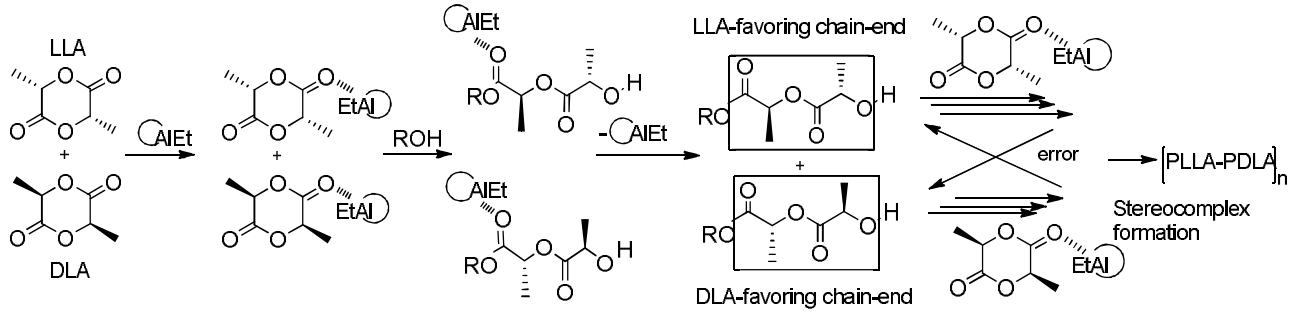
Figure 1. Aluminum alkyl complexes **1-6** supported by Salen ligands

Table 1. Polymerization of *rac*-LA Using **1d**, **2d**, **2e** and **3f**

Entry	Complex	Time (h)	Conv (%)	$M_n \times 10^{-3}$	PDI	P_m	T_m(°C)
1	**1d**	5.2	79	14.1	1.23	/	/
2	**2d**	1.3	94	20.0	1.11	0.81	170
3	**2e**	14	95	22.4	1.06	0.91	192
4	**3f**	19	93	20.0	1.09	0.97	207

Conditions: [LA]/[Al]/[BnOH] = 100 / 1 /1, toluene, 70 °C. P_m = probability of *meso* linkages.[37]

A series of aluminum ethyl complexes **1-6** (Figure 1) supported by salen ligands were systematic explored by Chen and Nomura respectively.[31-35] The living polymerization of *rac*-LA for highly isotactic poly(*rac*-LA) using these aluminum ethyl complexes **1a-e**, **2a-e** and **3d-f** as catalysts in the presence of benzyl alcohol without any chiral auxiliaries were reported by Nomura, and the catalysts were prepared in situ by mixing $AlEt_3$ with corresponding ligands, and were characterized by ^{1}H NMR. The spectroscopic data for these complexes are consistent with monomeric chelated metal-alkyl units.[31] The catalytic reactivity of **2** with more flexible propylene backbone was much higher than that of **1** with ethylene backbone (Table 1, entry 1 and 2), and the larger *t*Bu in the aromatic rings generally gave a higher isotacticity (Table 1, entry 3). The highest selectivity was obtained with *t*BuMe$_2$Si-substituted **3f**, and the P_m of the obtained poly(*rac*-LA) was 0.97 (Table 1, entry 4). Extensive studies suggested that the initiation reaction should proceed without formation of the corresponding alkoxide complexes, and an activated monomer mechanism is the most likely one for the initiation and polymerization reaction (Scheme 2).



Scheme 2. Activated monomer mechanism of stereoselective polymerization of *rac*-LA

Table 2. Polymerization of rac-LA Using **3a**, **3e**, **3g** and **1g**

Entry	Complex	M/I	Time (h)	Conv (%)	$M_n \times 10^{-3}$	PDI	P_m	T_m(°C)
1	**1g**	57.2	14	94.3	24.3	1.49	0.70	/
2	**3g**	58.1	3	96.3	20.23	1.36	0.71	/
3	**3e**	57.4	9	95.4	13.05	1.09	0.90	191.0
4	**3a**	58.9	22	96.3	13.51	1.38	0.67	/

Conditions: [Al]/[BnOH] = 1 /1, toluene, 70 °C.

Chen reported the crystal structures of **1g**, **3a**, **3e**, **3g**, **5e** and **6e**, which were all monomeric species with a five-coordinated central aluminum in the solid state. The geometries of central aluminum in **3e** and **5e** were described as a five-coordinate distorted-tetrahedral, while complexes **1g**, **3a**, **3g** and **6e** were described as a five-coordinate distorted-trigonal bipyramidal. The deviation of geometry among these Salen aluminum ethyl complexes indicated that the modification of the bridging part in the ligand leads to a dramatic change in the coordination geometry of the metal center. These aluminum complexes acted as living catalysts in the ROP of *rac*-lactide in the presence of isopropyl alcohol or BnOH, and electron-withdrawing substituents dramatically raised the polymerization rate (Table 2, entry 2). Lin and co-worker also reported a series of aluminum methyl complexes supported by a series of salen-type ligands with sterically bulky cumyl groups (−CMe$_2$Ph) at the ortho and para positions.[36]

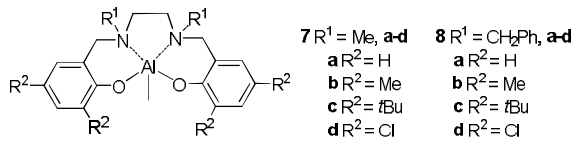


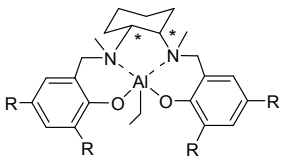
Figure 2. Aluminum alkyl complexes **7-8** supported by Salan ligands

Table 3. Polymerization of *rac*-LA Using **7a**, **8a** and **8d**

Entry	Complex	Time (h)	Conv (%)	$Mn \times 10^{-3}$	PDI	P*r*/P*m*
1	**7a**	23	97	18.92	1.04	0.32:0.68
2	**7d**	24	94	12.50	1.11	0.88:0.12
3	**8a**	21	98	21.18	1.08	0.21:0.79
4	**8d**	21	94	17.77	1.06	0.96:0.04

Conditions: [LA]/[Al]/[BnOH] = 100 / 1 /1, toluene, 70 °C. P_r and P_m are the probability of hetero- and iso-tactic enchainment determined by ^{1}H NMR spectroscopy.[37]

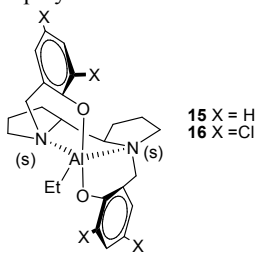
Gibson reported a new family of aluminum methyl catalysts stabilized by tetradentate phenoxyamine (salan-type) ligands,[38] and the ligands were synthesized via the stepwise condensation of the *N*,*N*-disubstituted ethylenediamine with the appropriate salicylaldehydes, following by reduction. The reactions of aminophanols with $AlMe_3$ at 110 °C overnight afforded the desired methyl complexes **7**-**8** (Figure 2), which showed quite remarkable stereocontrol in polymerization of racemic lactide in the presence of BnOH. When the phenoxide units contain halogen atom at the 3 and 5 positions, the tacticity was changed dramatically to a strong heterotactic bias (Table 3), which was the first time aluminum-based systems have been found to give heterotactic PLA. The single-crystal X-ray analysis of **7b** revealed a distorted-trigonal bipyramidal coordination geometry at the aluminum center.



