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# Aluminum complexes of mono-pyrrolidine ligands for the controlled ring opening polymerization of lactide

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Supporting Information Placeholder

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**ABSTRACT:** In this paper we report the full characterization (solution-state NMR spectroscopy and solid-state structures) of a series of Al(III) half-salan complexes and their exploitation for the ring opening polymerization of *rac*-lactide. Depending on the ligand employed and stoichiometry of the complexation, structures of the form Al(X)<sub>2</sub>Me or Al(X)Me<sub>2</sub> were isolated. Interestingly Al(2)<sub>2</sub>Me and Al(2)Me<sub>2</sub> produce PLA with a strong isotactic bias ( $P_m$  up to 0.80) whereas all other complexes produced atactic PLA. This is in contrast to recent studies on similar salan ligand systems. PLA with predictable molecular weights and narrow distributions were achieved. The results are discussed in terms of steric and electronic properties of the ligands.

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## INTRODUCTION

Currently, there is a tremendous desire to develop new polymeric materials that are biodegradable and sourced from annually renewable raw materials.<sup>1</sup> Unquestionably one of the most important polymers that fulfil these criteria is polylactide (PLA). PLA is prepared from the ring opening polymerization (ROP) of the cyclic ester monomer, lactide (LA). LA is typically utilized as either the enantiomerically pure L-LA or as a racemic mixture of D and L monomers (*rac*-LA). When *rac*-LA is utilized either atactic, heterotactic or isotactic PLA can be prepared, with the physical properties of the polymer being intrinsically linked to the polymer's microstructure. The microstructure can be controlled by judicious choice of metal center and ligand. For example, there are many elegant stereoselective polymerizations employing groups 1-4 metal centers,<sup>2</sup> lanthanides,<sup>3</sup> indium,<sup>4</sup> zinc<sup>5</sup> and pertinent to this study aluminum.<sup>6</sup> This follows on from seminal contributions by Feijen,<sup>6a</sup> Chisholm,<sup>7</sup> Gibson<sup>8</sup> and Coates<sup>2p,9</sup> in the early part of this century. More recently, a tremendous amount of effort has been focussed on understanding the subtle interplay between the metal-center and ligand and the consequence this has on the stereochemistry of the resulting polymer.<sup>2o,2v</sup> Subtle changes in selectivity have been observed by Williams for phosphasalen lanthanide complexes and by Ma for a series aminophenolate Zn(II)/Mg(II) complexes.<sup>2o,10</sup> However, it is fair to say that there is a degree of serendipity in the stereochemical outcome of the polymerization, with unpredictable tacticities achieved from metal-ligand combinations. Furthermore, subtle changes to the ligand can significantly alter the rate of polymerization.<sup>6f</sup> In this regard we have shown that simply reducing a salalen to a salan dramatically increases the rate of ROP of *rac*-LA.<sup>6f</sup> Tolman and co-workers have demonstrated, with a series of Al(III)-salen complexes, that the ortho substituent on the phenyl ring of the salen can induce distortions which can have a massive impact on the rate of polymerization of caprolactone. In this case it is shown that bulky substituents distort the geometry around the

Al(III) center, which is believed to be responsible for the observed increase in polymerization rate.<sup>11</sup>

