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Bis(salicylamidine) ligands (FAlen): a variant of Salen with “à la carte” denticity

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Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR-CNRS 6302), Université de Bourgogne.

ABSTRACT: Ethylene and phenylene-bridged bis(salicylamidine) ligands have been readily prepared from ethylene or phenylene diamine and iminium chloride derivatives generated *in situ* from *N,N*-dialkyl salicylamides. The former, in its diprotonated form (FAlenH₂), reacts with AlMe₃ to afford a zwitterionic dimethyldiphenoxyaluminate complex with the FAlen ligand monoprotated and in a bidentate κ^2O -fashion. Phenylene-bridged proligand behaves differently, yielding neutral methyl aluminum complex bearing FAlen ligand κ^3O,N,O' -coordinated. From these complexes, methyl anion abstraction with B(C₆F₅)₃ or reaction with Schrock's alcohol led to the corresponding aluminum cationic or alkoxy complexes in which a κ^4O,N,N',O' -coordination mode of the FAlen ligands is observed. X-Ray diffraction studies of the proligands and of the complexes show that the amidine functions feature a *trans*-configuration when the *N*-amidine atom is not coordinated to the metal and conversely a *cis*-configuration when it is. DFT calculations showed that *trans-cis* isomerization of the amidine functions occurs upon coordination with the

metal ion with very low energy barriers. They also confirm the intuition that the denticity of the FAlen ligands in the complexes is directly related to the electron richness of the metal ion. At last, FAlen Al complexes were used as initiators for the controlled ring-opening polymerization (ROP) of *rac*-Lactide to afford PLA with slight isotactic bias.

INTRODUCTION

Tetradentate N₂O₂ Schiff-bases, derived from salicylaldehydes and 1,2-diamines, also known under the name of salen, are ubiquitous ligands able to give complexes with most metal ions of the periodic table (Figure 1).¹ Metal-salen complexes find application in many fields ranging from catalysis,² chemical sensors,³ molecular magnets,⁴ energy storage⁵ to biological applications.⁶ In catalysis, salen complexes are considered as benchmark catalysts for a wide array of reactions, like the coupling of CO₂ and epoxides into cyclic or polymeric carbonates,⁷ the stereocontrolled polymerization of *rac*-lactide (LA)⁸ or the stereoselective epoxidation of unfunctionalized alkenes.⁹ One of the keys to the success of salen-type ligands is their ease of access and modularity. Their steric and electronic characteristics can indeed be easily tuned by choosing appropriate diimine bond and phenyl ring substituents. More drastic modifications of the ligand were also made by replacing either one or both imines functions with an amine¹⁰ or with an iminophosphorane.¹¹ These systems were found to be very efficient, sometimes even outperforming the parent salen ligands.¹² In this context, we recently developed phenoxy-amidines (FA), a new variant of phenoxy-imines (FI), *aka* hemi-salen, in which the imine function is replaced by a *N,N,N'*-trisubstituted amidine (Figure 1).¹³ Amidines differ from imines in that the nitrogen lone pair electrons of the amidine NR₂ group is involved in resonance, thus making them much more basic and more stable towards nucleophiles than imines. We envisioned that the strong

σ and π -donor character of the amidine function will provide additional stability to the metal ion resulting in robust complexes. The first proof of concept was obtained with phenoxy-amidine-Zn complexes that can promote the ROP of *rac*-lactide contaminated with up to 4 mol% lactic acid (a protic impurity often present in technical grade lactide), while phenoxy-imine-Zn analog catalysts are inactive under the same conditions. Based on the same strategy, we sought to develop an amidine-variant of salen ligands. Herein, we report the synthesis of these ligands, which we named FAlen (Figure 1), their coordination chemistry with Al as well as preliminary results in ROP of *rac*-lactide.

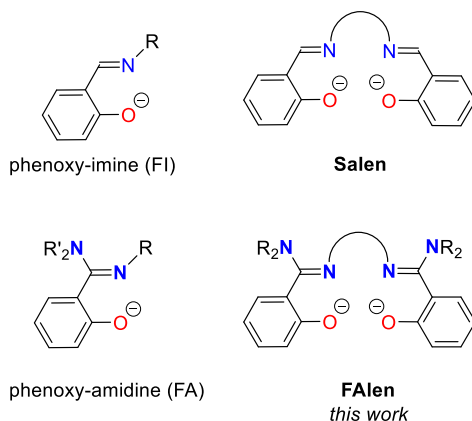


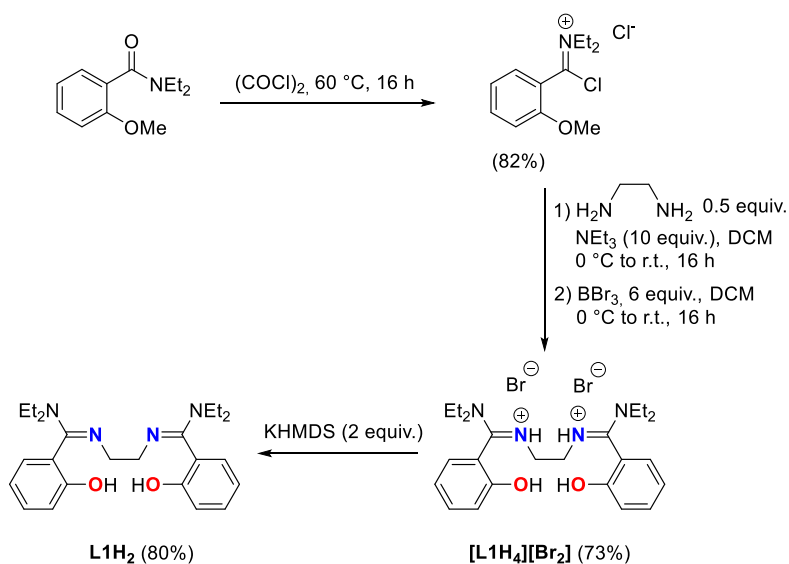
Figure 1. Phenoxy-imine (FI), salen, phenoxy-amidine (FA) and FAlen ligands.

RESULTS AND DISCUSSION

We first reacted ethylene diamine (0.5 equivalents) with the chloroiminium chloride derivative generated from *N,N*-diethyl-2-methoxybenzamide (Scheme 1). After deprotection of the phenol group from methyl ether, the bis-(phenol-amidinium) salt [**L1H₄**]**Br₂** was obtained in 73% yield (Scheme 1). Its ¹H NMR spectrum shows low field shifted protons at 9.7 ppm and at 9.59 ppm corresponding to OH and NH protons, respectively. The NEt₂ protons give two set of signals due

to restricted rotation around the N-C amidine bond. A diastereotopic split is further observed for the methylene protons of both the ethyl groups and the ethylene bridge due to atropisomer axial chirality, generated by the restricted rotation of Csp²-Csp² bond of the phenol moieties. The structure of [L1H₄]⁺Br₂⁻ was confirmed by XRD analysis (Figure 2). The two amidinium moieties feature a *trans* configuration (relative position of NEt₂ vs ethylene linker) and a small ΔCN value of 0.005 Å (ΔCN = d(C-N) - d(C=N)) reflecting the high delocalization along the N=C-N moiety. Deprotonation of [L1H₄]⁺Br₂⁻ with two equivalents of KHMDS yielded the proligand L1H₂, which exhibits a ¹H NMR spectrum with broad signals difficult to assign.

Scheme 1. Synthesis of the FAlen proligand L1H₂.



Suitable crystals for X-Ray diffraction study were obtained by slow evaporation of dichloromethane solution of L1H₂ under air. The ORTEP view shows two molecules of L1H₂ and one molecule of water imbricated in complicated intra- and intermolecular hydrogen bonds network (Figure. 2). If, each proligand is globally neutral and consistent with the L1H₂ formula, one of them combines a phenoxy-amidine and a phenol-amidinium fragment while the other

combines a phenate-amidinium and a phenol-amidine fragment. Noteworthy all the amidine or amidinium functions showed a *trans*-configuration.