9 R = H , (*R*,*R*) **12** R = H, (*rac*)
10 R = Cl, (*R*,*R*) **13** R = Cl, (*rac*)
11 R = Me, (*R*,*R*) **14** R = Me, (*rac*)

Figure 3. Aluminum alkyl complexes **9**-**14** supported by chiral Salan ligands

Salan aluminum ethyl complexes **9**-**14** (Figure 3) were prepared according to the genral Route I from the corresponding chiral salan ligands and $AlEt_3$ in toluene at 70 °C overnight.[39] Suitable single crystals of **9** and **14** were grown from saturated toluene solutions at room temperature. X-ray analysis revealed that the complexes were asymmetric with a five-coordinated central aluminium atom. The geometry of complex **9** adopts an intermediate between trigonal bipyramidal and square pyramidal. The packing modes in the unit cell of **14** showed a racemate crystallization and the metal center is in a trigonal bipyramidal geometry. In the presence of 2-propanol, the aluminium ethyl complexes acted as efficient initiators for the ROP of *rac*-LA and of *meso*-LA, and the **13**/propan-2-ol systems afforded syndiotactically biased PLAs from *meso*-LA with a Pr value of 0.73. Microstructural analysis of the resulting polymers and detailed kinetics studies indicated the coexistence of a CEM (chain-end control mechanism) and a SCM (site control mechanism) in lactide polymerization.

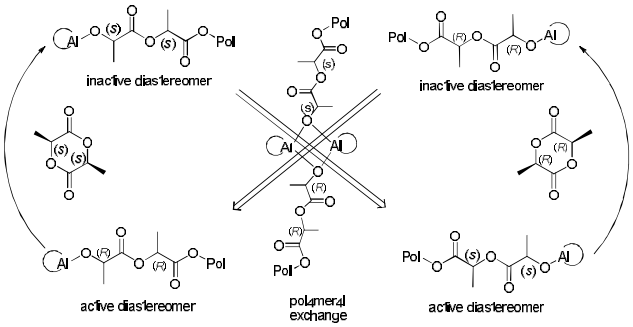


15 X = H
16 X =Cl

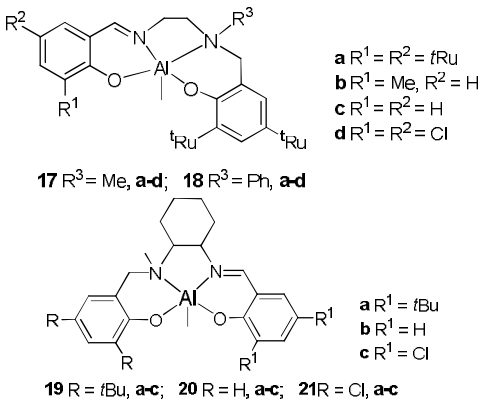
(*R*,*R*), (*S*,*S*) and (*rac*)

Figure 4 . Aluminum alkyl complexes **15**-**16** bearing chiral 2,2'−bipyrrolidine-based Salan ligands

Recently, the alkylaluminum complexes **15**-**16** (Figure 4) bearing chiral 2,2'−bipyrrolidine-based Salan ligands were reported by Kol and co-workers,[40] which showed the switch of stereochemical control from isoselectivity to hetereoselectivity in the *rac*-LA polymerization with the cocatalyst benzyl alcohol. The racemic complex **16** for the polymerization of *rac*-LA at 70 °C led to a highly heterotactic PLA with a P_r = 0.86, and lowering the polymerization temperature to 50 °C gave PLA with a $P_r \geq 0.98$! A highly heterotactic PLA was assumed to be produced by an insertion/autoinhibition/exchange mechanism (Scheme 3).



Scheme 3. Proposed mechanism for the high heteroselectivity induced by *rac*-**16**. The two salan ligand enantiomers are schematically represented as opposite chiral environments



17 R^3 = Me, **a**-**d**; **18** R^3 = Ph, **a**-**d**

a R^1 = R^2 = *t*Ru
b R^1 = Me, R^2 = H
c R^1 = R^2 = H
d R^1 = R^2 = Cl

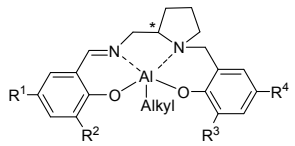
19 R = *t*Bu, **a**-**c**; **20** R = H, **a**-**c**; **21**R = Cl, **a**-**c**

a R^1 = *t*Bu
b R^1 = H
c R^1 = Cl

Figure 5. Aluminum alkyl complexes **17**-**21** supported by Salalen ligands

Jones synthesized a novel family of salalen aluminum methyl complexes **17**-**21** (Figure 5), which were experimentally and theoretically studied for the ROP of *rac*-LA.[41-43] Complexes **17b**, **17d**, **18a**, **18d** and **19a** were characterized by single crystal X-ray diffraction, and the geometries of central aluminum of those complexes are described as a five-coordinate highly distorted-trigonal bipyramidal. Complexes **17**-**18** were shown to be active for the polymerization of *rac*-LA with narrow molecular weight (PDI = 1.04 at the best) in the presence of 1 equiv. of BnOH to generate the alkoxide *in situ*, and the complexes **18** with N-Ph substituent have a slight isotactic bias in the polymerization. Complexes **19a** gave lower conversions than **19b** in the ROP of *rac*-lactide, which is presumably due to increased steric hindrance against the approach of the lactide to the metal centre. It is noteworthy that the alkoxide generated *in situ* from the aluminum alkyl complexes **20a** and **21a** gave a higher conversion

than the corresponding alkoxide complexes in the ROP of *rac*-lactide, and an activated monomer mechanism was suggested. It was found that chloro groups on the imine moiety increased the degree of heterotactic enchainment in the polymer.

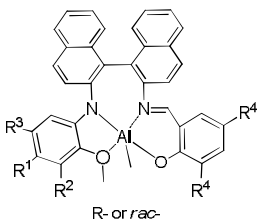


(*S*)-**22** $R^1 = R^2$ = Cl; R^3 = Ad; R^4 = Me; Alkyl = Me
(*R*)-**23** $R^1 = R^2$ = *t*Bu; $R^3 = R^4$ = Cl; Alkyl = Et

Figure 6. Aluminum alkyl complexes **22-23** supported by chiral salalen ligands

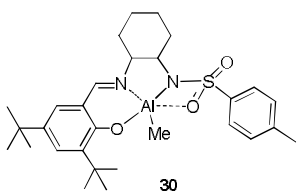
Recently, Lamberti and co-workers synthesized aluminum alkyl complexes **22** and **23** (Figure 6) supported by aminomethylpyrrolidine based chiral salalen ligands.[44] The corresponding alkoxide complexes were prepared either by treatment of the aluminum alkyls with equimolar amounts of 2-propanol or by direct reaction of the corresponding ligand precursors with $Al(O^iPr)_3$, which formed as single diastereomers. These complexes catalyzed the ROP of *rac*-LA, leading to a new polymeric microstructure, namely the gradient isotactic multiblock PLA. They demonstrated that both SCM and CEM mechanisms are active in the polymerization reactions catalyzed by these aluminum complexes. Single crystals of **23** were crystallized from pentane at −35 °C. The aluminum adopts a geometry intermediate between trigonal bipyramidal (with the imine-side phenolate O-donor and the pyrrolidine N-donor occupying the apical positions) and square pyramidal (with the ethyl group at the axial vertex), and the geometry is retained in solution. The PLA obtained by using catalyst **22** in the presence of 2-propanol, has a narrow molecular weight distribution (PDI = 1.09).