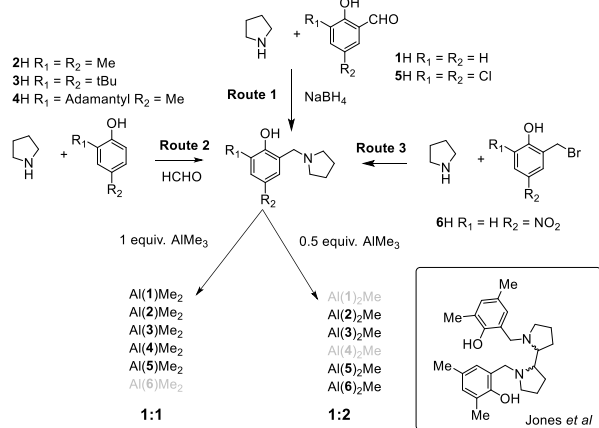
Recently, we have demonstrated the importance of bipyrrrolidine derived salan ligands for controlling the stereochemical outcome for *rac*-LA polymerization.<sup>2u,2v</sup> For example, when a meso-bipyrrrolidine salan ligand, Figure 1, is complexed to Zr(IV) the resulting initiator shows a high isotactic tendency ( $P_m$  up to 0.86).<sup>2u</sup> Interestingly, when the same ligand is complexed to Al(III) highly heterotactic PLA is produced ( $P_r$  up to 0.87).<sup>2v</sup> Moreover, for the tBu analogue, atactic PLA was produced in the melt (130 °C) after 48 hours and it was shown that the complex was inactive in solution.<sup>2v</sup> The In(III) complex of the meso tBu bipyrrrolidine produced heterotactic PLA in solution ( $P_r$  up to 0.84).<sup>4b</sup> The exact reasons for these dramatic switches in selectivity and activity are still open to debate. Kol has also successfully shown the importance of these pyrrolidine rings in salalen complexes of Al(III) for the controlled isotactic selective polymerization of *rac*-LA.<sup>2s,12</sup> As part of ongoing studies in the area of pyrrolidine systems we have prepared a series of mono-pyrrolidine ligands and their respective Al(III) complexes. These were and screened for the ROP of *rac*-LA to further investigate how the ligand affects the stereochemical outcome of the polymerization. Moreover, the ligand framework could provide a more rigid environment around the aluminum center which could influence the stereochemical outcome of the ROP.

## RESULTS AND DISCUSSION

### Ligand and Complex Preparation

The ligands are easily prepared by one of three methods, Scheme 1. Route 1 employs a reductive amination to prepare ligand **1/5H**, route 2 utilizes a modified Mannich reaction (**2-4H**) or route 3 *via* an S<sub>N</sub>2 reaction mechanism (**6H**).<sup>13</sup> In our hands these approaches were found to be the optimal synthesis for each ligand. The ligands themselves are relatively simple, which is a pre-requisite for large-scale applications (in-fact **1H** is commercially available). However, to our surprise, there is

only one crystallographically characterized metal complex of this class of ligand: Shen and co-workers have prepared a series of La(III) complexes, which have been screened for the polymerization of  $\epsilon$ -caprolactone.<sup>14</sup> All ligands synthesized here have been characterized *via*  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy and high resolution mass spectrometry. In the  $^1\text{H}$  NMR spectrum there was a sharp singlet at ca. 4 ppm for the methylene protons, Ar-CH<sub>2</sub>-N. The ligands were reacted with either 0.5 or 1 equiv. of AlMe<sub>3</sub> in an attempt to form the desired complexes, Scheme 1. A further aim of this study was to compare these ligands to the bipyrrolidine complexes we have recently published in an attempt to gain an insight into the high heteroselectivity of the Al-bipyrrolidine system.<sup>2v</sup>



Scheme 1: Synthesis of the ligands and attempted complexes used in this study, and our previous bipyrrolidine ligand for comparison. Those in pale grey were attempted but could not be isolated in a pure form.

Whilst scheme 1 shows all attempted synthesis only the following complexes could be isolated Al(1)Me<sub>2</sub>, Al(2)Me<sub>2</sub>, Al(3)Me<sub>2</sub>, Al(4)Me<sub>2</sub>, Al(5)Me<sub>2</sub>, Al(2)<sub>2</sub>Me, Al(3)<sub>2</sub>Me, Al(5)<sub>2</sub>Me, Al(6)<sub>2</sub>Me and characterized *via* single crystal X-ray diffraction. Table 1 has the key metric data for the complexes and representative structures for Al(X)<sub>2</sub>Me and Al(X)Me<sub>2</sub> where X = 2, are shown in Figure 1. In the other cases shown in scheme 1 a mixture of mono and bis-ligated complexes were observed in the crude mixture (regardless of stoichiometry), which could not be purified by recrystallization. It is relatively facile to distinguish between the two forms *via*  $^1\text{H}$  NMR spectroscopy, for example in the preparation of Al(1)Me<sub>2</sub> it was clear that a mixture of both forms {Al(1)Me<sub>2</sub> and Al(1)<sub>2</sub>Me} were observed in solution, see supporting information Figure S7. The mono-ligated complexes are tetrahedral in geometry with X-Al-Y angles close to 109°, Table 1. Whereas Al(X)<sub>2</sub>Me are pseudo trigonal bipyramidal, as observed by the  $\tau$  values being greater than 0.5, which are in agreement with other half salan-Al complexes in the literature.<sup>8</sup> As expected the Al-N distances for the mono-ligated system {1.9971(18) – 2.040(2) Å} are significantly shorter than the bis-ligated system {2.1131(17) – 2.1397(17) Å}. The metric data for both systems are in agreement with similar half-salan Al(III) reported complexes in the CCDC.<sup>8,15</sup> Moreover, comparing the systems there is little difference in the Al-O {1.760(2) – 1.7918(16) Å} and Al-C distances {1.954(3) – 1.987(4) Å} depending on the stoichiometry