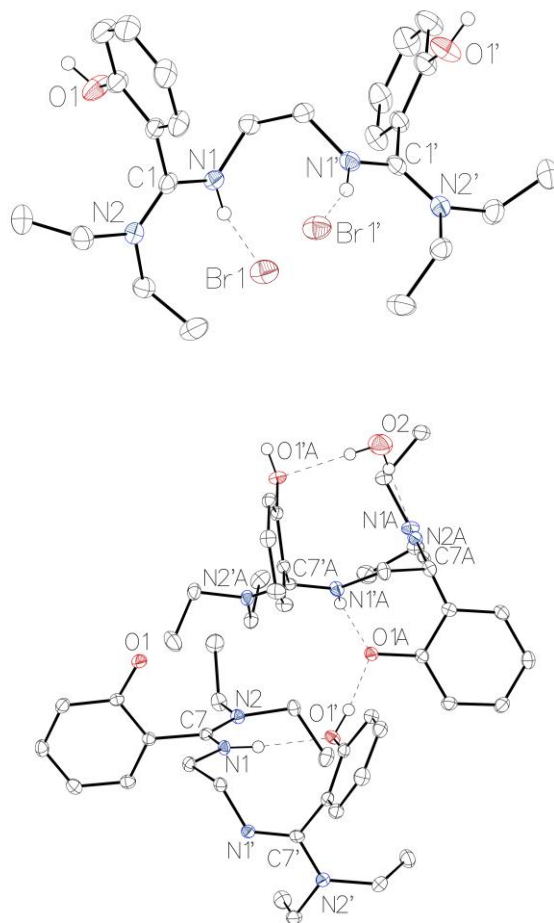


Figure 2. ORTEP views of $[\mathbf{L1H}_4]\mathbf{Br}_2$ (top) and $[\mathbf{L1H}_2]_2\cdot\mathbf{H}_2\mathbf{O}$ (bottom). Thermal ellipsoids are drawn at 30% probability plot. H atoms not involved in H-bonds are omitted for clarity. Selected distances (Å): $[\mathbf{L1H}_4]\mathbf{Br}_2$ C1-N1 = 1.321(3), C1-N2 = 1.318(3); $[\mathbf{L1H}_2]_2\cdot\mathbf{H}_2\mathbf{O}$: C7-N1 = 1.320(3), C7-N2 = 1.330(2), C7'-N1' = 1.288(3), C7'-N2' = 1.373(3), C7A-N1A = 1.294(3), C7A-N2A = 1.369(3), C7'A-N1'A = 1.316(3), C7'A-N2'A = 1.330(3).

For the coordination chemistry study, the proligand $\mathbf{L1H}_2$ was generated *in situ* from the well characterized bisamidinium salt $[\mathbf{L1H}_4]\mathbf{Br}_2$ using two equivalents of KHMDS. The alkane metathesis pathway from $\mathbf{L1H}_2$ and AlMe_3 (1 equiv.) yielded a new compound **1** whose ^1H NMR

spectrum was not consistent with the expected (L1)AlMe-like complex (Scheme 2). Instead, a labile proton at 7.8 ppm and two AlMe signals at -1.08 ppm and -0.61ppm were observed. The compound was crystallized and its XRD analysis shows the FAlen L1 ligand in κ^2O coordination mode. Two methyl groups complete the coordination sphere of aluminum giving a dimethyldiphenoxyaluminate with a tetrahedral geometry ($\tau_4' = 0.91$)¹⁴. One of the two amidine functions is protonated and serves as counter-ion. The expected *trans-cis* amidine isomerization previously observed with phenoxy-amidine ligands did not occur in this case, giving rise to a FAlen ligand coordinated in a κ^2O fashion.

Scheme 2. Synthesis of the FAlen aluminate complex **1**.

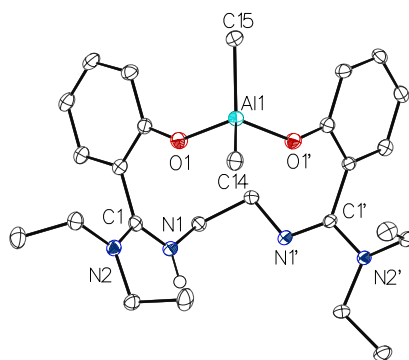
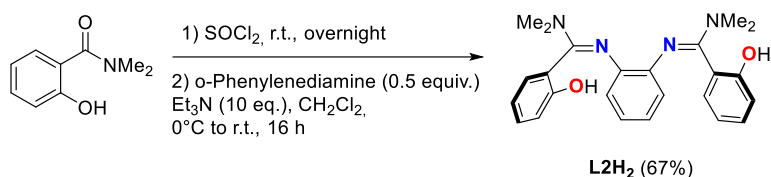


Figure 3: ORTEP views of **1**. Thermal ellipsoids are drawn at 30% probability plot. Hydrogen atoms and THF solvent molecule, except amidinium protons, are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected distances (Å) and angles (°): Al1-O1 = 1.781(2), Al1-O1' = 1.775(2), Al1-C14 = 1.976(3), Al1-C15 = 1.990(3), C1-N2 = 1.330(4), C1-N1 = 1.320(4), C1'-N2' = 1.383(4), C1'-N1' = 1.292(4), O1'-Al1-O1 = 105.2(1), C14-Al1-C15

= 117.6(1), O1-A11-C14 = 105.9(1), O1-A11-C15 = 109.5(1), O1'-A11-C14 = 105.9(1), O1'-A11-C15 = 111.8(1).

We then decided to develop a new FAIen ligand **L2** by introducing a phenylene rather than an ethylene linker between two *N,N*-dimethyl-substituted phenoxy-amidine groups. We hypothesized that this should result in a ligand with a better preorganized structure to wrap the metal ion. The proligand **L2H₂** was first synthesized in 36% overall yield according to the same procedure as **L1H₂** using 2-methoxy-*N,N*-dimethylbenzamide and *o*-phenylenediamine. The yield was further improved substantially to 67% by *in-situ* generating Vilsmeier-type reagent from unprotected 2-hydroxy-*N,N*-dimethylbenzamide and thionyl chloride, and subsequent addition of *o*-phenylene diamine (Scheme 3).

Scheme 3. Synthesis of the FAIen proligand **L2H₂**.



In the solid-state, the structure of **L2H₂** shows a zwitterionic form with one of the two phenol-amidine fragments protonated at N1' and the other deprotonated at O, both being connected by an intramolecular (O⁻⋯HN⁺) hydrogen bond. Both amidine and amidinium moieties feature *trans*-configuration and small ΔCN values of 0.061(3) and 0.001(3) Å, respectively (Figure 4). The ¹H NMR spectrum of **L2H₂** in CD₂Cl₂ at 298 K is consistent with a C₂-symmetric compound. It indeed shows only six signals in the aromatic proton region and two broad signals at δ = 3.21 and 2.77 ppm for the NMe₂ groups due to the restricted rotation about the amidine bounds. The apparent inconsistency between the solid-state and solution structures of **L2H₂** and the absence of phenol

proton signals could be explained by rapid exchanges of protons in solution between the phenol and amidine functions.

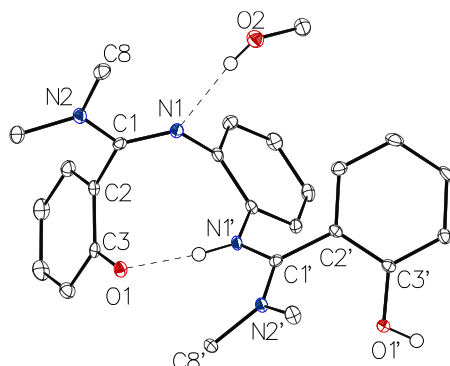
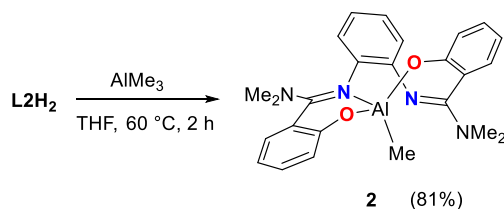


Figure 4: ORTEP views of **L2H2**·**MeOH**. Thermal ellipsoids are drawn at 30% probability plot. H atoms not involved in H-bonds are omitted for clarity. Selected distances (Å): **L2H2** C1'–N1'–H⁺ = 1.326(2), C1'–N2' = 1.327(2), C1=N1 = 1.298(2) / C1–N2 = 1.359(2).

