FULL PAPER

Iron (III) Salalen Complexes for the Polymerisation of Lactide

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Abstract: Herein, we report the preparation and characterisation of iron (III) salalen complexes, with variation of ligand substituents and backbone investigated. Six new complexes were prepared and characterised by elemental analysis, mass spectrometry and X-ray crystallography. These complexes have been applied for the ring opening polymerisation (ROP) of *rac*-lactide in propylene oxide. Fe(**1**)Cl was found to have a moderate isotactic preference (P_m = 0.75 – 0.80) and demonstrated good molecular weight control in solution (Đ = 1.02 – 1.18). Fe(**2**-**7**)Cl were also active for ROP and activities could be related to ligand structure.

Introduction

There is a growing need for a shift in manufacturing towards more sustainable products and processes. This is increasingly true for the production of plastics, the majority of which are derived from crude oil.[1] Plastics have rapidly become widely used in many applications due to their durability and lightweight properties. They are widely used for single use applications, especially in packaging and more high value healthcare sectors.[2] However, the very properties that make plastics useful has now been recognised to be a severe drawback. Plastic waste persists in the environment and it is estimated that 79% is accumulated in landfills or, worse, in the environment.[2] A potential solution to these issues is a switch to more sustainable and degradable plastics. A candidate for replacing conventional packaging materials is poly(lactic acid) (PLA). PLA has the added benefit of being renewable and biodegradable. PLA is preferentially formed through ring opening polymerisation (ROP) of the cyclic dimer, lactide.[3–5] A key challenge in this field is the stereoselective ROP of a racemic blend of lactide monomers (*L* /*D*) to give a stereoblock or stereocomplexed PLA, a polymer with improved thermal properties.[6] This can be achieved by application of metal initiator complexes capable of differentiating between the two enantiomers. A range of metal/ligand systems have been shown to achieve this. Aluminium salen complexes of Spassky, Feijen and Nomura demonstrated strong isotactic bias.[7–13] These works show the capability of both chiral and achiral complexes in achieving stereocontrol. Aluminium salan complexes have also been reported for the stereocontrolled ROP of *rac*-LA.[14–16] Further examples of isoselectivity have been reported with metals including Na(I)/K(I),[17–21] Mg(II),[22] Zn(II),[23–25] Ga(III),[26,27] Y(III),[28–31] Lu(III),[32,33] In(III),[27,34–37] and Zr(IV)/Hf(IV). [38,39]

There are a limited number of papers concerning Fe mediated ROP of lactide, particularly Fe(III). Benefits of this metal include high abundance, low cost, and biocompatibility. In some cases, such complexes may also be air stable. Simple ferric alkoxides, $Fe(OR)_3$, have been shown to be active for lactide polymerisation under solvent free conditions.[40] For this system, no epimerisation was observed but intermolecular transesterification was operational. Fe(III) clusters with benzyl alkoxide and ethoxide have also shown activity for ROP,[41] with good molecular weight control and rapid polymerisation at 70°C. Formation of amidinate alkoxide complexes reduces activity while maintaining good control.[42] Interestingly, Byers and co-workers report electrochemically switchable Fe(III)/Fe(II) systems which were inactive for lactide ROP as Fe(III) but active when reduced.[43,44] [ONO] Fe(III) complexes have also been demonstrated for ROP of lactide.[45,46] Iron (III) salen complexes have been reported by Duan and co-workers.[47,48] These complexes generally had an isotactic bias for the ROP of *rac*-LA, with a chain end controlled mechanism being suggested.

Salalens are an important ligand class, enabling selective, controlled catalysis when complexed to a range of metal centres.[49-63] An advantageous feature of these ligands is the variability in the structure, with there being many points of functionalisation. Jones and co-workers first demonstrated the use of Al(III) salalen complexes for the ROP of *rac*-LA.[64] This study involved an ethylene diamine backbone with a range of aryl and amine nitrogen substituents. Resultant polymer tacticity was found to depend on identity of the group on the amine nitrogen centre. The effect of the ortho aryl substituents upon tacticity was also elucidated by DFT calculations.[65] Use of a phenylene backbone caused a switch in tacticity, when compared to ethylene based salalens, with the same aryl and nitrogen substituents.[66] The use of chiral ligand backbones has also been shown influence catalytic activity and the resultant polymer stereochemistry.[67–69] This was particularly highlighted by Kol and co-workers who utilised chiral aminomethylpyrrolidine Al(III) complexes for the ROP of lactide.[69] For this system, stereocontrol was dictated by aryl substituents with both chain end and enantiomorphic site control mechanisms being operational. Salalen complexes of other metals {Ti(IV), Zr(IV), Hf(IV), Y(III), Sm(III) and Nd(III)} have also been successfully applied to the ROP of lactide.[66,70–74] Recently, Lamberti and co-workers have reported the first example of an Fe(III) salalen {Fe(**1**)Cl}.[75] However, the polymerisation of *L*-LA was unsuccessful under the conditions tested.