or ligand, both in relatively tight ranges. The Al(X)Me<sub>2</sub> structures appear to be maintained in solution, this is exemplified for Al(3)Me<sub>2</sub> where discrete and relatively sharp resonances are observed for the –CH<sub>2</sub>– moieties in the solution-state NMR (C<sub>6</sub>D<sub>6</sub>). Further in all cases, one sharp 6H Al-Me resonance is observed at ca. –0.5 ppm. On an NMR scale Al(2)Me<sub>2</sub> was reacted with either 1 or 2 equivalents of BnOH, resultant spectra showed the rapid reaction of Al-Me with BnOH, to generate the alkoxide (SI figure 16, 17). DOSY investigations showed a reduction in the diffusion constant upon reaction with BnOH (SI figure 18), as might be expected by the removal of –Me by –OCH<sub>2</sub>Ph, although this does not conclusively rule out the formation of a dimeric alkoxide species. However, in the presence of a coordinating monomer, such as lactide, a monomeric active species is highly likely.

For the solid-state complexes of the form Al(X)<sub>2</sub>Me the ligands bind to the aluminum center so that the nitrogen moieties are *trans* to one another, N(1)-Al(1)-N(2) being in the range 169.29(7) – 172.06(7)°. Obviously, this differs from our bipyrrolidine system (and other tetra-dentate salan systems in the CCDC) in which the tetradentate nature of the ligand dictates them to be *cis* to each other.<sup>2v</sup> All metric data are in agreement within the series regardless of the ligand's substituent. In solution the complexes appear to have a degree of fluxionality as indicated by broad resonances in the region ca. 2-4 ppm for the pyrrolidine ring and –CH<sub>2</sub>– methylene. In an attempt to aid resolution a solution of Al(3/5)<sub>2</sub>Me in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> were investigated *via* variable temperature  $^1\text{H}$  NMR spectroscopy. The resulting spectra were complex with multiple resonances being observed, see supporting information figure S13 and S14. When heated sharp resonances indicative of a monomeric species were observed, this is important at the polymerization takes place at higher temperatures. However, in all cases at room temperature analysis of the aromatic region of the  $^1\text{H}$  NMR spectrum indicated the required number of resonance for this motif and there is single 6H resonance for the Al-Me moiety. However, as the system cooled the Al-Me resonance splits into two signals. This coupled with a significantly more complex aliphatic region at low temperature potentially indicates that multiple coordination motifs are present in solution upon cooling.

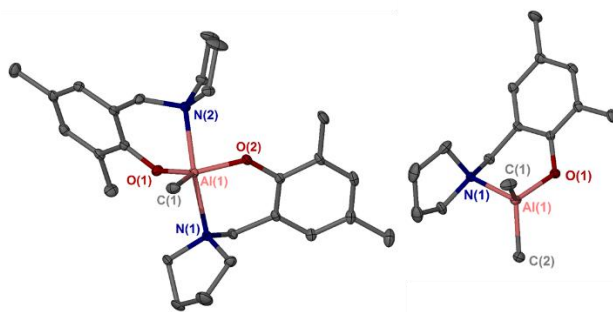


Figure 1: Solid-state structures for Al(2)<sub>2</sub>Me (left) and Al(2)Me<sub>2</sub> (right), ellipsoids are shown at the 30% probability level and all hydrogen atoms and solvent of crystallization have been removed for clarity

**Table 1:** Selected bond lengths (Å) and angles (°) for the complexes characterized *via* single crystal X-ray diffraction. The  $\tau$  values have been determined *via* the method of Atwood et al.<sup>16</sup>