The reaction of **L2H2** with one equivalent of AlMe₃ in THF at 60°C for 2 h afforded (**L2**)AlMe complex **2** in 81% yield (Scheme 4). X-Ray analysis of crystals of **2** indicates that the Al atom has a pseudo-tetrahedral geometry with the FAIen **L2** ligand in κ^3O,O,N coordination mode and a methyl ligand occupying the fourth coordination site (Figure 5).

Scheme 4. Synthesis of the FAIen methyl Al complex **2**.



The Al atom is located in the FAIen cavity at a distance of 2.97 Å from the *trans*-amidine atom N1', which is shorter than the sum of the van der Waals radii (3.39 Å). Assuming that both amidine functions in the proligand **L2H2** are *trans* in solution, in agreement with the solid-state structure

and the known greater thermodynamic stability of *trans*-amidine, it means that *trans-cis* isomerization of one of the two amidine functions occurred upon coordination. Surprisingly, the ^1H and ^{13}C NMR spectra of **2** in CD_2Cl_2 at 298 K shows a set of signals consistent with a C_s symmetric structure. We hypothesized that a dynamical process must take place in solution and can explain this inconsistency.

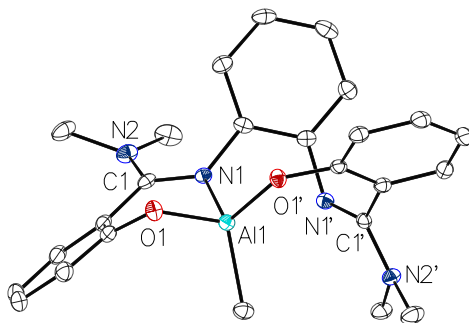


Figure 5: ORTEP views of **complex 2**. Thermal ellipsoids are drawn at 50% probability plot. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles ($^\circ$): Al1-O1 = 1.787(1), Al1-O1' = 1.734(1), Al1-C16 = 1.956(1), Al1-N1 = 1.930(1), C1-N2 = 1.352(2), C1-N1 = 1.326(2), C1'-N2' = 1.365(2), C1'=N1' = 1.299(2), O1'-Al1-O1 = 104.4(1), N1-Al1-C16 = 119.8(1), O1-Al1-C16 = 109.9(1), O1-Al1-N1 = 93.3(1), O1'-Al1-C16 = 117.6(1), O1'-Al1-N1 = 108.1(1).

To get some insights on the fluxional behavior of **2**, we performed DFT calculation at the M06-2x/6-31+G(d,p) computational level (in DCM) (Figure 6). First of all, it shows that amidine functions easily isomerize during coordination with the metal by rotation around the C=N bond with very shallow energy barriers ($\Delta G^\ddagger \leq 12.9 \text{ kcal.mol}^{-1}$). These energy values are consistent with a dynamic process occurring in solution at room temperature or even below (the ^1H NMR spectra of **2** did not change significantly down to 193 K, see Fig. S27). The FAlen ligand can thus momentarily have the two amidine functions in a *cis*-configuration, ideally suited for κ^4 -coordination and the formation of stepped and umbrella-shaped complexes (B1/B2 and C). All

these complexes are in fast equilibrium in solution at room temperature, but the enantiomeric κ^3 -coordinated complexes (A1/A2) were found more thermodynamically stable than the κ^4 -forms (B1/B2 and C), as observed experimentally. It should be noted that a much higher energy barrier ($\Delta G^\ddagger = 20.4 \text{ kcal}\cdot\text{mol}^{-1}$) was estimated for *trans-cis* amidine isomerization within a hemiFAlen proligand (2-hydroxy-*N,N*-dimethyl-*N'*-propylbenzamidine), in agreement with values previously reported in the literature (See SI, Fig. S48-S49).¹⁵

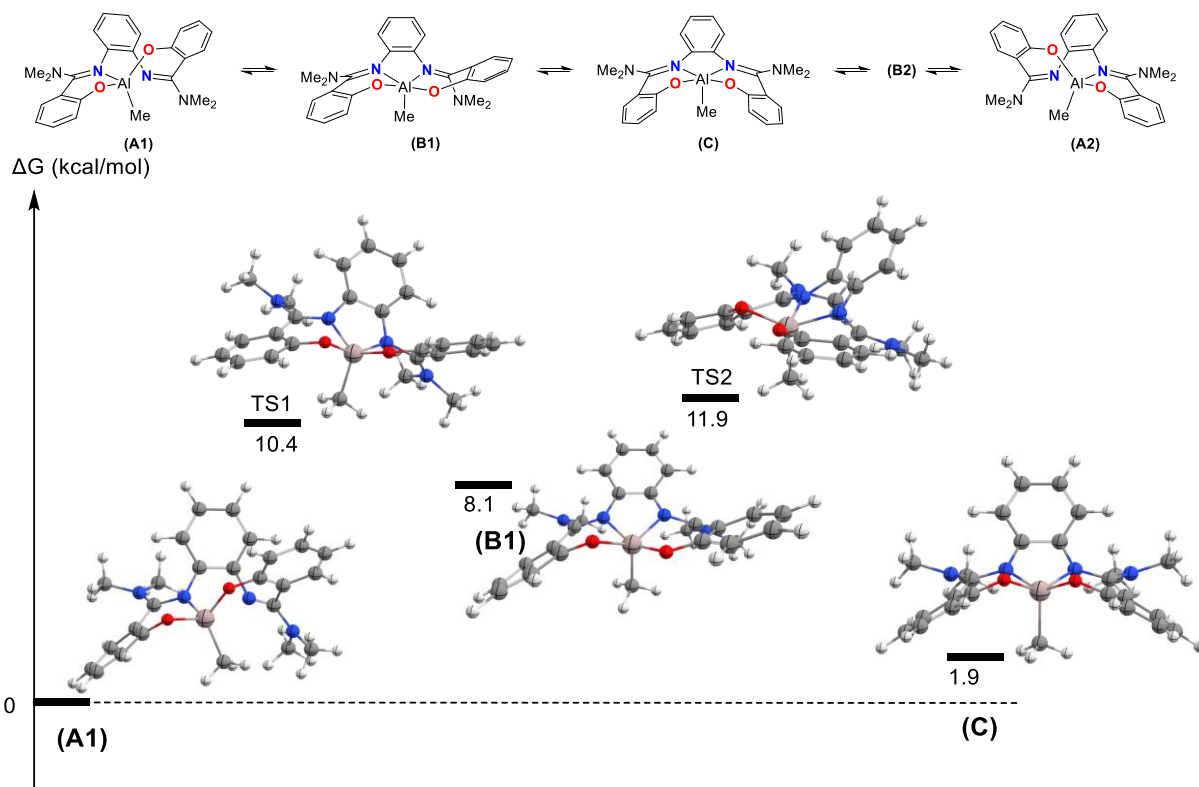
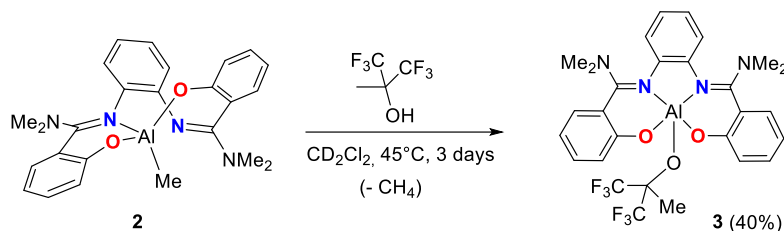


Figure 6: Dynamic behavior of complex **2**. Gibbs Free energy profiles computed at the M06-2X/6-31+G(d,p) theory level in DCM.

We then hypothesized that by decreasing the electron density at the Al center, the κ^4 -FAlen coordination mode should be thermodynamically favored over the κ^3 -form. For this, we carried out the alcoholysis of **2** with Schrock's alcohol (Scheme 5). After 3 days at 45°C in CD_2Cl_2 , a single complex **3** was formed. Its ^1H NMR spectrum was consistent with a C_s symmetric structure,

showing only 6 signals for the aromatic protons and one broad signal for the NMe₂ groups. The high field shifted AlMe signal of **2** located at $\delta = -1.12$ ppm was replaced by a signal at $\delta = 0.67$ ppm corresponding to the AlOC(CF₃)₂Me group.