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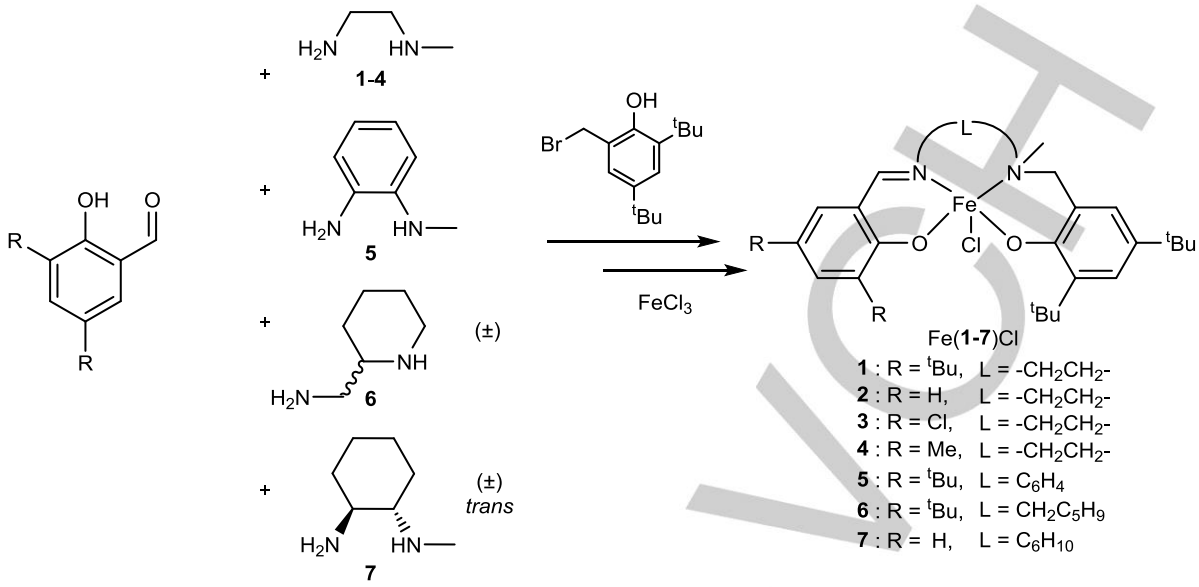

Scheme 1. Synthesis of ligands and complexes used in this study.

In this work, we have prepared a range of salalen ligands based on literature examples,[66–68,72] and explored further Fe(III) salalen complexes. Different aryl and backbone substituents were used to investigate structure-activity-relationships in the ROP polymerisation of *rac*-LA.

Results and Discussion

Complexation of salalen ligands to Fe(III) was achieved with anhydrous ferric chloride in the presence of triethylamine (Scheme 1). Complexation was initially carried out in refluxing THF in air {Fe(**1,2,6**)Cl}. After filtration and recrystallisation (see ESI for solvents), the product was confirmed by high-resolution mass-spectrometry (HR-MS) and elemental analysis. Mass spectrometry confirmed the coordination of ligand to metal, achieving ionisation by loss of Cl·. For the complexation of **2**, X-ray crystallography indicated an oxo-bridged structure, [Fe(**2**)]$_2$O. Despite this, elemental analysis was consistent with Fe(**2**)Cl and it is suggested that the oxo bridged dimer may have formed during prolonged exposure to the solution for recrystallisation. As a precaution, however, subsequent complexations were carried out under argon in dry toluene {Fe(**3,4,5,7**)Cl}. Once again, elemental analysis and HR-MS conformed to the expected product. MALDI-ToF was also used to further characterise some of the complexes, showing a good match of experimental and theoretical isotopic distribution patterns (See ESI).