	Al(1)Me <sub>2</sub>	Al(2)Me <sub>2</sub>	Al(3)Me <sub>2</sub>	Al(4)Me <sub>2</sub>	Al(5)Me <sub>2</sub>	Al(2) <sub>2</sub> Me	Al(3) <sub>2</sub> Me	Al(5) <sub>2</sub> Me	Al(6) <sub>2</sub> Me
Al(1)-O(1)	1.7745(10)	1.7644(18)	1.760(2)	1.7769(17)	1.7606(14)	1.770(2)	1.7916(13)	1.7873(17)	1.7846(15)
Al(1)-O(2)	-	-	-	-	-	1.770(2)	1.7870(14)	1.7830(15)	1.7918(16)
Al(1)-N(1)	2.0300(11)	2.040(2)	2.029(2)	2.047(2)	1.9971(18)	2.139(3)	2.1261(18)	2.125(2)	2.1131(17)
Al(1)-N(2)	-	-	-	-	-	2.132(3)	2.1377(18)	2.125(2)	2.1397(17)
Al(1)-C(1)	1.9639(14)	1.954(3)	1.963(3)	1.964(3)	1.964(2)	1.987(4)	1.981(2)	1.973(2)	1.983(2)
Al(1)-C(2)	1.9579(14)	1.956(3)	1.956(3)	1.952(3)	1.956(2)	-	-	-	-
O(1)-Al(1)-N(1)	98.13(4)	97.43(8)	97.46(9)	97.45(8)	95.58(7)	87.77(11)	87.85(6)	89.55(7)	89.48(7)
N(1)-Al(1)-N(2)	-	-	-	-	-	170.41(11)	172.06(7)	167.88(8)	169.29(7)
O(1)-Al(1)-O(2)	-	-	-	-	-	118.98(13)	117.28(7)	118.46(8)	119.41(7)
C(1)-Al(1)-O(1)	112.06(9)	111.22(11)	112.37(13)	111.88(10)	112.27(9)	118.66(15)	121.52(9)	119.08(9)	120.77(10)
$\tau$	-	-	-	-	-	0.81	0.84	0.77	0.81

## Polymerization Studies

The most pertinent comparison in the literature to the complexes herein is with our bipyrrrolidine salan system (either meso or homochiral versions).<sup>2u,2v</sup> When complexed to Al(III) this bipyrrrolidine ligand (with methyl substituents in the ortho/para position) produces either heterotactic PLA (meso chirality) or atactic (homochiral ligand) PLA. For example, with the meso-bipyrrrolidine-Al-Me complex at 100:1:1 (LA:Init:BnOH) in toluene at 80 °C a conversion of 87% was achieved after 120 hrs ( $M_n = 21550$ ,  $\bar{D} = 1.05$ ,  $P_r = 0.87$ ). However, with the tBu substituted ligand atactic PLA was observed and it was concluded that with this bipyrrrolidine system heterotactic PLA was due to a combination of steric bulk of the ortho substituent and the meso chirality of the ligand. In the current study we have removed any effect ligand chirality may have on the stereochemical outcome of the polymerization. However, the coordination motif is now subtly different to our previously reported study.<sup>2v</sup>

The complexes were tested for the ROP of *rac*-LA in solution with the addition of BnOH to generate the alkoxide *in-situ*, Table 2. MALDI-ToF mass spectrometry indicated the BnO- and H- end groups as expected (entry 12), a major series with a repeat unit of 144 gmol<sup>-1</sup> and a minor series of 72 gmol<sup>-1</sup> was observed due to transesterification. We suggest that the mechanism for polymerization is the classical coordination insertion mechanism, as both sets of complexes react with BnOH in solution (see SI Figure 16,17).<sup>17</sup> For the Al(X)<sub>2</sub>Me complexes there is relatively good agreement between the observed molecular weights and theoretical molecular weight with narrow distributions observed in all cases. However, for Al(3)<sub>2</sub>Me the observed molecular weight was considerably higher than the theoretical, this may well be related to the increase steric bulk of the ortho substitute hindering the formation of the Al-alkoxide, thus reducing the concentration of the active species in solution or poor initiation. Al(2)<sub>2</sub>Me was also trialed in the melt (entries 3-4). Without the addition of BnOH the polymer molecular weight was not predictable, however with the addition of BnOH there was excellent agreement and PLA with a narrow  $\bar{D}$  was isolated. The polymer tacticity, assessed by <sup>1</sup>H{<sup>1</sup>H} NMR spec-

troscopy, showed Al(2)<sub>2</sub>Me produced PLA with a moderate isotacticity ( $P_m = 0.71$ ) whereas all other Al(X)<sub>2</sub>Me complexes afforded atactic PLA.