Scheme 5. Synthesis of the FAlen alkoxy Al complex **3**.



Suitable crystals for X-Ray diffraction study were obtained by slow diffusion of pentane in a dichloromethane solution of **3** (Figure 7). In the solid state, the Al atom has a square-based pyramidal geometry ($\tau_5 = 0,01$)¹⁶ with the FAlen ligand in basal position and in κ^4 -coordination mode. The alkoxy ligand occupies the apical position, in the cavity formed by the FAlen ligand in an umbrella-shaped conformation. The Al-O1/O1' and Al-N1/N1' distances are 1.816(2)-1.815(2) Å and 1.977(2)-1.987(2) Å, respectively, in the same range as those observed in analogous Salen(Al) complexes.¹⁷

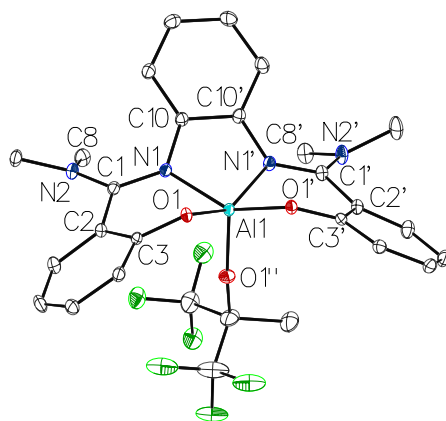


Figure 7. ORTEP views of **3**. Thermal ellipsoids are drawn at 30% probability plot. Hydrogen atoms, DCM solvent and disordered parts are omitted for clarity. Selected distances (Å) and angles

(°): C1=N1 = 1.324(3), C1-N2 = 1.364(3), C1'=N1' = 1.327(3), C1'-N2' = 1.361(3), Al1-N1 = 1.987(2), Al1-N1' = 1.977(2), Al1-O1 = 1.815(2), Al1-O1' = 1.816(2), Al1-O1'' = 1.733(2), O1-Al1-O1' = 89.9(1), N1-Al1-O1 = 87.4(1), N1-Al1-N1' = 79.8(1), N1'-Al1-O1' = 87.3(1), O1'-Al1-O1'' = 106.0(1), N1-Al1-O1'' = 104.4(1), N1'-Al1-O1'' = 105.8(1).

DFT calculations carried out on complex **3** revealed a dynamic behavior similar to that of **2** (see SI, Fig. S50), with however lower energy for the κ^4 -complex (C') than for the κ^3 -form (A1') (Figure 8). NBO studies were then carried out in order to evaluate the residual charge of aluminum in these different complexes and to see if a correlation exists between the electronic richness of the metal and the coordination mode of the ligand. Expectedly, NBO analysis show higher positive charge on Al in the alkoxy complex with respect to the alkyl complex. Coordination of the second amidine function decreases the charge on Al in both cases. It should be noted that the most stable complex in each series has almost the same charge on Al. It therefore seems that the FAlen ligands can adapt their mode of coordination and their geometry according to the electronic richness of the metal ion.

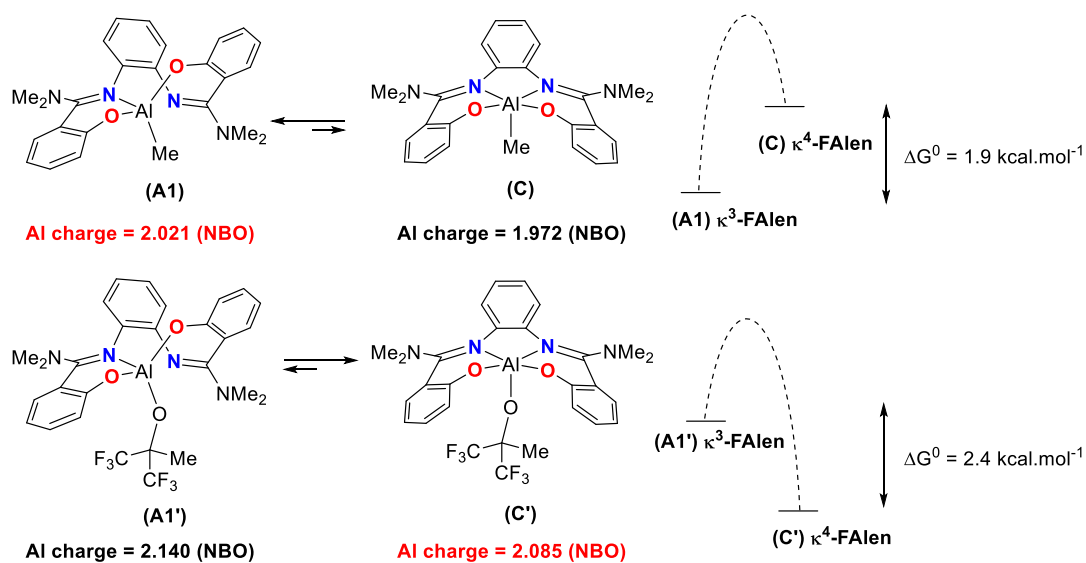
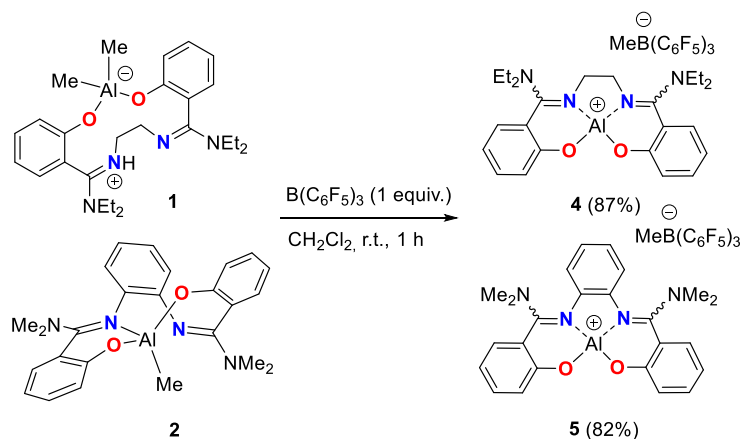


Figure 8. NBO charges on Al and free Gibbs energies of the κ^3 and κ^4 -coordination modes in complexes **2** and **3**.

With the aim to obtain even more electron-deficient Al species, we sought to synthesize Al cations from complexes **1** and **2**. Methyl anion abstraction was first carried out from complex **1** in CH_2Cl_2 using one equivalent of tris(pentafluorophenyl)borane (Scheme 6). The resulting ^1H NMR spectrum showed very broad signals very difficult to assign. Suspecting the formation of aggregates, we added deuterated pyridine to the NMR sample. It greatly simplified the spectrum giving rise to an NMR pattern consistent with a C_s symmetry structure. Moreover, we noticed the disappearance of the two AlMe_2 signals present in the ^1H NMR spectrum of **1**, and the appearance of a new signal at $\delta = 0.68$ ppm, related to the presence of $\text{MeB}(\text{C}_6\text{F}_5)_3$ anion.

Scheme 6. Synthesis of the aluminum cations **4** and **5**. For simplicity, **4** and **5** are represented as mononuclear complexes rather than as aggregates.



Suitable crystals for X-Ray diffraction study were obtained by diffusion technique from the NMR sample ($\text{CD}_2\text{Cl}_2/\text{pentane}/\text{Py-D}_5$). The ORTEP view presented on Figure 9 shows a dimeric structure in which the two cationic Al units are bridged by the oxygen atoms of one of the phenoxy groups of each FAlen ligand. The aluminum atom adopts a pseudo-octahedral geometry defined

by the four O₂N₂ atoms of the FAlen ligand in the equatorial plane. The O atom of a bridging aryloxy group and the N atom of an additional pyridine ligand occupy the two axial positions. Thus, the ethylene-bridged FAlen ligand **L1** was shown to be able to adopt a κ^4 -coordination modes with an umbrella-shaped conformation like **L2** in complex **3**. The bond lengths Al-O, Al-O', and Al-N are broadly comparable to those reported for similar octahedral aluminum cations with Salen-type ligands. Similarly, the reaction of B(C₆F₅)₃ with complex **2** afforded the cationic complex **5** which was then characterized by NMR in CD₂Cl₂/Pyridine-D₅ and crystallized as bis(pyridine) adduct of a dicationic dinuclear Al complex (Figure 9).