Once isolated, complexes were stored in air, showing no signs of decomposition and no loss in catalytic activity. For Fe(**1**/**4**/**5**/**6**)Cl, X-ray crystallography confirmed the solid-state structure, revealing a five coordinate geometry in each case (Table 1, Figure 1). Geometric preference, τ, has been quantified using the two largest coordination angles.[76] A slight preference for a trigonal bipyramidal geometry was generally observed (τ = 0.56 - 0.68, Table 1). The structure of Fe(**1**)Cl, has recently been reported, with data recorded at room temperature.[75] The structure reported herein is based upon data recorded at 150 K. This complex is observed to be disordered over two sites in a ratio of 92:8. Fe(**1**)Cl has the moderate preference towards a trigonal bipyramidal geometry (τ = 0.66). This preference is greater than that of the corresponding salen (τ = 0.47).[47] In all cases, the axial axis is occupied by O(1) and the secondary amine, N(2). A deviation from the anticipated axial angle is generally seen for each complex {Fe(**1**)Cl, O(1)-Fe-N(2) = 164.77(8)°}.

Table 1. Selected bond lengths (Å) and angles (°) of Fe(**1,4,5,6**)Cl

	Fe(**1**)Cl	Fe(**4**)Cl	Fe(**5**)Cl	Fe(**6**)Cl
τ	0.66	0.56	0.68	0.56
Fe-O(1)	1.9081(18)	1.8941(15)	1.892(4)	1.8977(15)
Fe-O(2)	1.8445(16)	1.8734(16)	1.835(4)	1.8532(14)
Fe-N(1)	2.047(2)	2.044(7)	2.064(4)	2.0634(17)
Fe-N(2)	2.300(2)	2.269(2)	2.260(5)	2.2486(18)
Fe-Cl(1)	2.2432(7)	2.2264(8)	2.236(2)	2.2492(7)
O(1)-Fe-N(2)	164.77(8)	157.48(9)	162.18(17)	161.92(7)
O(2)-Fe-N(1)	117.14(8)	123.48(19)	121.2(2)	128.35(7)
O(2)-Fe-Cl(1)	117.14(6)	116.56(56)	120.79(15)	116.33(5)
N(1)-Fe-N(2)	78.99(8)	76.8(2)	76.32(18)	78.73(6)
N(1)-Fe-Cl(1)	124.94(6)	119.03(18)	116.58(16)	114.72(5)

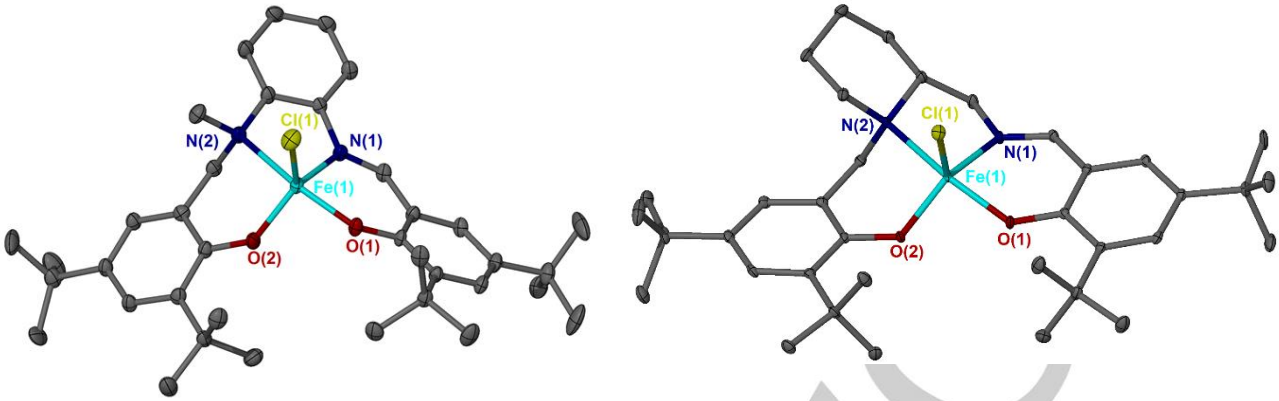

Figure 1. Solid-state structures of Fe(**5**)Cl (left) and Fe(**6**)Cl (right). Ellipsoids are shown at 30% probability level and all hydrogen atoms have been omitted for clarity.