For the Al(X)Me<sub>2</sub> systems again there was good agreement between the theoretical and calculated molecular weight and MALDI-ToF indicated the desired end groups. The high degree of control was exemplified by a linear relationship between conversion and molecular weight for Al(2)Me<sub>2</sub>, Figure 2, with a gradient of ca. 144 gmol<sup>-1</sup> indicative of one chain growing per metal center and the  $\bar{D}$  remained below 1.10. Furthermore, when the equivalents of BnOH was varied (entry 12 vs. 13) then there is a concomitant reduction in the observed molecular weight, and without BnOH (entry 14) there is a small degree of conversion. This system is also active under melt conditions (entries 15 and 16) with high conversion in a relatively short timeframe. Noteworthy, is that at a ratio of 1000:1:10 under melt conditions a 92% conversion was achieved in just 30 mins with a predictable molecular weight and narrow distribution. This is a significantly shorter timeframe than the tetradentate salan complex.<sup>2v</sup>

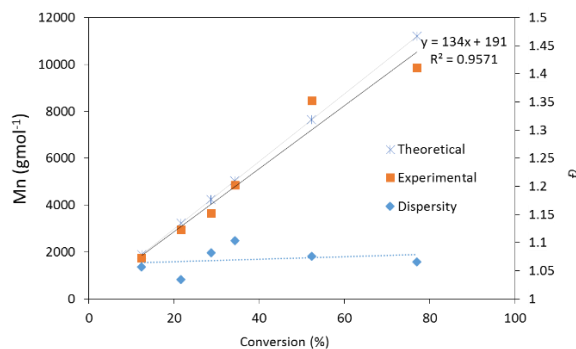


Figure 2: Plot of measured  $M_n$  and  $\bar{D}$  vs. conversion for the polymerization of *rac*-LA with Al(2)Me<sub>2</sub> (80 °C, 100:1:1 LA:Init:BnOH, solvent: toluene).

**Table 2:** Solution and Melt polymerization for the range of Al(III) complexes prepared. [<sup>a</sup> toluene solvent, <sup>b</sup> solvent free (melt conditions); <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub>; <sup>d</sup> determined from analysis of the <sup>1</sup>H NMR spectrum; <sup>e</sup> as determined from <sup>1</sup>H{<sup>1</sup>H} NMR; <sup>f</sup> as determined by GPC (THF) calibrated using RI, viscometer and light scattering detectors using the Universal calibration method via multi-detection software; <sup>g</sup> Theoretical molecular weight calculated from conversion {[LA]/[BnOH]} × (Conv. × 144.13) + 108.14 (rounded to the nearest 50).]

Entry	Initiator	[LA]:[I]:[BnOH]	Temp./°C	Time/ h	Conv./ % <sup>d</sup>	<i>P<sub>m</sub></i> <sup>e</sup>	<i>M<sub>n</sub></i> <sup>f</sup>	<i>D<sub>f</sub></i>	Calc <i>M<sub>n</sub></i> <sup>g</sup>
1	Al(2) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	6	38	0.72	4210	1.02	5550
2	Al(2) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	24	95	0.71	8780	1.04	13750
3	Al(2) <sub>2</sub> Me	100:1:0	130 <sup>b</sup>	0.25	60	0.62	18500	1.24	8750
4	Al(2) <sub>2</sub> Me	100:1:1	130 <sup>b</sup>	0.25	94	0.58	14850	1.10	13650
5	Al(2) <sub>2</sub> Me	100:1:1	25 <sup>c</sup>	120	17	-	-	-	2550
6	Al(3) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	48	32	0.52	24250	1.28	4650
7	Al(5) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	6	36	0.49	4650	1.18	5300
8	Al(5) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	24	96	0.48	11950	1.17	13950
9	Al(6) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	6	48	0.61	4350	1.07	6950
10	Al(6) <sub>2</sub> Me	100:1:1	80 <sup>a</sup>	24	72	0.59	12750	1.10	10400
11	Al(1)Me <sub>2</sub>	100:1:1	80 <sup>a</sup>	6	84	0.53	8250	1.06	12154
12	Al(2)Me <sub>2</sub>	100:1:1	80 <sup>a</sup>	6	73	0.80	9250	1.05	10550
13	Al(2)Me <sub>2</sub>	100:1:2	80 <sup>a</sup>	6	52	0.68	6050	1.06	7400
14	Al(2)Me <sub>2</sub>	100:1:0	80 <sup>a</sup>	6	23	-	-	-	3350
15	Al(2)Me <sub>2</sub>	100:1:1	130 <sup>b</sup>	0.16	73	0.61	12550	1.23	10550
16	Al(2)Me <sub>2</sub>	1000:1:10	130 <sup>b</sup>	0.5	92	0.56	18200	1.10	13300
17	Al(3)Me <sub>2</sub>	100:1:1	80 <sup>a</sup>	24	16	-	-	-	2400
18	Al(4)Me <sub>2</sub>	100:1:1	80 <sup>a</sup>	24	12	-	-	-	1850
19	Al(5)Me <sub>2</sub>	100:1:1	80 <sup>a</sup>	6	74	0.61	8800	1.06	10700
20	Al(5)Me <sub>2</sub>	100:1:2	80 <sup>a</sup>	6	68	0.55	5300	1.07	4950