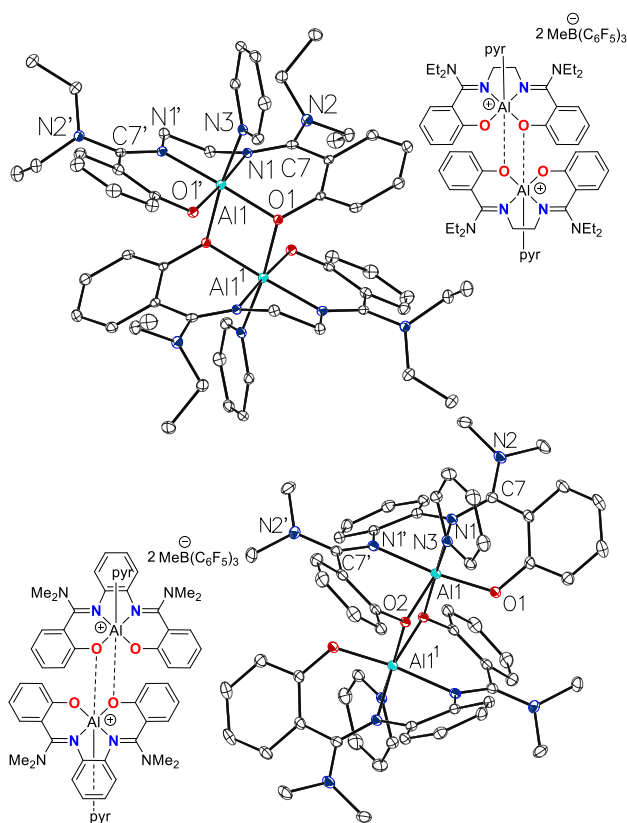


Figure 9. ORTEP views of the bis(pyridine) adduct of the dimeric form of complexes **4** and **5**. Thermal ellipsoids are drawn at 30% probability plot. Hydrogen atoms and counterions are omitted for clarity. ¹1-x, 2-y, 1-z and ¹1-x, -y, 1-z symmetry element used for **4** and **5** respectively. Selected

distances (Å) and angles (°): N1-Al1 = 1.971(2), O1-Al1 = 1.881(2), N1'-Al1 = 1.984(2), O1'-Al1 = 1.789(2), N3-Al1 = 2.063(2), O1¹-Al1 = 2.013(2), O1-Al1-O1' = 95.4(1), O1'-Al1-N1' = 93.6(1), N1'-Al1-N1 = 82.4(1), N1-Al1-O1 = 88.4(1), N3-Al1-O1 = 95.4(1), N3-Al1-O1¹ = 173.2(1), N1'-Al1-O1 = 167.1(1), O1'-Al1-N1 = 175.9(1) for compound **4** ; N1-Al1 = 1.983(2), O1-Al1 = 1.810(2), N1'-Al1 = 2.016(2), O2-Al1 = 1.899 (2), N3-Al1 = 2.050(2), O2¹-Al1 = 1.951(2), O1-Al1-O2 = 103.4(1), O2-Al1-N1' = 87.3(1), N1'-Al1-N1 = 78.6(1), N1-Al1-O1 = 90.4(1), N3-Al1-O1 = 89.6(1), N3-Al1-O2¹ = 166.5(1), N1'-Al1-O1 = 168.1(1), O2-Al1-N1 = 165.6(1) for compound **5**.

Salen aluminum complexes have been widely used as initiator for the Ring Opening Polymerization (ROP) of lactide. Spassky firstly showed that simple (salen)AlOMe can initiate the ROP of *rac*-lactide with moderate activity but with slight isotactic bias.¹⁸ These results triggered intensive research in the field and a great variety of salen-type ligands with different diimine linkers and substituents on the phenolate rings have been synthesized and tested allowing the identification of highly isoselective catalysts, albeit moderately active.⁸ We therefore choose this benchmark reaction to test the efficiency of the FAlen ligands. Polymerization runs were first conducted at 90°C in toluene in the presence of 1 equiv. of *i*PrOH as the alcohol source (Table 1). The FAlen dimethyl aluminate complex **1** and the (FAlen)AlMe complex **2** led to comparable results affording PLAs in 94-95% conversion after 24 h (entries 1 and 5). The cationic system **4** and **5** were much less active in the same conditions, affording only 48% and 18% of conversion, respectively (entries 8-9). At lower temperatures, complex **1** was clearly the most effective achieving complete conversion of the monomer after 7 h at 50°C while complex **2** afforded only 68% conversion after 15 h at 70°C (entries 3 and 6). At room temperature, in dichloromethane, complex **1** is the only one still active with monomer conversion reaching 74% after 9 h (entry 4).

The GPC analysis of the different polymer samples showed a good agreement between experimental and theoretical M_n values and relatively narrow molecular weight distributions ($\mathcal{D} = 1.11-1.44$). NMR analysis showed PLA chains with slight isotactic bias ($P_m = 0.53-0.62$). The kinetic of the reaction with complex **1**, at 25 °C in CH_2Cl_2 (Fig. 10), showed a linear relationship between $\ln([\text{LA}]_0/[\text{LA}]_t)$ and time with a rate constant k_{app} of $0.0027 \pm 0.0003 \text{ min}^{-1}$ comparable to the one previously obtained with the parent (salen)AlMe complex, at 70 °C and higher catalyst loading ($k_{\text{app}} = 0.0035 \text{ min}^{-1}$, $[\text{LA}]_0/[\text{initiator}]/[\text{PhCH}_2\text{OH}] = 50/1/1$, toluene, 70 °C).⁸ The evolution of the M_n and PDI values with conversion confirmed the well-controlled character of the polymerization, when promoted by complex **1** and isopropanol as co-initiator. Noteworthy, the MALDI-ToF spectrum obtained in these conditions showed only one series of PLA chains terminated with isopropoxy ester with a peak spacing of 144 Da and no intercalated peak due to secondary transesterification reactions (See SI, Fig. S47).

Table 1. ROP of *rac*-lactide mediated by FAlen-Al complexes **1,2, 4** and **5**^a

Entry	Init.	T (°C)	t (h)	Conv (%) ^c	$M_{n, \text{exp}}^d$	$M_{n, \text{theo}}^e$	\mathcal{D}	P_m^f
1	1	90	24	94	11 400	13 500	1.31	0.53
2	1	70	15	99	10 200	14 400	1.44	0.63
3	1	50	7	99	12 000	14 400	1.11	0.62
4	1 ^b	25	9	74	7 500	10 700	1.11	0.57
5	2	90	24	95	12 100	13 700	1.37 ^g	0.54
6	2	70	15	68	8 300	9 800	1.22	0.56
7	2 ^b	25	9	0	-	-	-	-
8	4	90	24	48	4 500	6 900	1.11	-
9	5	90	24	18	-	-	-	-

^a Polymerization conditions: $[rac\text{-LA}]_0 = 1\text{ M}$, 100 equiv. of $rac\text{-LA}$, 1 equiv of $i\text{PrOH}$ and 1 equiv of metal catalyst, toluene. ^b Reactions performed in CH_2Cl_2 . ^c Monomer conversion. ^d Measured by GPC in THF (30 °C) using PS standards and corrected by applying the appropriate correcting factor (0.58). ^e Calculated using $M_{n,theo} = [rac\text{-LA}]_0/[catalyst]_0 \times M_{LA} \times \text{conversion}$. ^f Determined from the methine region of the HD ^1H NMR spectrum. ^g GPC chromatogram presents bimodal profile.