2.1.2 Aluminum alkyl complexes supported by hemisalen ligands



R- or *rac*-

24 $R^1 = R^2 = R^3 = R^4$ = H
25 $R^1 = R^2 = R^3$ = H, R^4 = *t*Bu
26 $R^1 = R^2 = R^3$ = H, R^4 = Cl
27 R^1 = F, $R^2 = R^3 = R^4$ = H
28 R^1 = H, $R^2 = R^3$ = *t*Bu, R^4 = Cl
29 R^1 = F, $R^2 = R^3$ = H, R^4 = Cl

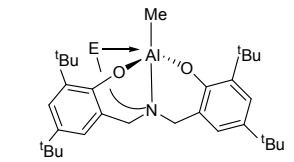


30

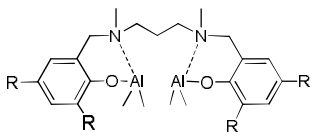
Figure 7. Aluminum alkyl complexes **24-30** supported by hemisalen ligands

A series of aluminum methyl complexes **24-30** (Figure 7) supported by asymmetric O,N,N,O-tetradentate hemisalen ligands were synthesized.[45,46] Crystals of (*S*)-**26** and (*rac*)-**27** suitable for an X-ray structure determination were obtained from a mixed THF and hexane solution, and the structural analysis revealed that complexes (*S*)-**26** and (*rac*)-**27** are mononuclear complexes with aluminum atoms in distorted square pyramidal environments. These aluminum methyl complexes serve as single-site, living catalysts for the polymerization of L-LA and *rac*-LA in the presence of the cocatalyst 2-propanol at 70 °C. The activities of these complexes decreased as the substituent size on the benzene ring increased, while electron-withdrawing substituents increased the polymerization rate. Microstructural analysis of the polymers catalyzed by these complexes reveals that the asymmetric O,N,N,O-tetradentate ligands have the ability to control the tacticity of the polymer, and the end group analysis of the oligomers of L-LA indicated the actual initiator is the isopropoxyl aluminum species. The aluminum methyl complex **30** can be obtained by the reaction of sulfonamide/Shiff base ligand with $AlMe_3$ in toluene at 100 °C for 36 h in 89% yield, and the geometry around aluminum is a distorted square pyramid with methyl group at the axial positions and the nitrogen and oxygen atoms at the basal positions. The corresponding aluminum benzyloxy derivative was an efficient initiator for the ROP lactide under controlled manner with isotactic selectivity.

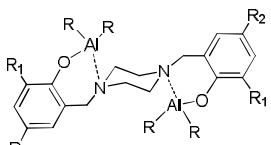
2.1.3 Aluminum alkyl complexes supported by amine phenolate ligands



31 E = CH_2Py
32 E = $CH_2CH_2NMe_2$



33 R = Br (a(; *t*Bu (b(cumyl (c(



34 R =Me a-c
35 R = Et a-c

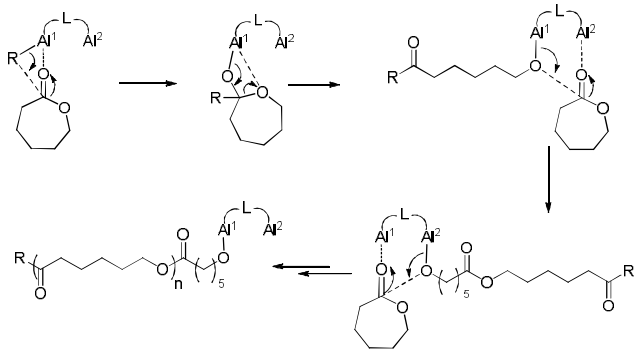
a $R^1 = R^2$ = Me
b R^1 = *t*Bu, R^2 = Me
c $R^1 = R^2$ = *t*Bu

Figure 8. Aluminum alkyl complexes **31-35** supported by amine phenolate ligands and quinolinolato ligands

Amine bis(phenolate) ligand precursors are known for several decades, and can be easily prepared by a modified Mannich reaction. Treatment of amine bis(phenolate) ligand precursors with 1.1 molar equivalent of $AlMe_3$ in toluene afforded the aluminium methyl complexes **31-32** (Figure 8).[47] Suitable crystals of **31** for structural determination were obtained from a mixed toluene and hexane solution. The structural analysis confirmed a symmetric monomeric form with five-coordinated aluminium center and the central Al atom adopts distorted trigonal bipyramidal geometry. Further reactions of **31** or **32** with one equivalent of benzyl alcohol afforded the corresponding

benzyloxy derivatives, and which were found to catalyze the polymerization of ε-caprolactone with very narrow PDIs in a living manner at 25 °C or 50 °C in toluene. The end group analysis of a polymer product indicated the ring cleavage of a lactone occurred between the acyl-oxygen bond to form an aluminium alkoxide intermediate, which further reacted with excess lactones to form polyesters.

Binuclear aluminum complexes have been a focus of current research in the polymerization of lactide and cyclic esters. Ma and Yao reported a series of dinuclear aluminum dialkyl complexes **33-35** supported by bridged phenoxy-amine ligands (Figure 8).[48-51] The dinuclear complex **33** exhibited high degree of control towards the copolymerization of *L*-LA and ε-CL in the presence of 2-propanol, producing blocky, gradient, tapered and random copolymers. Single crystals suitable for X-ray diffraction determination were successfully obtained for complexes **33b** and **33c**. The dinuclear aluminum complexes **34-35** showed higher activities in initiating the ROP of ε-CL in the absence of alcohols under mild conditions, and a plausible mechanism was proposed highlighting the cooperation between the two Al centers in dinuclear complexes supported by piperazidine-bridged bis(phenolato) ligands (Scheme 4). The polymerization accelerated dramatically in the presence of BnOH using these dinuclaer aluminum complexes as the initiators. The end-group analysis of the oligomers using **35a** as initiator showed that the benzyloxy group formed *in situ* is an active center for initiating the polymerization, and the monitoring of this process by ^{1}H NMR indicated that the nucleophilic attack onto a monomer was favored by the aryloxo group rather than by the ethyl group in the absence of BnOH. The solid state structures of **34a-c**, **35a** have been determined by X-ray diffraction analysis. Recently, Wang et al also reported two classes of dinuclear aluminum complexes supported by amino- or imino-phenolate ligands,[52] which are efficient catalysts for the ROP of *rac*-lactide in the presence of BnOH.



Scheme 4. Plausible mechanism for the polymerization of ε-CL initiated by bimetallic Al complexes

2.1.4 Aluminum complexes supported by enolic Schiff base and fluorinated alkoxy-imino ligands

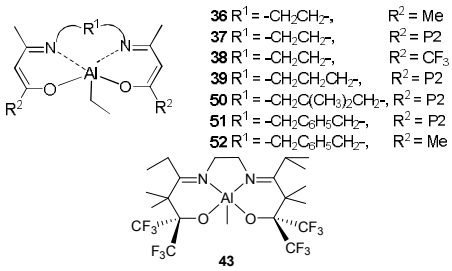


Figure 9. Aluminum alkyl complexes **36-43** supported by enolic Schiff base and fluorinated alkoxy-imino ligands

A series of enolic Schiff base aluminum (III) ethyl complexes **36-42** (Figure 9) were prepared by treatment of corresponding linked β-ketimine ligands with triethyl aluminum at 80 °C for 12 h in toluene.[53, 54] Crystals of **37**, **39** and **40** suitable for X-ray diffraction were grown from a mixture of toluene and pentane at -10 °C. X-ray diffraction data showed that these complexes were five-coordinated monomers, and the monomric forms were retained in solution. The coordination geometries of **37** are square pyramidal, while the coordination geometries of **39**, **40** are trigonal bipyramidal. The complexes **39**, **40** having higher backbone flexibility showed higher stereoselectivity in the ROP of *rac*-lactide (P_m = 0.76 and 0.78 respectively). The higher backbone flexibility was suitable for the metal coordination sphere to open the inserting monomer ring. Thus, the dimethyl-substituted complex **40** displayed the highest activity in the presence of 2-propanol. Carpentier and co-workers developed new families of fluorinated alkoxy-imino ligand, and the corresponding tetradentate aluminum methyl complexe **43** were prepared (Figure 9).[55-57]

2.2 Tridentate

Aluminum methyl complexes supported by ligands bearing *ONO* or *NNO* moiety.