For Al(2)Me<sub>2</sub> PLA with a strong isotactic bias was observed with *P<sub>m</sub>* = 0.80. Analysis of the <sup>1</sup>H{<sup>1</sup>H} NMR spectrum showed a reduced *sis* tetrad, indicative of PLA possessing a “blocky” nature is formed. Moreover, the *sii*, *iis* and *isi* tetrads are approximately 1:1:1 which is indicative of a chain end mechanism in operation.<sup>2v</sup> It is interesting that regardless of stoichiometry complexes with 2H have an isotactic tendency. This is in stark contrast to the Al(III) complex of the tetradentate version.<sup>2v</sup> It is not uncommon that minor changes to the substituents on the phenyl group of salan/salen or salalen ligands to induce difference stereochemical outcomes.<sup>2v,18</sup> However, it is far less common to compare two bidentate ligands to the tetradentate system. The exact reason for the dramatic switch is not fully known but is potentially related to change in coordination motif of the ligand around the metal center which in turn will alter the path of lactide coordination to the metal center.

The rate of polymerization has been investigated and Table 3 shows a comparison of *k<sub>app</sub>* for a representative sample of initiators. The mono-ligated systems appear to be faster {Al(2)<sub>2</sub>Me vs. Al(2)Me<sub>2</sub> and Al(5)<sub>2</sub>Me vs. Al(5)Me<sub>2</sub>} which may be related to the reduce steric crowding around the Al(III) center facilitating facile coordination of the monomer. As expected as the size of the ortho substituent increases (H – Me –tBu) there is a reduction in the apparent first order rate constant. Again this can be explained in terms of steric crowding around the metal center. The polymerization of L-LA was investigated with Al(2)<sub>2</sub>Me and in this case polymerization rate was faster than

with *rac*-LA, which is to be expected from an isoselective initiator.

**Table 3:** *k<sub>app</sub>* values for various initiators. Temperature = 80 °C, solvent C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, [LA]<sub>0</sub> = 0.69 moldm<sup>-3</sup>.

Initiator	Conditions (LA:Init:BnOH)	<i>k<sub>app</sub></i> /mins <sup>-1</sup>
Al(2) <sub>2</sub> Me	100:1:1 <i>rac</i> -LA	6.5 × 10 <sup>-4</sup>
Al(2) <sub>2</sub> Me	100:1:1 L-LA	10.2 × 10 <sup>-4</sup>
Al(5) <sub>2</sub> Me	100:1:1 <i>rac</i> -LA	5.6 × 10 <sup>-4</sup>
Al(1)Me <sub>2</sub>	100:1:1 <i>rac</i> -LA	19.2 × 10 <sup>-4</sup>
Al(2)Me <sub>2</sub>	100:1:1 <i>rac</i> -LA	18.8 × 10 <sup>-4</sup>
Al(2)Me <sub>2</sub>	100:1:2 <i>rac</i> -LA	19.7 × 10 <sup>-4</sup>
Al(3)Me <sub>2</sub>	100:1:1 <i>rac</i> -LA	1.3 × 10 <sup>-4</sup>
Al(5)Me <sub>2</sub>	100:1:1 <i>rac</i> -LA	13.5 × 10 <sup>-4</sup>

## Conclusions

In conclusion nine half-salan Al(III) complexes have been prepared and fully characterized in solution and in the solid-state. The ligands have been chosen to investigate the steric and electronic effects on the polymerization. Complexes Al(2)<sub>2</sub>Me and Al(2)Me<sub>2</sub> produce PLA with a high isotactic bias, which is in stark contrast to previously reported complexes.<sup>2v</sup> The other complexes produced predominately atactic PLA. It therefore appears that the steric requirements are the overriding requirement for the production of isotactic PLA. Moreover, it is interesting to compare this half salan to the full bipyrrrolidine salan, which has a high heterotactic enchainment. This illustrates the

very subtle interplay between ligand coordination and selectivity. Such a change between bidentate half salan and tetradentate salan ligands, to our knowledge, is unprecedented.