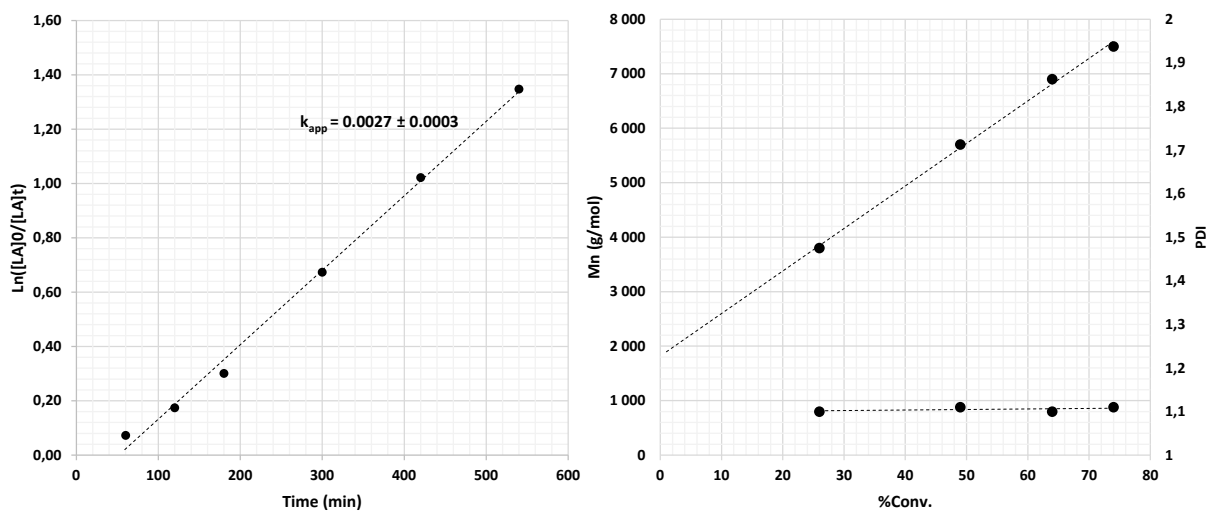


Figure 10. Left: First-order logarithmic plot for the polymerization of $rac\text{-LA}$ at 25°C in DCM using **1** with $i\text{PrOH}$ as initiator (100:1:1). Right: M_n and PDI against conversion.

CONCLUSION

We have described a new variant of the ubiquitous salen by incorporating two amidine moieties in the ligand backbone. These new ligands, named FAlen, provide access to a series of aluminum complexes and showed quite unique coordination chemistry compared to salen. In the solid state, (FAlen)Al(III) complexes were found either in κ^2O,O' , κ^3N,O,O' or κ^4N,N',O,O' coordination mode. DFT calculations have shown that amidines easily isomerize within the complexes which confers fluxional properties and versatile denticity to FAlen. Finally, (FAlen)Al complexes were tested for the ROP of $rac\text{-Lactide}$ in the presence of $i\text{PrOH}$ as co-initiator. The (FAlen- κ^2)AlMe₂

aluminate complex **1** was the most efficient complex, being able to initiate the ROP of LA at room temperature making it much more active than its parent salen complex. Efforts are currently underway to study further the flexible coordination mode of FAlen with other metals and to develop new FAlen ligands with different diamidine linkers and substituents on the phenolate platforms.

EXPERIMENTAL SECTION

General considerations

All reactions, except when indicated, were carried out under an atmosphere of argon using conventional Schlenk techniques and Ar glovebox. DCM, diethyl ether, THF, toluene, and pentane were dried using a MBRAUN SPS 800. Analyses were performed at the “Plateforme d’Analyses Chimiques de Synthèse Moléculaire de l’Université de Bourgogne”. Elemental analyses were performed by Mr Marcel Soustelle and Ms Tiffanie Régner on CHNS ThermoFisher Scientific Flash EA 1112 analyzer. Reagents were commercially available and used as received. High resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL ESI-MS (ElectroSpray Ionization Mass Spectrometry). All X-Ray experimental procedure and crystal data are detailed in SI. NMR spectra (^1H , ^{13}C) were recorded on Bruker 300 Avance Neo, Bruker 400 Avance Neo, Bruker 500 Avance Neo, or Bruker 600 Avance HD spectrometers. All acquisitions were performed at 298 K. Chemical shifts are quoted in parts per million (δ) relative to TMS (for ^1H and ^{13}C). For ^1H and ^{13}C spectra, values were determined by using solvent residual signals (*e.g.* CHCl_3 in CDCl_3) as internal standards. The apparent multiplicity of the ^1H signals is reported. Assignment of ^1H and ^{13}C signals (when possible) was done through the use of 2D experiences (COSY, HSQC and HMBC). Nomenclature: the positions of carbon and hydrogen atoms in the aromatic rings of FAlen ligands were labelled according to Figure 10.

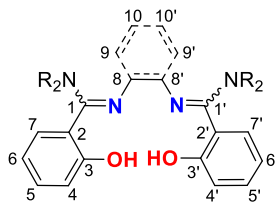


Figure 10. Numbering scheme for the assignment of the NMR spectra

Synthesis of *N,N*-diethyl-2-methoxy-chlorobenzimidium chloride. *N,N*-diethyl-2-methoxybenzamide (1 equiv., 25 mmol, 5.18 g) was dissolved in toluene (25 mL) and oxalyl chloride (5 equiv., 125 mmol, 10.9 mL) was added. The mixture was stirred 16 h at 60 °C. The volatiles were evaporated, and the residue was washed with diethyl ether (5 x 50 mL), and dried to give the pure product as a beige solid (5.39 g, 82 %). **Elemental Analysis:** calcd for C₁₂H₁₇Cl₂NO: C, 54.98; H, 6.54; N, 5.34. Found: C, 54.60; H, 6.71; N, 5.43. **¹H NMR** (300 MHz, CDCl₃): δ (ppm) = 8.09 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H, H7), 7.61 (ddd, *J* = 8.6, 7.5 Hz, 1.7 Hz, 1H, H5), 7.20 (pseudo td, *J* = 7.6 Hz, 0.9 Hz, 1H, H6), 7.06 (d, *J* = 8.5 Hz, 1H, H4), 4.82 (m, 1H, N(CH₂CH₃)₂), 4.45 (m, 1H, N(CH₂CH₃)₂), 4.29 (m, 2H, N(CH₂CH₃)₂), 3.94 (s, 3H, OMe), 1.66 (t, *J* = 7.4 Hz, 3H, N(CH₂CH₃)₂), 1.46 (t, *J* = 7.3 Hz, 3H, N(CH₂CH₃)₂). **¹³C{¹H} NMR** (75 MHz, CDCl₃): δ (ppm) = 171.7 (C1), 154.6 (C2), 135.4 (C5), 129.6 (C7), 122.3 (C6), 120.4 (C2), 111.7 (C4), 56.5 (CH₃ + CH₂ overlapping, OMe, N(CH₂CH₃)₂), 54.7 (N(CH₂CH₃)₂), 13.1 (N(CH₂CH₃)₂), 12.6 (N(CH₂CH₃)₂).

Synthesis of [L1H₄][Br₂]. *N,N*-diethyl-2-methoxy-chlorobenzimidium chloride (2 equiv., 4 mmol, 1.05 g) was solubilized in DCM (40 mL) and cooled to 0°C. Triethylamine (10 equiv., 20 mmol, 2.70 mL) was added, and then slowly ethylenediamine (1 equiv., 1 M in DCM, 2.00 mmol, 2.00 mL). The mixture was stirred 16 h while warming to rt. The mixture was hydrolysed with NaOH solution (1 M, 30 mL), diluted with water (30 mL), and extracted with DCM (3 x 40 mL). The gathered organic layers were dried with MgSO₄, and concentrated to give the crude methoxy-

protected FAlen ligand as an oil. The oil was solubilized in DCM (40 mL) and cooled to 0°C. Boron tribromide (6 equiv., 1 M solution in DCM, 12.0 mmol, 12.0 mL) was slowly added, and the mixture stirred 16 h while warming to rt. The mixture was cooled to 0°C and slowly quenched with water (50 mL), and extracted with DCM (3 x 50 mL), and further extracted with chloroform (3 x 40 mL). The gathered organic layers were dried with MgSO₄, and concentrated to give the bis(salicylamidinium) [L1H₄][Br₂] as a beige solid (840 mg, 73 %). **HR-MS (ESI-pos):** calcd for [C₂₄H₃₅N₄O₂]⁺ [M+H]⁺: 411.27545. Found: 411.27406 (- 3.4 ppm). **¹H NMR (500 MHz, CD₂Cl₂):** δ (ppm) = 9.70 (s, 2H, OH), 9.59 (broad signal, 2H, NH), 7.60 (d, *J* = 8.3 Hz, 2H, H4), 7.39 (ddd, *J* = 8.5, 5.5, 3.5 Hz, 2H, H5), 6.98-6.92 (m, 4H overlapping, H6 + H7), 4.13 (m, 2H, N(CH₂CH₃)₂), 3.87 (m, 2H, N(CH₂CH₃)₂), 3.38-3.22 (m, 6H, H8 + N(CH₂CH₃)₂), 3.22-3.15 (m, 2H, H8), 1.44 (t, *J* = 7.2 Hz, 6H, N(CH₂CH₃)₂), 1.12 (t, *J* = 7.2 Hz, 6H, N(CH₂CH₃)₂). **{¹H}¹³C NMR (125 MHz, CD₂Cl₂):** δ (ppm) = 163.5 (C1), 154.4 (C3), 133.7 (C5), 126.9 (C7), 120.7 (C6), 118.5 (C4), 114.6 (C2), 48.2 (N(CH₂CH₃)₂), 44.9 (N(CH₂CH₃)₂), 44.7 (C8), 13.7 (N(CH₂CH₃)₂), 12.3 (N(CH₂CH₃)₂).