The largest equatorial angle is either N(1)-Fe-Cl(1) {Fe(**1**)Cl, 124.94(6)°} or O(2)-Fe-N(1) {Fe(**6**)Cl, 128.35(7)°} being dependent on the steric constraints of ligand coordination. The reduction of steric bulk of the aryl substituents {Fe(**1**)Cl, R = ^{t}Bu vs. Fe(**4**)Cl R = Me} caused a decrease in geometric preference (τ = 0.56). Increasing the planarity of the backbone {Fe(**1**)Cl, L = -CH_2CH_2- vs. Fe(**5**)Cl, L = C_6H_4} had minimal effect on the geometric preference (τ = 0.68). Restricting the conformation of the backbone {Fe(**1**)Cl, L = -CH_2CH_2- vs. Fe(**6**)Cl, L = $CH_2C_5H_9$} also reduced the trigonal bipyramidal preference (τ = 0.56). The crystal data for [Fe(**2**)]$_2$O was poor but unambiguously showed the µ-oxo complex. Crystals for X-ray crystallography were also prepared for the complex based on **3**. However, this structure was found to be [Fe(**3**)]$_2$O (Figure 2). The elemental analysis of this complex conforms to the expected product of Fe(**3**)Cl, suggesting the solid-state structure is not representative of the bulk sample. The µ-oxo complex is most likely formed due prolonged recrystallisation time. Each iron centre is five coordinate with preference towards square based planarity (τ = 0.35) with the bridging oxygen in the apical position. The two ligands are rotated by 90° into a staggered arrangement and oxo bridge is observed to be bent {Fe(1)-O(3)-Fe(1#) = 159.63(12)°}.

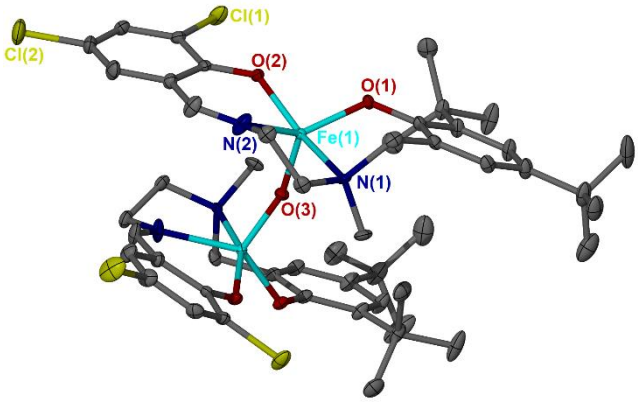

Figure 2. Solid-state structure of [Fe(**3**)]$_2$O. Ellipsoids are shown at 30% probability level and all hydrogen atoms have been omitted for clarity

Coordination bond lengths are similar to those reported for µ-oxo-Fe(III) salen complexes, however, there is variation in the deviation from linearity of the bridge.[77] The observation of µ-oxo complexes for only **2** and **3** could be related to a reduction in steric bulk and increased metal Lewis acidity respectively.

Polymerisation

Polymerisation of *rac*-LA was carried out in propylene oxide (PO), which was purified by vacuum distillation prior to use. PO acted as both solvent and co-initiator as demonstrated in previous studies.[47,75] For all studies reported, the monomer was singly recrystallised before use. For the majority of solution polymerisations, a ratio of 100:1 [LA]:[Fe] was employed. Importantly, no activity was observed when the polymerisation was carried out in toluene with the addition of catalytic amounts of PO. For Fe(**1**)Cl, polymerisation was attempted for a range of conditions (Table 2). At 60°C, high conversion was achieved after 3 days. This agrees with recent work of Lamberti and co-workers, who observed no conversion after 4 hours.[75] A moderate isotactic bias was achieved under these conditions (P_m = 0.77). The stereocontrol likely originates from a chain-end mechanism as was observed by Duan and co-workers for iron salen complexes.[48] The stereocontrol could be enhanced at 40°C (P_m = 0.80) albeit with a reaction time of 7 days. Polymerisation at 80°C required less time to achieve high conversion while maintaining good isoselectivity. At this temperature, Fe(**1**)Cl is found to be more active than the analogous Al(III) complex as well as being more isoselective {Al(**1**)Me, 80°C, 3 days, 73%; P_m = 0.61}.[64] This increase in activity could be due to greater accessibility of the metal centre due to lengthened bond distances or increased Lewis acidity of Fe(III) compared to Al(III). Batch kinetics were carried out for Fe(**1**)Cl under these conditions (Figure 3). An induction period was observed within the first six hours, after which the LA is consumed with a first order dependence (k_{app} = 0.105 ± 0.01 hr^{-1}, R^2 = 0.97). This induction period is likely related to the *in situ* generation of the active alkoxide species. Compared to the corresponding iron (III) salen complex, Fe(**1**)Cl is less active but demonstrates greater molecular weight control and stereocontrol.[47]

Table 2. ROP of *rac*-LA with Fe(**1**)Cl

Init.	T/ °C	Time /days	Conv. %[a]	P_m[b]	M_n[c]	Đ[c]
Fe(**1**)Cl	40	7	80	0.80	11900	1.11
Fe(**1**)Cl	60	3	76	0.77	10800	1.18
Fe(**1**)Cl[d]	60	2	62	0.78	4550	1.12
Fe(**1**)Cl	80	1	72	0.79	9400	1.11
Fe(**1**)Cl[e]	80	1	63	0.75	6300	1.07
Fe(**1**)Cl[f]	80	1	78	0.67	11250	1.02