## EXPERIMENTAL SECTION

The preparation and characterization of all metal complexes was carried out under inert argon atmosphere using standard Schlenk or glovebox techniques. All chemicals used were purchased from Aldrich and used as received except for *rac*-LA which was recrystallized from dry toluene. Dry solvents used in handling metal complexes were obtained *via* SPS (solvent purification system). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual protio solvent peaks. CDCl<sub>3</sub>/C<sub>6</sub>D<sub>6</sub> were dried over CaH<sub>2</sub> prior to use with metal complexes. Coupling constants are given in Hertz. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University. All details are given as supporting information, but a representative synthesis is provided below. The following general synthesis for the 1:2 metal:ligand complexes was followed: The ligand (1.0 mmol) was dissolved in toluene (10 ml), to this AlMe<sub>3</sub> (0.5 mmol) was added slowly. After 1 hour the solvent was removed and the resulting product recrystallized from a hexane/toluene mixture, typically crystals were isolated after cooling to -20 °C overnight. Al(5)<sub>2</sub>Me isolated as a yellow powder (64 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, δ<sub>H</sub>, ppm, 298 K); 7.38 (2H, d, J = 2.3 Hz, ArH), 6.52 (2H, d, J = 2.3 Hz, ArH), 3.55 (2H, m, NCH<sub>2</sub>), 3.15 (4H, m, NCH<sub>2</sub>), 2.79 (4H, m, NCH<sub>2</sub>), 1.32 (8H, m, CH<sub>2</sub>), -0.69 (3H, s, CH<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, δ<sub>C</sub>, ppm): 154.7 (C-O), 129.0 (Ar), 125.8 (Ar), 125.5 (Ar), 124.5 (Ar), 121.0 (Ar), 57.1 (NCH<sub>2</sub>), 53.1 (NCH<sub>2</sub>), 22.4 (CH<sub>2</sub>), 21.3 (CH<sub>2</sub>), -12.3 (CH<sub>3</sub>). Elemental (CHN) Analysis; (Cald: C<sub>23</sub>H<sub>27</sub>N<sub>2</sub>Cl<sub>4</sub>O<sub>2</sub>Al<sub>1</sub>) C: 51.90%, H: 5.11%, N: 5.26%, (Exp.) C: 51.65%, H: 5.06%, N: 5.03%. For the synthesis of mono-ligated complexes, a solution of ligand (1.0 mmol) dissolved in toluene (5 ml) was added slowly to a solution of AlMe<sub>3</sub> (1.0 mmol) in toluene (5 ml). Work up procedures follow the methods for bis-ligated complexes. Al(5)Me<sub>2</sub> isolated as a white solid (59 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, δ<sub>H</sub>, ppm); 7.38 (1H, d, J = 2.8 Hz, ArH), 6.47 (1H, d, J = 2.8 Hz, ArH), 2.89 (2H, s, CH<sub>2</sub>), 2.38 (2H, m, NCH<sub>2</sub>), 1.61 (2H, m, NCH<sub>2</sub>), 1.11 (2H, m, CH<sub>2</sub>), 1.01 (2H, m, CH<sub>2</sub>), -0.57 (6H, s, CH<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, δ<sub>C</sub>, ppm): 155.3 (C-O), 130.5 (Ar), 127.7 (Ar), 125.5 (Ar), 123.8 (Ar), 120.9 (Ar), 58.4 (NCH<sub>2</sub>), 54.0 (NCH<sub>2</sub>), 22.4 (CH<sub>2</sub>), -11.3 (CH<sub>3</sub>). Elemental (CHN) Analysis; (Cald: C<sub>13</sub>H<sub>18</sub>N<sub>1</sub>Cl<sub>2</sub>O<sub>1</sub>Al<sub>1</sub>) C: 51.66%, H: 6.00%, N: 4.64%, (Exp.) C: 50.85%, H: 5.89%, N: 5.25%.

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Crystallographic data (CIF)

Summary of NMR, GPC and kinetic data (PDF)

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### Notes

The authors declare no competing financial interest.

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