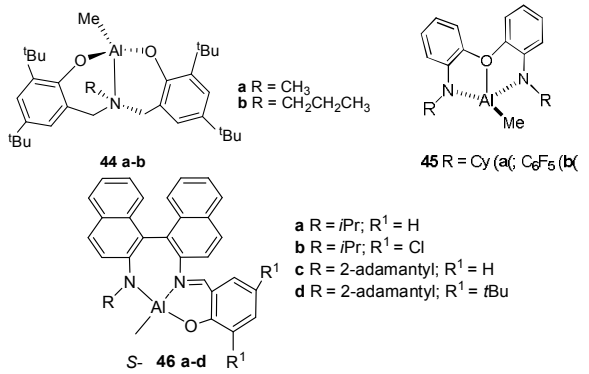


Figure 10. Aluminum monoalkyl complexes **44-46** supported by ligands bearing *ONO* or *NNO*

Monoalkyl aluminum complexes **44-46** (Figure 10) bearing the bulky substituents on the ligands were synthesized by reactions of $AlMe_3$ with the corresponding proligands.[58-60] The aluminum methyl complexes **44a-b** can catalyze the polymerization of ε-caprolactone more actively than complexes **31**, **32** supported by pendant amine bis(phenolate) in the presence of benzyl alcohol.

The catalytic performances of complexes **45a** and **45b** as ROP initiators of *rac*-lactide (*rac*-LA), ε-caprolactone (ε-CL), and trimethylene carbonate (TMC) were estimated in the presence of BnOH acting as an effective chain transfer agent. The more Lewis acidic aluminum methyl **45b** displayed significantly better ROP activity than its analogue **45a**. Crystals of **44a-b** and **45a** for structural determination were obtained from a concentrated hexane solution. Their structures exhibited a monomeric forms with four-coordinate aluminum center and the coordination geometry around the Al center can be described as a distorted tetrahedral.

Recently, a series of aluminum methyl complexes **46a-d** bearing tridentate *N,N,O*-type binaphthyl-Schiff-base (hemi-salen) ligands were prepared.[60] These aluminum complexes were employed for ring-opening polymerization of L-lactide and *rac*-lactide in the presense of isopropanol. The end-group analysis of the oligo(lactide) revealed that the actual initiator of the polymerization was the aluminum alkoxide propagating species.

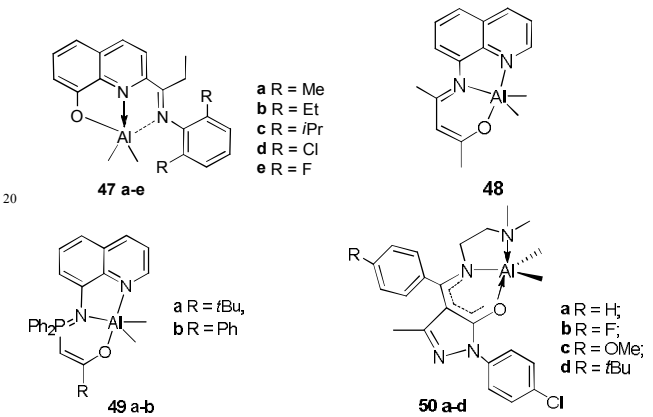


Figure 11. Aluminum dialkyl complexes **47-50** supported by ligands bearing *NNO*

The aluminum methyl complexes **47a-e** (Figure 11) bearing 2-(arylimino)quinolin-8-olates were reported by Sun et al.[61] Single crystals of complexes **47a** and **47c** were obtained from a mixed toluene and *n*-heptane solution at -30 °C. The geometry around the Al metal center can be described as a distorted trigonal pyramid. In the presence of BnOH, the aluminum complexes **47a-e** can efficiently initiate the ROP of ε-CL, while the polymerization did not take place without BnOH. The formation of Al–alkoxide species can act as the initiator *via* a coordination insertion mechanism. Wang designed quinoline-based N,N,O-tridentate ligands involving iminophosphoranyl moiety or ketiminate moiety. The aluminum methyl complexes **48-49** (Figure 8) supported by these ligands were synthesized.[62] Complexes **48** and **49b** were characterized by single crystal X-ray diffraction and the coordination geometry of the aluminum center can be best described as a distorted trigonal bipyramid. They are active catalysts for the ROP of ε-CL in the presence of BnOH, giving polymers with good control over the molecular weight and distribution.

The complexes **50a-d** (Figure 11) are also active catalysts for ring-opening polymerization of L-lactide (L-LA) in the presence of benzyl alcohol.[63] The complex **49b** performed efficiently not only in a "living" fashion but also in an "immortal" manner,[64] giving polymers with the expected molecular weights and narrow PDIs.

2.3 Bidentate

2.3.1 Aluminum alkyl complexes supported by phenoxy-imine and phenoxy-amine ligands

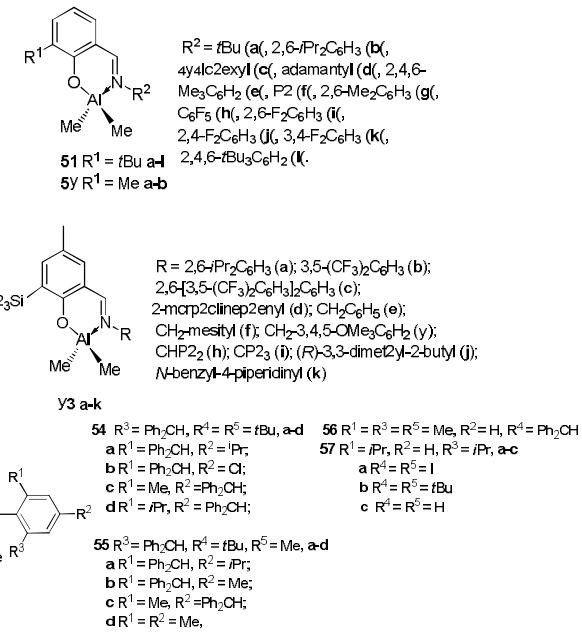
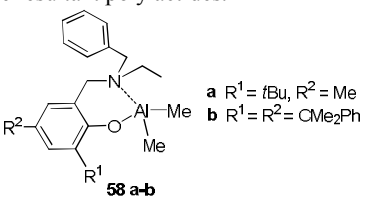


Figure 12. Aluminum alkyl complexes **51-57** supported by phenoxy-imine ligands

In 2001, Gibson and co-workers reported the synthesis of a series of aluminum methyl complexes and their conversion to the corresponding THF-coordinated monoalkylaluminum cations with $B(C_6F_5)_3$ supported by phenoxy-imine ligands.[65] Subsequently, it was reported that the *in suit* mixed catalyst systems consisting of $AlEt_3$ and 2.0 equiv. of phenoxy-imine derivatives showed good catalytic activity for ROP of ε-CL in the presence of BnOH at 25 °C.[66] However, no studies concerning the catalytically active species and isolation of the aluminum alkyl complexes were made. Nomura and co-worker isolated a series of monomeric dialkyl aluminum complexes **51-52** (Figure 12) supported by phenoxy-imine ligand, and the ring-opening polymerization of ε-CL or δ-valerolactone (VL) or *rac*-lactide (LA) using these aluminum alkyl complexes in the presence of *n*BuOH or BnOH were investigated.[67-71] The polymerization did not take place in the absence of alcohols, suggesting that the polymerization may be initiated by Al-alkoxide *via* a coordination insertion mechanism. Systematic studies demonstrated that the auxiliary ligands might significantly influence polymerization behavior of these catalysts, and the imino substituent (R^2) rather than the aryloxo substituent (R^1) strongly affected the catalytic activity in the ROP. The catalysts bearing fluorinated aromatic substituents were found to effectively polymerize *rac*-lactide at 80 °C and ε-CL at 50 °C. The structures of **51a-h** and **52a-b** were determined by X-ray crystallography, and these complexes hold a distorted tetrahedral geometry around Al.