Conditions: *rac*-LA (0.4 g), [LA]:[Fe] = 100:1, PO (2 ml); [a] Determined by ^{1}H NMR spectroscopy; [b] Probability of isotactic enchainment, determined by ^{1}H{^{1}H} NMR spectroscopy;[78] [c] Determined *via* GPC (triple detection analysis); [d] [LA]:[Fe] = 50:1. [e] [LA]:[Fe]:[BnOH] = 100:1:1. [f] Toluene, [LA]:[Fe]:[Et_3N]:[BnOH] = 100:1:1:1.

The molecular weight control of this initiator is good under all conditions, with predictable M_n and narrow dispersities being achieved (Đ = 1.07 – 1.18). However, there is bimodality for all polymers derived from Fe(**1**)Cl and PO. These distributions have been treated together to give the molecular weight value (see ESI). Doubling the amount of initiator effectively halves the molecular weight demonstrating the dependence on initiator concentration (60°C; [LA]:[Fe] = 100:1, 76%, M_n = 10800 Da; [LA]:[Fe] = 50:1, 62%, M_n = 4550 Da). Addition of one equivalent of benzyl alcohol (80°C; [LA]:[Fe]:[BnOH] = 100:1:1) was observed to reduce the achieved molecular weight. This demonstrates a tendency for alkoxide exchange at the metal centre once initiation has occurred. MALDI-ToF analysis of polymer derived from Fe(**1**)Cl confirmed the role of propylene oxide, with chloropropanol being identified as the polymer α end group. This is also evidence for the operation of a coordination-insertion mechanism. For polymer produced at 40 °C, the MALDI-ToF spectra shows a series centred on 9914 Da which is similar to the molecular weight found by GPC analysis. Separation of peaks is observed to be 144 Da with a minor series of lower intensity with a separation of 72 Da indicating a small degree of undesired transesterification. Both series are asymmetric with a tail towards lower molecular weight.

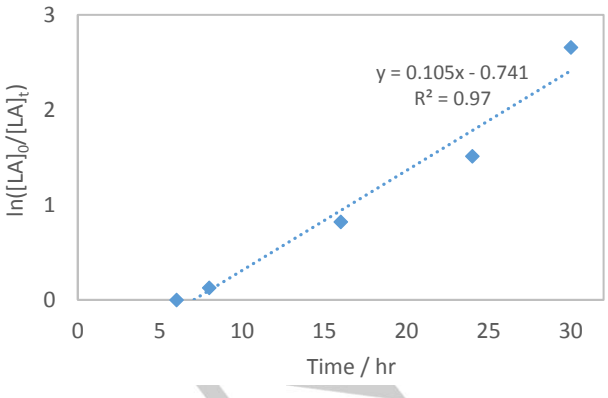

Figure 3. Semi-logarithmic plot of ROP of *rac*-LA with Fe(**1**)Cl (80°C, $[LA]_0$ = 1.39 M).

Table 3. ROP of *rac*-LA with Fe(**2-7**)Cl

Init.	T/ °C	Time /days	Conv. %[a]	P_m[b]	M_n[c]	Đ[c]
Fe(**2**)Cl	60	0.25	76	0.61	10300	1.30
Fe(**2**)Cl	80	0.17	42	0.62	6400	1.09
Fe(**3**)Cl	60	0.25	80	0.56	7650	1.11
Fe(**3**)Cl	80	0.17	93	0.54	11150	1.14
Fe(**4**)Cl	60	2	94	0.59	10700[d]	1.27[d]
Fe(**4**)Cl	80	1	93	0.61	11850[d]	1.35[d]
Fe(**5**)Cl	60	4	85	0.64	11600	1.06
Fe(**5**)Cl	80	2	92	0.56	12700	1.17
Fe(**6**)Cl	80	3	59	0.69	5250	1.13
Fe(**6**)Cl	80	4	92	0.62	8750	1.22
Fe(**7**)Cl	60	1	60	0.54	10400	1.03
Fe(**7**)Cl	80	0.67	95	0.56	12150	1.09

Conditions: *rac*-LA (0.4 g), [LA]:[Fe] = 100:1, PO (2 ml); [a] Determined by ^{1}H NMR spectroscopy; [b] Probability of isotactic enchainment, determined by ^{1}H{^{1}H} NMR spectroscopy; [c] Determined *via* GPC (triple detection analysis);[78] [d] Determined *via* GPC (RI only due to anomalous light scattering signals).