Synthesis of 1. In glovebox, KHMDS (79.8 mg, 0.4 mmol, 2 equiv.) were added to [L1H₄][Br₂] (114 mg, 0.2 mmol) in 10 mL of dried THF. After stirring 4 h at r.t., a 2M solution of AlMe₃ in hexanes (100 μL, 0.2 mmol, 1 equiv.) in 2 mL of THF was added and the reaction mixture was stirred for another 2 h at r.t. The supernatant was cannulated and after removing the THF, the solid was washed twice with 5 mL of pentane to give aluminum complex **1** as a beige solid (58 mg, 62%). **Elemental analysis:** calcd for (C₂₆H₃₉AlN₄O₂)₁₀₀(C₂H₆SiO)₇₀: C, 63.47; H, 8.40; N, 10.81. Found: C, 63.40; H, 8.13; N, 11.66. **¹H NMR (400 MHz, TDF):** δ (ppm) = 7.80 (broad signal, 1H, NH), 7.11-7.04 (m, 2H, H5), 6.89 (dd, *J* = 8.4, 0.8 Hz, 2H, H4), 6.80 (dd, *J* = 7.5, 1.8 Hz, 2H, H7), 6.56 (td, *J* = 7.3, 1.3 Hz, 2H, H6), 3.39 (broad signal, 8H, N(CH₂CH₃)₂), 3.21-3.12 (m, 2H, H8),

3.00-2.91 (m, 2H, H8), 1.20 (broad signal, 12H, N(CH₂CH₃)₂), -0.61 (s, 3H, AlMe), -1.04 (s, 3H, AlMe). ¹H¹³C NMR (125 MHz, TDF): δ (ppm) = 166.06 (C1), 160.86 (C3), 132.08 (C5), 128.41 (C7), 122.80 (C2), 121.82 (C4), 116.81 (C6), 49.36 (C8), 43.68 (N(CH₂CH₃)₂), 14.04 (N(CH₂CH₃)₂), -4.98 (AlMe), -8.86 (AlMe).

Synthesis of L2H₂. 2.0 g (12.1 mmol) of 2-hydroxy-*N,N*-dimethylbenzamide were solubilized into 10 mL of SOCl₂. The mixture was stirred overnight at r.t. and the solvent was then evaporated under vacuum. 15 mL of dried CH₂Cl₂ was added and further evaporated. A solution of the crude product and 8.4 mL (60.5 mmol, 5 equiv.) of triethylamine in 50 mL of dried CH₂Cl₂ was then cooled to 0 °C and 598.6 mg (5.5 mmol, 0.45 equiv.) of *o*-phenylenediamine were added. The mixture was allowed to reach r.t. and stirred for 2 h 30. After hydrolysis with 50 mL of distilled water, the product was extracted with CH₂Cl₂ (4 x 50 mL). The organic phases were combined and dried over MgSO₄ before being evaporated. The crude product was taken back in 50 mL of diethyl ether and a 1M solution of HCl in diethyl ether was added up to pH = 1. The brownish product was filtrated under vacuum and washed with 3x40 mL of diethyl ether. The whitish solid was suspended in 10 mL of distilled water and a 5M aqueous solution of NaOH was added up to pH = 9-10. The product was extracted with 50 mL of CH₂Cl₂. The organic phase was washed with 3x10 mL of distilled water before being dried over MgSO₄ and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using MeOH as eluent to afford 1.48 g of L2H₂ (67% yield). **Elemental Analysis:** calcd for C₂₄H₂₆N₄O₂: C, 71.62; H, 6.51; N, 13.92. Found: C, 71.84; H, 6.62; N, 13.94. ¹H NMR (600 MHz, CD₂Cl₂): δ (ppm) = 7.08 (td, *J* = 7.7, 1.8 Hz, 2H, H5), 6.98 (dd, *J* = 7.6 Hz, 1.8 Hz, 2H, H7), 6.80 (broad signal, 2H, H6), 6.75 (d, *J* = 8.2 Hz, 2H, H4), 6.55 (m, 2H, H10), 6.40 (broad signal, 2H, H9), 3.21 (broad signal, 6H, NMe₂), 2.77 (broad signal, 6H, NMe₂). ¹H¹³C NMR (150 MHz, CD₂Cl₂): δ (ppm) = 161.56 (C1),

155.30 (C2), 144.56 (C8), 130.41 (C5), 129.08 (C7), 124.01 (C2), 123.91 (C10), 123.37 (C9), 120.21 (C4 or C6), 119.96 (C4 or C6), 39.86 (NMe₂), 37.89 (NMe₂).

Synthesis of 2. In glovebox, 250 μ L (0.5 mmol, 1 equiv.) of AlMe₃ (2M in hexanes) were added to a solution of 201 mg (0.5 mmol) of proligand **L2H₂** in 10 mL of dried THF. The mixture was stirred at 60 °C for 2 h. After cooling down to r.t., the solvents were evaporated under vacuum. The crude product was washed with 8 mL of dried pentane, affording 180 mg of complex **2** (81% yield). **Elemental Analysis:** calcd for C₂₅H₂₇AlN₄O₂: C, 67.86; H, 6.15; N, 12.66. Found: C, 67.96; H, 6.17; N, 12.17. **¹H NMR (500 MHz, CD₂Cl₂):** δ (ppm) = 7.33 (dd, J = 8.0, 1.8 Hz, 2H, H7 + H7'), 7.25 (td, J = 8.7, 1.9 Hz, 2H, H5 + H5'), 6.80-6.73 (overlapping signals, 6H, H4 + H4' + H6 + H6' + H10 + H10'), 6.46 (m, 2H, H9 + H9'), 3.00 (s, 6H, NMe₂), 2.90 (s, 6H, NMe₂), -1.12 (s, 3H, AlMe). **¹H¹³C NMR (125 MHz, CD₂Cl₂):** δ (ppm) = 165.40 (C1 + C1'), 162.32 (C3 + C3'), 141.59 (C8 + C8'), 133.50 (C5 + C5'), 131.33 (C7 + C7'), 123.41 (C10 + C10'), 122.91 (C9 + C9'), 122.52 (C4 + C4'/C6 + C6'), 119.71 (C2 + C2'), 117.04 (C4 + C4'/C6 + C6'), 42.40 (NMe₂), 40.57 (NMe₂), -13.60 (AlMe).