Recently, the aluminum dialkyls **53-57** stabilized by a series of bulky phenoxy-imine ligands were synthesized (Figure 12).[72,73] The distorted tetrahedral geometry of complexes **53k**, **54a**, **55b** and **55d** were confirmed by single crystal analysis. These complexes exhibited high activities toward the ROP of *rac*-lactide at 100 °C in combination with an alcohol (*i*PrOH or BnOH) as co-initiator, and the nature of the ligands significantly affected the observed catalytic activities of the catalysts and the properties of the resultant polylactides.



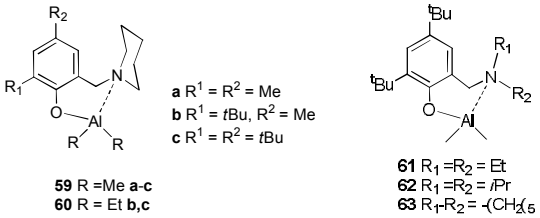
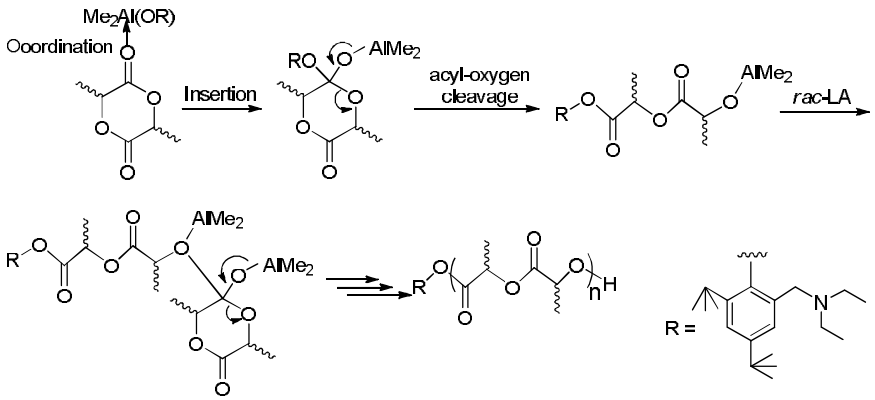


Figure 13. Dialkyl aluminum complexes **58-63** supported by amine phenolate ligands

A series of dimethyl aluminum complexes **58-63** containing aminophenolate ligands were synthesized by the reactions of $Al(alkyl)_3$ with the ligands in 1:1 stoichiometric ratio (Figure 13).[49-50,74] The catalytic activities of complexes **61-63** towards the ring opening polymerization (ROP) of *rac*-LA and L-LA were examined, and the heterotactic enrichment (P_r = 0.72-0.74) in the PLA obtained from *rac*-LA were achieved. The MALDI-TOF mass and ^{1}H NMR spectra of low oligomers showed that the aminophenoxide ligand initiates the ROP (Scheme 5), which was supported by DFT studies on the molecular geometries of all these complexes.



Scheme 5. Proposed mechanism for the ring opening polymerization of *rac*-LA using **61**.

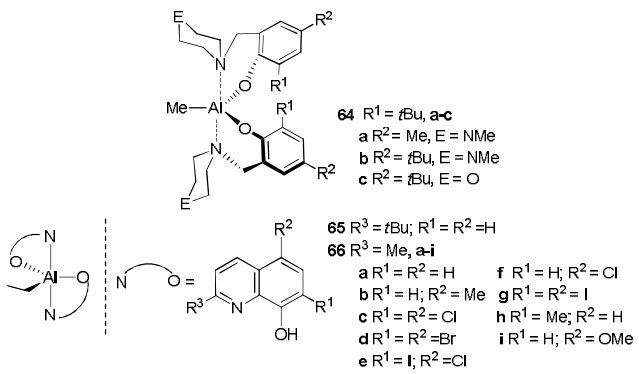
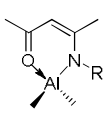


Figure 14. Monoalkyl aluminum complexes **64-66** supported by amine phenolate ligands and quinolinolato ligands

Reactions of $AlMe_3$ with 2 equiv. of monoanionic piperazinyl- or morpholinyl-amine-phenolate ligands gave the aluminum alkyl complexes **64a-c** (Figure 14).[75] The geometries of these complexes are slightly distorted from trigonal bipyramidal as revealed by single-crystal X-ray diffraction analysis. The complexes exhibited efficient catalytic activity in the polymerization of ε-CL in the presence of BnOH, while lower catalytic activity was observed in the absence of BnOH. Williams reported the synthesis of a series of bis(8-quinolinolato) aluminum ethyl complexes **65-66** (Figure 11).[76] Crystals of complexes **66e** and **66f** suitable for X-ray diffraction experiments were grown from toluene and pentane, respectively. The structures of the two complexes are closely related, and both crystallized as racemic mixtures. The complexes **66a-i** were active initiators for *rac*-lactide polymerizations in the presence of ^{i}PrOH. However, the polymerization proceeded very slow, with full conversion being achieved after 135 h at 75 °C (1/100 loading of initiator/lactide). The complex **65** with *tert*-butyl substituent at the R^3 position showed the best catalytic activity.

2.3.2 Aluminum alkyl complexes supported by ketimine ligands

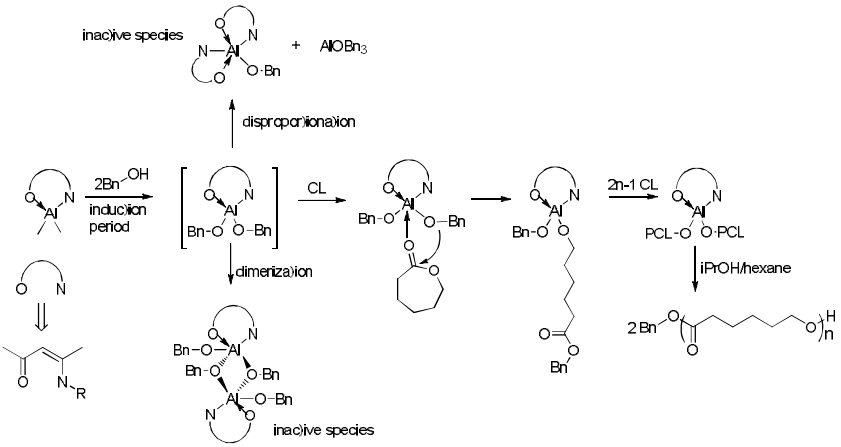


67 a-t

R = benzyl (**a**); CH_2(2-pyridyl) (**b**); $CH_2CH_2NMe_2$ (**c**); CH_2(2-THF)(**d**); C_6H_5 (**e**); 4-$OMeC_6H_4$(**f**); 2-FC_6H_4 (**g**); 4-FC_6H_4 (**h**); 4-ClC_6H_4 (**i**); 4-$NO_2C_6H_4$ (**j**); C_6F_5 (2); 2,4,6-$Cl_3C_6H_2$ (**l**); 2,4,6-$Br_3C_6H_2$ (**m**); 2,4,6-$Me_3C_6H_2$ (**n**); 2,6-*i*$Pr_2C_6H_3$; (**o**); 2-*i*PrC_6H_4 (**p**); 2,6-$Me_2C_6H_3$ (**q**); 2,6-$Cl_2C_6H_3$ (**r**); 4-*i*PrC_6H_4 (**s**); 2-$OMeC_6H_4$ (**t**)

Figure 15. Aluminum alkyl complexes **67a-t** supported by ketimine ligand

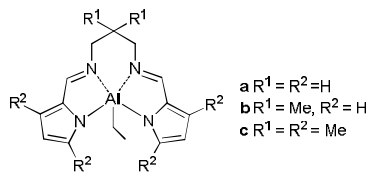
A series of aluminum methyl complexes **67a-t** (Figure 15) supported by varied ketimine ligands were prepared.[77-79] The catalytic activity for ROP of ε-CL using complexes **67a-p** as pre-catalysts were reported, and the plaussible mechanisms were reported (Scheme 6). The aluminum complexes bearing ketiminato ligands bearing sterically bulky and electron-withdrawing substituents showed greater catalytic reactivity as indicated by kinetic studies.