A similar spectrum was found at 60°C, with identical end groups (M_p = 8331 Da; $M_{n,gpc}$ = 10800 Da). At 80 °C, the degree of transesterification is reduced however, there are peaks related to cyclic oligomer at lower molecular weight. Polymerisation with an equivalence of BnOH affords a symmetrical MALDI-ToF spectrum with two overlapping series. The major series has the expected BnO-/-H end groups with a small degree of transesterification peaks. The second series has end groups attributable to initiation by PO. There is good agreement of theoretical and experimental molecular weight. There is no evidence of different end groups in MALDI-ToF related to the second peak observed in GPC. From MALDI-ToF data of polymer derived from Fe(**2**-**7**)Cl, the second series in GPC is inferred to be due to the initiation of polymerisation by propane-1,2-diol (PD). This diol is likely an impurity of PO, and is present despite distillation of PO prior to use. This evidence is likely absent from MALDI-ToF spectra of polymer derived from Fe(**1**)Cl due the size and intensity of the higher molecular weight series. For example, analysis of the higher molecular weight series (by GPC), for the 80°C polymerisation, indicates an M_n of 19250 Da, which would be less likely to ionise and be detected in MALDI-ToF analysis (see ESI). Polymerisation activity of Fe(**1**)Cl was also tested in the presence of a catalytic amount of triethylamine and benzyl alcohol, which is common for other trivalent halides.[79–81] Similar activity (toluene, 80°C, [LA]:[Fe]:[Et_3N]:[BnOH] = 100:1:1:1) is seen compared to experiments with PO. However, there is a reduction in stereocontrol (P_m = 0.67) but this may also be related to the change of polymerisation solvent and, hence, polarity (PO *vs.* toluene). The GPC chromatogram is monomodal with a narrow distribution of chain lengths and the molecular weight is as expected based on conversion (M_n =11250 Da, Đ = 1.02). The monomodality suggests the previous bimodality observed when PO is used is not due to the initiator, supporting the PD initiation hypothesis. MALDI-ToF analysis confirms the BnO-/-H end groups (See ESI). The spectrum is symmetrical with no indication

of transesterification reactions. The distribution is centred around 6903 Da which is lower than the theoretical molecular weight.