Synthesis of 3. In glovebox, 17.7 mg (0.04 mmol) of complex **2** were introduced in a Young NMR tube and solubilized in 0.5 mL of CD₂Cl₂. Then 5 μ L (0.04 mmol, 1 equiv.) of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol were added with a micro syringe and the tube was heated at 45 °C for 3 days. Crystals (10 mg, 40% yield) were then obtained by slow diffusion of pentane and analysed by NMR and XRD. **Elemental Analysis:** calcd for (C₂₈H₂₇AlF₆N₄O₃)₁₀₀(CH₂Cl₂)₁₀₀: C, 50.23; H, 4.22; N, 8.08. Found: C, 50.15; H, 4.74; N, 7.79. **¹H NMR (400 MHz, CD₂Cl₂):** δ (ppm) = 7.55 (dd, J = 8.2, 1.8 Hz, 2H, H7), 7.36 (m, 2H, H5), 7.08 (m, 2H, H9/H10), 7.01 (d, J = 7.6 Hz, 2H, H4), 6.75 (t, J = 7.5 Hz, 2H, H6), 6.67 (m, 2H, H9/H10), 3.07 (broad signal, 12H, NMe₂), 0.67 (s, 3H, OCH₃(CF₃)₂). **¹H¹³C NMR (101 MHz,**

CD₂Cl₂): δ (ppm) = 168.35 (C3), 166.20 (C1), 137.63 (C8), 134.76 (C5), 131.60 (C7), 124.16 (C9/C10), 123.76 (C4), 119.90 (C9/C10), 117.40 (C2), 115.93 (C6), 43.88 (NMe₂), 17.97 (OCH₃(CF₃)₂). **¹H¹⁹F NMR (470 MHz, CD₂Cl₂)**: δ (ppm) = -80.38 (s).

Synthesis of 4. In glovebox, complex **1** (94 mg, 0.2 mmol) and B(C₆F₅)₃ (102 mg, 0.2 mmol, 1 equiv.) were introduced in a Schlenk tube, solubilized in 4 mL of dry CH₂Cl₂ and allowed to stir one night at room temperature. After solvent removing, a white solid was obtained (167mg, 87% yield). The complex (cca 10 mg) was dissolved in CD₂Cl₂ to give a white suspension which became clear when 0.1 mL of Pyridine-D₅ was added. The signals detected by ¹H NMR analysis were large at the beginning but after one night the signals became sharp and allow the characterization of the aluminum cation **4**. **Elemental Analysis:** calcd for (C₄₃H₃₅AlBF₁₅N₄O₂)₁₀₀(C₂H₆OSi)₁₀₀: C, 52.14; H, 3.99; N, 5.40. Found: C, 51.76; H, 4.25; N, 5.15. **¹H NMR (500 MHz, CD₂Cl₂ + Pyridine-D₅, 298K)**: δ (ppm) = 7.26-7.18 (m, 4H, H5 + H7), 6.91 (d, *J* = 7.8 Hz, 2H, H6), 6.58 (t, *J* = 7.8 Hz, 2H, H4), 3.64 (s, 4H, H8), 3.38 (q, *J* = 7.0 Hz, 8H, N(CH₂CH₃)₂), 1.11 (t, *J* = 7.0 Hz, 12H, N(CH₂CH₃)₂), 0.69 (s, 3H, BMe). **¹H¹³C NMR (125 MHz, CD₂Cl₂ + Pyridine-D₅)**: δ (ppm) = 172.53 (C1), 166.64 (C3), 148.30 (m, CF), 139.31 (m, CF), 138.21 (m, CF), 137.38 (m, CF), 135.78 (C5 or C7), 132.83 (C7 or C5), 123.80 (C4), 1118.66 (C2), 117.47 (C6), 47.84 (N(CH₂CH₃)₂), 47.03 (C9), 15.01 (N(CH₂CH₃)₂), 11.20 (BMe). **¹⁹F NMR (470 MHz, CD₂Cl₂ + Pyridine-D₅)**: δ (ppm) = -132.81 (d, *J* = 19.1 Hz, 2F), -165.0 (t, *J* = 20.2 Hz, 1F), -167.59 (m, 2F).

Synthesis of 5. In glovebox, 88.5 mg (0.2 mmol) of complex **2** and 102.4 mg (0.2 mmol, 1 equiv.) of BCF were introduced in a Schlenk tube and solubilized in 4 mL of dry CH₂Cl₂. The mixture was stirred at r.t. for 1 h and the volatiles were evaporated under vacuum in glovebox. The crude product was then washed with pentane and dried under vacuum to afford 157 mg of complex

5 as a yellowish powder (82% yield). **Elemental Analysis:** calcd for $(C_{43}H_{27}AlBF_{15}N_4O_2)_{100}(CH_2Cl_2)_{48}$: C, 52.47; H, 2.83; N, 5.63. Found: C, 52.54; H, 3.12; N, 5.50.

1H NMR (400 MHz, CD_2Cl_2 + Pyridine- D_5): δ (ppm) = 7.46-7.31 (overlapping signals, 4H, H7/H5), 7.17-7.05 (overlapping signals, 4H, H4 + H9), 6.81 (m, 2H, H10), 6.67 (t, J = 7.8 Hz, 2H, H6), 3.13 (broad signal, 12H, NMe_2), 0.89 (s, 3H, BMe). **$\{^1H\}^{13}C$ NMR (101 MHz, CD_2Cl_2 + Pyridine- D_5):** δ (ppm) = 168.26 (C3), 165.29 (C1), 138.87 (C8), 136.14 (C5/C7), 132.45 (C5/C7), 126.55 (C9), 124.61 (C4), 122.23 (C10), 117.21 (C2 + C6), 44.70 (NMe_2), 10.98 (CH_3 , BMe , deducted from HSQC). CF not seen. **^{19}F NMR (470 MHz, CD_2Cl_2 + Pyridine- D_5):** δ (ppm) = -132.77 (d, J = 19.9 Hz, 2F), -165.03 (t, J = 20.7 Hz, 1F), -167.59 (m, 2F).

Polymer synthesis procedure: Under argon, 288.3 mg (2.00 mmol) of *rac*-Lactide and 0.01 equiv. of catalyst are weighed in a vial then mixed in the chosen solvent. Afterwards, 0.01 equiv. of co-initiator is added with a 5 μ L Hamilton then the vial is crimped and let stirred at the desired temperature.

Gel Permeation analysis: The number-average, weight-average masses (M_n and M_w respectively) and molar distribution (M_w/M_n) of the polyester samples were determined by size exclusion chromatography at 30°C with the Agilent 1260 Infinity system equipped with Varian 390-LC refractometer detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. A 5 μ m pre-column and two aligned Polypore 5 μ m (7.5 \times 300 mm) were used. Calibration were performed using polystyrene standards (900-1 000 000 g/mol) and raw values of M_n were thus obtained.

MALDI-ToF analysis: Mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-ToF-Microflex LRF, Bruker Daltonics). An external quadratic multi-point calibration was carried out before each measurement using polyethylene glycol (PEG) mixed in methanol

with dithranol (DIT). Analysis were performed with DIT as matrix (10 mg/mL) and sodium trifluoroacetic acid (10 mg/mL) as an additive. The polymer (10 mg/mL), the matrix and the additive were mixed in a volumetric ratio of 1/1/0.5 in THF. All the analysis was performed in positive reflectron mode.

Computational details: All Quantum mechanics calculations were performed using the Gaussian 16 package.¹⁹ Energy and forces were computed by density functional theory with the hybrid meta GGA M06-2X exchange-correlation functional.²⁰ The DCM solvent effects were modelled by means of the continuum model as implemented in Gaussian. Geometries were optimized and characterized with the 6-31+G(d,p) basis set. Gibbs free energies have been computed at 298K and 1 atm using unscaled density functional frequencies. Transition states were localized using the string theory²¹ as implemented in Opt'n Path.²² Molecular structures are drawn with the Chemcraft software.²³

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.xxxxxxx. full experimental details and analyses for compounds [L1H₄]Br₂, [L2H₂], 1-5 ; computational details ; GPC analysis and MALDI-TOF spectra ; crystallographic tables (PDF); Crystallographic Information Files (CIF).

AUTHOR INFORMATION

Corresponding Authors

Raluca Malacea-Kabbara* Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR 6302, Université de Bourgogne, 9 avenue Alain Savary 21000 Dijon (FR). Email: raluca.malacea@u-bourgogne.fr; <https://orcid.org/0000-0002-6684-1967>.

Paul Fleurat-Lessard* Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR 6302, Université de Bourgogne, 9 avenue Alain Savary 21000 Dijon (FR). Email: Paul.Fleurat-Lessard@u-bourgogne.fr; <http://orcid.org/0000-0003-3114-2522>.

Pierre Le Gendre* Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR 6302, Université de Bourgogne, 9 avenue Alain Savary 21000 Dijon (FR). Email: pierre.le-gendre@u-bourgogne.fr; <https://orcid.org/0000-0003-2635-5216>.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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