Scheme 6. Possible mechanisms underlying polymerization by aluminum complexes supported by ketimine ligand

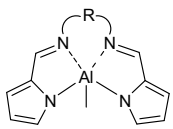
3. Aluminum alkyl complexes supported by *N*, *N* ligands

3.1 Tetradentate



a $R^1 = R^2 = H$
b R^1 = Me, R^2 = H
c $R^1 = R^2$ = Me

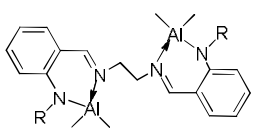
68 a-c



a R = $-CH_2CH_2-$
b R = $-CH_2CH_2CH_2-$
c R = $-CH_2CMe_2CH_2-$
d R = $-C_6H_4CH_2-$
e R = $-CH_2(CH_2)_2CH_2-$
f R = $-C_6H_4-$
g R = -*rac*-$C_6H_{10}-$

69 a-g

Figure 16. Aluminum alkyl complexes **68-69** supported by pyrrolyl ligands



70 R = 2,6-$Me_2C_6H_3$ (**a**); 2,6-*i*$Pr_2C_6H_3$ (**b**)

Figure 17. Aluminum alkyl complexes **70** supported by bridged anilido-aldimine ligands

The aluminum alkyl complexes **68-69** (Figure 16) based on a bis(pyrrolide) Schiff base ligands were prepared and characterized.[80, 81] The monomeric structure of complexes **68a-c** with a five-coordinated aluminum center were determined by NMR analysis, which acted as catalysts for the polymerization of (*S*,*S*)-LA to isotactic PLA, *rac*-LA to predominant isotactic PLA, and *meso*-LA to atactic PLA in the presence of 2-propanol as initiator. The ^{1}H NMR spectrum of PLA showed that the aluminum isopropoxides were the actual active species, and the single-site isopropoxide derivative of **68b** exhibits a much higher activity compared with the *in situ* formed aluminum isopropoxide from **68b**/2-propanol in *rac*-LA polymerization. However, the effect of catalyst architecture on the stereocontroling power of this initiator system remains elusive. Recently, Hormnirun and co-workers reported the catalytic performance of aluminum methyl complexes supported by this kind of ligands with a wide range of backbone linkers for *rac*-lactide and L-LA polymerizations. Density functional theory (DFT) study was also performed on the correlation between the structure of backbone linkers and the polymerization activity and the stereoselectivity. The molecular structure of **69c** features a monomeric form with a five-coordinate aluminum center in a geometry best described as distorted square-based pyramidal.

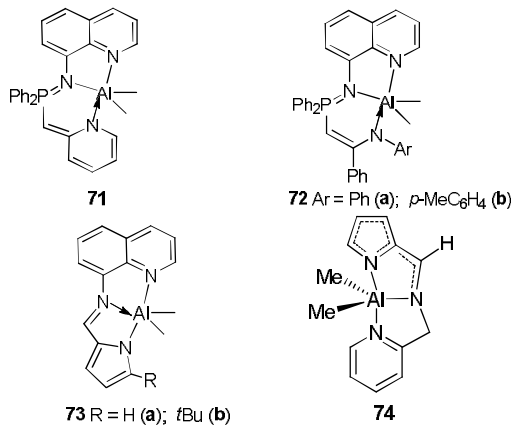
The bimetallic complexes **70a-b** (Figure 17) supported by bridged anilido-aldimine ligands showed good activity for the ROP of ε-CL in the presence of BnOH,[82] and no reaction took place in the absence of BnOH (Table 4, entries 1-2). The effect of the amount of BnOH was tested and it was found that the highest catalytic activity can be obtained with an Al : BnOH molar ratio of 2 : 1 for complex **70a** (Table 4, entries 3-5), and BnOH acts both as a chain initiator and a chain transfer reagent in the polymerization process.

Table 4. ROP of ε-CL initiated by complexes **70 a-b**

Entry	Cat	BnOH : M : CL	*t*	Yield (%)	$M_n \times 10^{-3}$	PDI
1	**70a**	0 : 2 : 100	24 h	0	-	-
2	**70b**	0 : 2 : 100	24 h	0	-	-
3	**70a**	4 : 2 : 100	1.5 h	89.0	7.3	1.12
4	**70a**	2 : 2 : 100	20 min	91.5	13.8	1.26
5	**70a**	1 : 2 : 100	10 min	96.5	19.7	1.53

Conditions: [Al] = 0.19 mM, [CL] = 3.0 M in toluene, 70 °C.

3.2 Tridentate

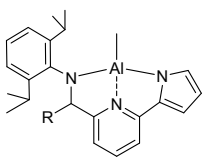


71 **72** Ar = Ph (**a**); *p*-MeC$_6$H$_4$ (**b**)

73 R = H (**a**); *t*Bu (**b**) **74**

Figure 18. Aluminum alkyl complexes **71-73** supported by quinoline-based ligands or pyrrolyl ligands

The aluminum alkyl complexes **71-74** (Figure 18) supported by quinoline-based or pyrrolyl N,N,N-chelate ligands were synthesized and characterized.[83-85] The molecular structures of complexes **71**, **72b**, and **74** were determined by single-crystal X-ray diffraction techniques, and the skeletal structure of these complexes are similar to a distorted trigonal-bipyramidal geometry. In the presence of benzyl alcohol, the aluminum complexes **71-72** are active catalysts in the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL), leading to polymers with good molecular weight control and narrow molecular weight distribution (Table entries 1-2). However, they are inactive toward the ROP of *rac*-lactide in the presence/absence of BnOH. Recently Sun et al reported the ROP of ε-CL using aluminum amidates as initiator in the presence of BnOH.[86]



75 R = H (**a**); 2-*i*PrC$_6$H$_4$ (**b**)

Figure 19 Aluminum alkyl complexes **75a-b** supported by pyrrolylpyridylamido ligand

The monomethylaluminum complexes **75a-b** pyrrolylpyridylamido as dianionic [−NNN−] tridentate ligands (Figure 19) were synthesized and tested as initiators in the ring-opening polymerization (ROP) of ε-caprolactone, L-lactide, and D,L-lactide.[87] In the presence of 1 equiv. of alcohol, they acted as highly active initiators in the ROP of ε-CL (Table 5, entry 5) and showed moderate activity in the ROP of lactides. End-group analysis of the obtained PLA samples performed by ^{1}H NMR spectroscopy showed that the polymer chains were end-capped with an isopropyl ester and a hydroxyl group.