Reduction of the size of aryl groups, with the same ethylene backbone, increases the polymerisation activity in the presence of PO (Table 3). For Fe(**2**/**3**)Cl (R = H/Cl), high conversion is generally achieved within 6 and 4 hours at 40 and 60°C respectively. However, the degree of stereocontrol is also reduced (P_m = 0.54 – 0.61). These complexes are also more active than the analogous aluminium species and give a reversed stereoselectivity {Al(**2**)Me, 80°C, 3 days, 73%; P_m = 0.26; Al(**3**)Me, 80°C, 1 day, 96%; P_m = 0.37}. The increased activity is likely a consequence of the reduced steric bulk {Fe(**2**)Cl} and enhanced Lewis acidity {Fe(**3**)Cl}. Despite an increase in temperature, a lower conversion is seen for Fe(**2**)Cl at 80°C compared to 60°C. This could be related to an induction period as seen for Fe(**1**)Cl. Another possibility is the formation of less active dimeric species, which was suggested by Duan and co-workers to rationalise the counterintuitive lower activity of less sterically demanding ligands.[47] The μ-oxo bridge solid-state structure of [Fe(**2**)]$_2$O could be seen as evidence for the latter case. MALDI-ToF analysis of polymer derived from these complexes at 80°C was performed (see ESI). For Fe(**2**)Cl, there are two symmetrical distributions; the higher molecular weight series was much weaker in intensity (M_p = 7592 Da). Peak spacing of this series was 144 Da, indicating the absence of side reactions. However, the residual mass was best accounted for by propanediol. This is likely to be propane-1,2-diol (PD), originating as an impurity of the PO. The lower molecular weight series (M_p = 4439 Da) was consistent with a chloropropanol end group, with a small degree or transesterification. Polymer derived from Fe(**3**)Cl has three overlapping series with transesterification reactions prevalent in each. The end groups, from high to low molecular weight, were identified to be PD, Cl-PO and none (cyclic). Increased bulk relative to these ligands {Fe(**4**)Cl,R = Me} requires more time to reach high conversion, being more similar to Fe(**1**)Cl (2 days, 60°C, 94%; 1 day, 80°C, 93%). Only a slight preference for isotactic PLA is achieved by Fe(**4**)Cl (P_m = 0.59 – 0.61). Reasonable control over molecular weight is demonstrated by Fe(**2**-**4**)Cl. Modifying the ligand backbone had the effect of reducing polymerisation activity and stereocontrol relative to Fe(**1**)Cl. Having a phenyl backbone, Fe(**5**)Cl required twice as long as Fe(**1**)Cl to reach high conversion (4 days, 60°C, 85%; 2 days, 80°C, 92%). Only a moderate degree of isoselectivity was achieved (P_m = 0.56 - 0.64). Reasonable molecular weight was achievable despite the extended reaction time. Once again, a high molecular weight series of PD capped PLA is observed by MALDI-ToF (See ESI). The expected chloropropanol end group is present as a more intense lower molecular weight series. At 80°C, both series have a small amount of peaks due to transesterification reactions. Fe(**5**)Cl was observed to be more active than Al(**5**)Me while having similar stereocontrol {Al(**5**)Me, 80°C, 4 days, 96%; P_m = 0.61}.[66] Use of an aminopiperidine backbone, Fe(**6**)Cl, inhibited reaction at 60°C. Polymerisation at 80°C required 3-4 days to reach high conversion. After 3 days, 59% conversion was achieved and this was increased to 92% after 4 days. A slight preference for isotactic PLA is observed (P_m = 0.62 – 0.69). Molecular weight is slightly lower than anticipated (M_n = 5250 - 8750 Da, Đ = 1.13 - 1.22). MALDI-ToF analysis of polymer produced after three days shows, again, two series with chloropropanol and PD end groups respectively (see ESI). Activity is improved relative to the analogous aluminium complex, however, similar tacticity is afforded {Al(**6**)Me, 80°C, 10 days, 88%; P_m = 0.63}.[67] Fe(**7**)Cl, in comparison to Fe(**2**)Cl, also has reduced polymerisation activity due to modification of the backbone. Use of the diaminocyclohexane backbone required 1 day and 16 hours to reach high conversion at 60°C and 80°C respectively. Good molecular weight control is achieved (Đ = 1.03 – 1.09) however there is no stereocontrol due to this complex. MALDI-ToF analysis shows three overlapping series around 5504 Da (See ESI). The major series is observed to have chloropropanol end groups while PD terminated PLA is the minor series. There is also a low molecular weight tail of cyclic oligomers. Activity is superior to the aluminium analogue {Al(**7**)Me, 80 °C, 4 days, 71%).[68] This reduction in activity on changing the backbone is likely related to a decreased flexibility of the complex and an increase in steric crowding around the metal centre.

Conclusions

Seven iron(III) salalen complexes have been prepared and characterised by mass spectrometry and elemental analysis. Both ligand substituents and backbone have been systematically varied to identify structure-activity-relationships. In some cases, X-ray crystallography was also performed to elucidate the solid-state structure. Fe(**1,4,5,6**)Cl were observed to be five coordinate each with a slight tendency towards trigonal bipyramidal geometry. An example of a μ-oxo Fe (III) salalen structure, [Fe(**3**)]$_2$O, has also been reported. All complexes were found to be active for the ROP of *rac*-LA. For Fe(**1**)Cl (R = ^{t}Bu, L = -CH_2CH_2-), there was a moderate isotactic preference (P_m = 0.75 – 0.80). Despite extended reaction times of 1 – 7 days, this initiator exerted good control over molecular weight (Đ = 1.09 – 1.18). For the same backbone, reducing the size of substituents was seen to increase activity but reduce stereocontrol {Fe(**2-4**)Cl, L = -CH_2CH_2-, R = H; Me; Cl}. Variation in the backbone caused a decrease in activity {Fe(**5-7**)Cl, L = C_6H_4; $CH_2C_5H_9$; C_6H_{10}} and this has been related to complex inflexibility.

Experimental Section

General experimental methods

All chemicals were commercially obtained from Sigma-Aldrich and used as received. This is with the exception of the *rac*-lactide, which was singly recrystallised from dry toluene, and propylene oxide (PO) and benzyl alcohol, which were distilled before use. For the synthesis of metal complexes under anhydrous conditions, dry solvents, MBraun LABmaster dp glovebox, standard Schlenk line techniques and oven-dried glassware were used. Dried and degassed reaction solvents, used in the preparation of these complexes, were collected under inert gas conditions from a Solvent Purification System (SPS).

Ligands were prepared and characterised following previously reported literature.[64,66–68] All ligands and complexes were characterised by electron-spray ionisation-mass spectrometry (ESI-MS) in positive mode. CHN elemental analysis was performed by Mr Stephen Boyer at London Metropolitan University.