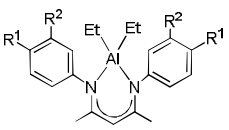
Table 5. ROP of ε-CL initiated by complexes **71-75**

Entry	Cat.	*T* (°C)	*t* (min)	Conv. (%)	$M_n \times 10^{-4}$	PDI
1	**71**	70	8	89	2.32	1.10
2	**72b**	70	6	92	3.31	1.11
3	**73a**	70	105	93	5.49	1.17
4	**74**	40	1260	96	1.24	1.54
5	**75b**	70	3	97	2.8	1.23

Conditions: [CL]/[Al]/[OH] = 200 / 1 /1 in toluene

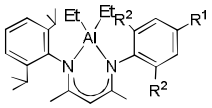
3. 3 Bidentate

3. 3. 1 Aluminum alkyl complexes supported by β-diketiminate ligand and amido phosphinimine ligands



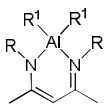
76 a-h

a $R^1 = R^2 = H$ e $R^1 = F$, $R^2 = H$
b $R^1 = CH_3$, $R^2 = H$ f $R^1 = H$, $R^2 = F$
c $R^1 = OMe$, $R^2 = H$ g $R^1 = CF_3$, $R^2 = H$
d $R^1 = Cl$, $R^2 = H$ h $R^1 = H$, $R^2 = CF_3$



77 a-e

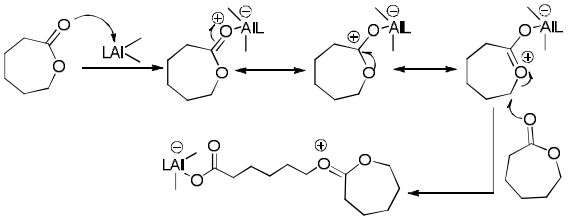
a $R^1 = R^2 = H$
b $R^1 = OMe$, $R^2 = H$
c $R^1 = Cl$, $R^2 = H$
d $R^1 = F$, $R^2 = H$
e $R^1 = H$, $R^2 = Me$



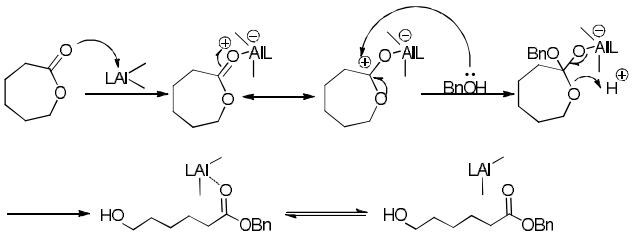
78 R^1 = Me, R = CH_3 (**a**(; *i*Pr (**b**(; *t*Bu (**c**(; Bn (**d**(; CH_2CH_2Ph (**e**(; $CHPh_2$ (**f**(
79 R^1 = Et, R = *t*Bu
80 R^1 = *i*Bu, R = *t*Bu

Figure 20. Aluminum alkyl complexes **76-80** supported by β-diketiminate ligands

Aluminum alkyl complexes **76-80** (Figure 20) bearing *N*-aryl or *N*-alkyl β-diketiminate ligand frameworks were synthesized readily *via* alkane elimination reactions.[88, 89] The aluminum ethyl complexes **76-77** initiated ROP of ε-CL with moderate activities as single component catalysts, affording polymers with broad molecular weight distributions and undefined end groups. End group analysis of the obtained oligomer sample excluded the possibility that the polymerization was initiated from the Al–alkyl bond; the Al-amido moiety was most likely the active site for initiation. The steric and electronic characteristics of the ancillary ligands exhibited a significant influence on the polymerization performance of the corresponding aluminum complexes. The complex **76h** with the *meta*-CF_3 substituted showed the highest catalytic activity.



Scheme 7. A plausible mechanism for ROP of ε-CL by **78c** in the absence of BnOH via a cationic mechanism



Scheme 8. A plausible mechanism for ROP of ε-CL by **78c** in the presence of BnOH via a monomer-activated mechanism

The complexes **78-80** were efficient initiators for ring-opening polymerization of ε-CL in the absence or in the presence of alcohol, affording narrow molecular weight distributions of the obtained polymers. In order to further elucidate the mechanism, the reaction of complex **78c** with ε-CL was monitored by ^{1}H NMR with 10:1 and 1:1 ε-CL/Al ratio in C_6D_6 at 60 °C in the absence of BnOH, which showed that the methyl groups remained attached to the Al center. In addition, no evidence was found to show that the monomer inserted into the Al-diketiminate bond. The reaction of complex **78c** with BnOH in 1:1 and 1:4 molar ratio were also monitored by ^{1}H NMR in $CDCl_3$ at room temperature, which showed the dissociation of ancillary ligand from the metal center. Similar phenomena were also found in the aluminum methyl complexes supported by triaza framework ligands.[90] A plausible cationic mechanism and a monomer-activated mechanism were proposed, respectively (Schemes 7 and 8). However these complexes were inactive toward the ROP of lactides. The complexes **77c**, **78a**, **78c** and **80** were monomeric structures as confirmed by X-ray diffraction study, and the geometry of these complexes shows a slightly distorted tetrahedron. Peng also reported dimethylaluminum complexes bearing a chiral diketiminate ligand, which exhibited activity for the ring-opening polymerization of ε-CL in the absence of an alcohol.[91]

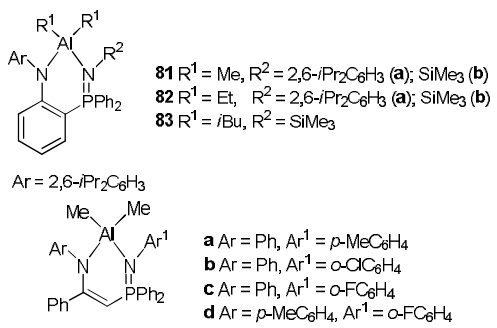


Figure 21. Aluminum alkyl complexes **81-84** supported by amido phosphinimine ligands

The complexes **81-84** were prepared by reactions of corresponding amido phosphinimine ligands with $AlMe_3$ (Figure 21).[92, 93] In the presence of BnOH, the complexes **84** were efficient catalysts for the ROP of ε-CL, and the end group analysis of the PCL showed that the polymerization may be initiated through insertion of the benzyl alkoxyl group to ε-CL followed by ring opening *via* acyl-oxygen cleavage.

3.3.2 Aluminum alkyl complexes supported by amino-amido ligands, diamido ligands and amidinate ligands

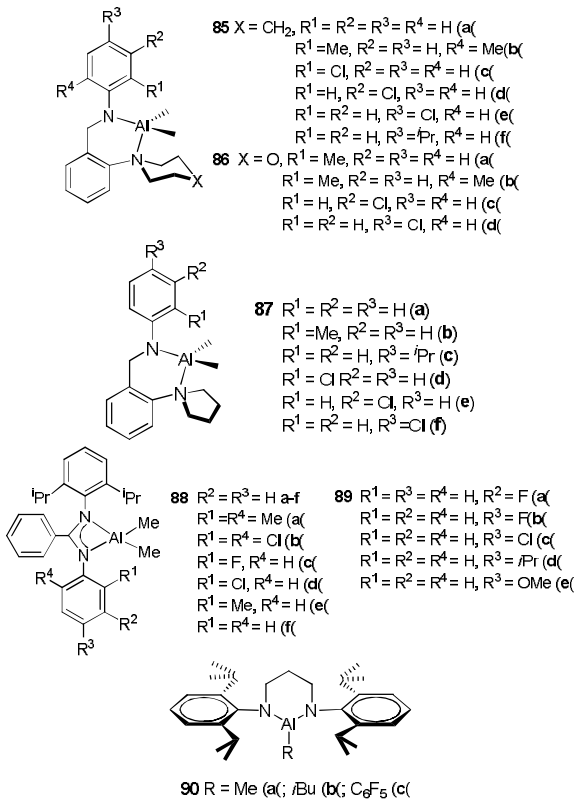
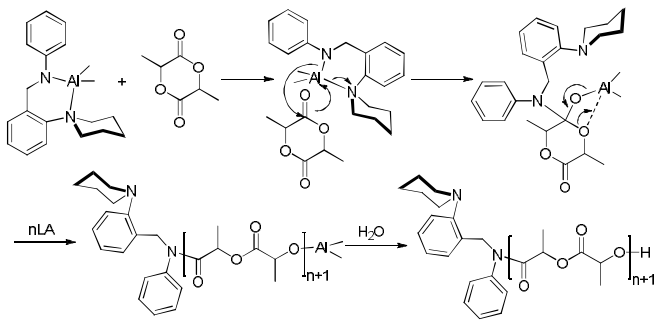


Figure 22. Aluminum alkyl complexes **85-90** supported by diamido ligands and amidinate ligands

A series of aluminum alkyl complexes **85-90** (Figure 22) supported by amino-amido ligands, diamido ligands or amidinate ligands were synthesized.[94-98] Without any co-initiator, the aluminum dimethyl complexes **85-87** could polymerize *rac*-LA or ε-CL in a well-controlled manner, producing polyesters with narrow molecular weight distributions. The results suggested that the ligands in these aluminum dimethyl complexes could act as initiating groups for the ROP of *rac*-LA or ε-CL in a living manner. Based on the end-group analysis of oligomer *via* ^{1}H NMR spectroscopy and ESI-TOF MS spectrometry, a coordination-insertion mechanism was proposed for the ROP of *rac*-LA with aluminum methyl complexes of **85-86** (Scheme 9).

The amidinate aluminium complexes **88-89** are also efficient initiators for the ROP of *rac*-lactide, and the ESI-TOF mass

spectrum of the oligomers indicated that both Al-N and Al-R initiation are possible. Complexes **90a-c** are active for ring-opening polymerization of ε-CL and cyclohexene oxide, producing high-molecular-weight polymers. The methyl group still attached to Al in complex **90a** after polymerization of ε-caprolactone, which indicated that the polymerization might be initiated by the amido group. The molecular structures determined by X-ray diffraction study indicated a bidentate chelating mode of the ligand.



Scheme 9. Proposed mechanism for lactide polymerization initiated by complex **85a**.

4. Aluminum alkyl complexes supported by other ligands bearing *S* or *P*-donor atoms

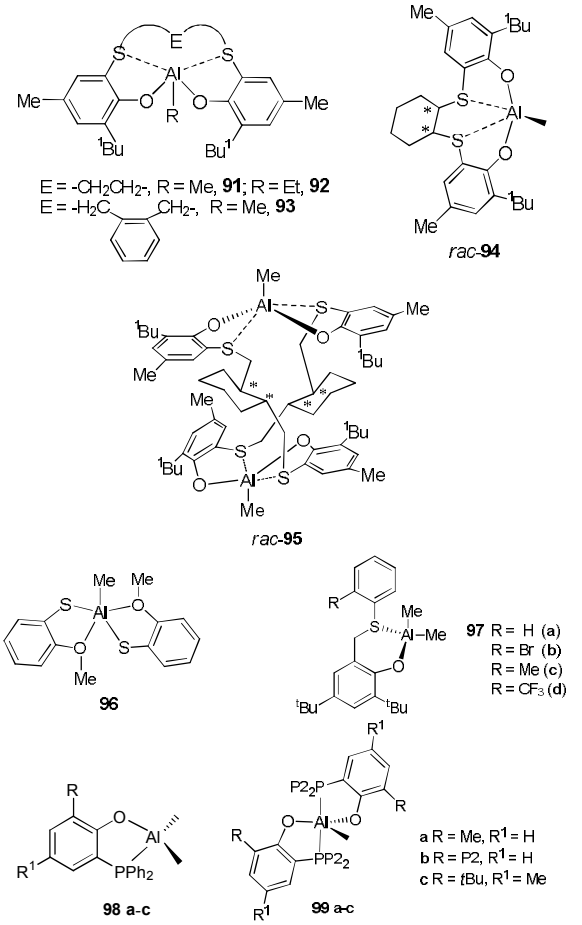


Figure 23. Aluminum alkyl complexes **91-99** supported by ligands bearing *S* or *P*-donor atoms

The aluminum methyl complexes **91-99** (Figure 23) supported by phenolate ligands with softer donor atoms (*S* or *P*) were prepared.[99-103] Okuda reported aluminum complexes **91-95** containing dianionic tetradentate OSSO-type ligands, which acted as efficient initiators for the *living* polymerization of *rac*-lactide in the presence of isopropyl alcohol. The modification of the linker in the ligand led to a change in the coordination geometry of the metal center. Reaction of $AlMe_3$ with the tetradentate (OSSO)-type bis(phenol) ligands in pentane gave the aluminum complexes *rac*-**94** and *rac*-**95**. The complex *rac*-**95** bearing bis(phenolato) ligand with a longer four carbon bridge between the two sulfur atoms gave a dinuclear structure. Single-crystal X-ray diffraction of *rac*-**94** showed strongly distorted trigonal bipyramidal geometry, while complex *rac*-**95** contained two square pyramidal aluminum centers. The polymerization activity of the monomeric complex *rac*-**94** was 8 times more active than the dimeric complex *rac*-**95** with the same monomer conversion.

The complexes **98** and **99** reacted with $B(C_6F_5)_3$ to yield the corresponding cationic Al species of the type $\{PO\}Al(Me)(THF)^+$ and $\{PO\}_2Al^+$, respectively. These cationic Al complexes initiated the ROP of ε-CL via successive ring-opening insertions of the monomer into the Al-OPhO bond of the ligand. So, the $\{PO\}^-$ chelating moiety may act as both a supporting ligand and an initiating group for the ROP of ε-CL in these cationic Al systems.

5. Outlook

This perspective highlights some selected fundamental works and recent advances in the field of aluminum(III) alkyl complexes supported by various ligands. The aim is to provide the readers with a knowledge of the design and characterization of aluminum alkyl complexes and their application in the ROP of cyclic esters, and the challenges needing to be addressed in this field. It is clear that the aluminum alkyl complexes containing tetradentate ligands produce polymers with high molecular weight and narrow molecular weight distribution in the ROP of cyclic esters, featuring a stereoregular polymerization of lactide. For bidentate aluminum complexes, most current studies have focused on the use of these complexes to catalyze the ROP of ε-caprolactone. Although current interest of the application aluminum alkyl complexes is chiefly focused on the ROP of cyclic esters, future efforts may focus on the following several aspects: 1) The development of new ligands with multi-heteroatoms for aluminium complexes with high activity towards useful transformations of small molecules with C-C double or triple bonds, C-N double or triple bonds, and C-H bonds, in addition to cyclic esters, is a promising area.[104-108] Isolation and characterization of active intermediates to understand the catalytic mechanism in the transformation of these small molecules should also be addressed. 2) The transformation of the aluminum compounds to other active species such as cationic aluminium species, low oxidation state aluminum compounds, and their applications to the activation of small molecules such as CO_2, CO and even N_2 would be highly challenging but meaningful in aluminium chemistry. 3) The development of

highly active chiral aluminum catalysts applicable for efficient asymmetric organic synthesis, and new aluminum reagents as efficient olefin polymerization cocatalysts would be highly desired. The aluminum chemistry is promised to have a bright and expanding future given the availability and unique properties of this element.

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Notes and references

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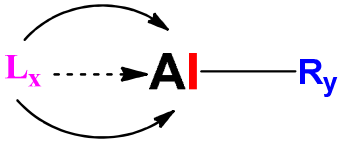
ARTICLE TYPE

Graphical Abstract

Aluminum alkyl complexes bearing various supporting ligands can be efficient catalysts for ring-opening polymerization of cyclic esters.



L = different ligands
R = Alkyl
x = 1; y = 2
x = 2; y = 1