All crystallographic data was collected on either a SuperNova or Excalibur, EOS detector diffractometer using CuKα (λ = 1.54184 Å) or Mo-Kα (λ = 0.71073 Å) radiation. All data was recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model, all refinement details are given in the .cif file. CCDC numbers 18466313-1866317 contains the necessary crystallographic data. Fe(**1**)Cl, ligand and chloro groups disordered over two positions in a ratio of 92:8; Constraints where necessary to aid convergence and the minor part has been refined with ADP restraints. Fe(**3**)Cl, ligand backbone was disordered over two positions in a ratio of 60:40. Fe(**5**)Cl diffracted poorly to high angle and the model presented is a testimony to modern diffractometers. Fe(**6**)Cl involves a two component twin with twinning (44%) by virtue of a 180° rotation about the (0.71, 0, -0.71) reciprocal axis.

General Complexation Procedure for Fe(1), Fe(2) and Fe(6) under air

The salalen ligand (1 mmol) was placed in a flask and dissolved in THF (30 mL). $FeCl_3$ (0.162 g, 1 mmol) was added as a black solid to the yellow solution and Et_3N (0.28 mL, 2 mmol) added dropwise. The reaction mixture was refluxed for 16 hours, filtered and washed with further THF. The solvent was removed *in vacuo* to afford a crude solid that was rinsed with hexane (5 mL) and dried to give a dark purple product.

General Complexation Procedure for Fe(3), Fe(4), Fe(5) and Fe(7) under argon

The salalen ligand (1 mmol) was placed in a Schlenk flask, dried and transferred into the glovebox. Toluene (10 mL) was added and $FeCl_3$ (0.162 g, 1 mmol) added as a solid to the yellow solution. Et_3N (0.28 mL, 2 mmol) was added dropwise and the flask heated at 80 °C for 3 days. The reaction mixture was filtered *via* cannula, washed with further toluene and solvent removed *in vacuo*. The crude solid was rinsed with hexane (5 mL) and dried to obtain a dark purple product.

General Polymerisation methods and procedures

All polymerisations were carried out using Schlenk flasks with J Youngs taps under inert conditions. Polymerisations were generally carried out in a ratio of 100:1 [LA]:[Fe].

PO polymerisations: Fe(**1**-**7**)Cl (0.0278 mmol) and *rac*-lactide (0.4 g, 2.78 mmol) were placed in a flask and distilled propylene oxide (2.0 mL) was added *via* syringe. The flask was placed in the pre-heated oil bath (40°C - 80°C) for the desired time duration. After this reaction time, the tube was cooled and an aliquot analysed by ^{1}H NMR spectroscopy ($CDCl_3$) to determine conversion to polymer. Solvent was then removed *in vacuo* and the residue washed with excess methanol (>30 mL).

Et_3N polymerisation: Fe(**1**)Cl (0.0694 mmol) and *rac*-lactide (1 g, 6.94 mmol) were placed in a flask and dry toluene (5 mL), and triethylamine (0.0694 mmol), and benzyl alcohol (0.0694 mmol) were added. The overall loading was 100:1:1:1 [LA]:[Fe]:[Et_3N]:[BnOH]. The flask was placed in the pre-heated oil bath (80°C) for the 24 hours. After this reaction time, the tube was cooled and an aliquot analysed by ^{1}H NMR spectroscopy ($CDCl_3$) to determine conversion to polymer. Solvent was then removed *in vacuo* and the residue washed with excess methanol (>30 mL).

All washed polymers were characterised by gel permeation chromatography (GPC). GPC was carried out at 1 ml min^{-1} at 35 °C with a THF eluent using a PLgel 5 µm MIXED-D 300 × 7.5 mm column. Molecular weights were determined using triple detection methods based on refractive index (RI), light scattering (LS) and viscometry. In two cases, only RI was used and a correction factor of 0.58 was applied to measured values.[82] Homonuclear decoupled NMR spectroscopy, ^{1}H{^{1}H}, was used to determine the probability of isotactic enchainment, P_m.[78] MALDI-ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB {trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile} as the matrix and ionized using NaTFA. Spectra were recorded in positive reflectron mode.

Materials characterisation (GPC, ESI-MS MALDI-TOF) facilities were provided through the Chemical Characterisation and Analysis Facility (CCAF) at the University of Bath.

Complex characterisation

Fe(1)Cl. The complex was prepared following the general complexation procedure under air and recrystallised using methanol / acetonitrile.

Yield = 0.220 g, 37%.

ESI-MS (AcCN): Calcd m/z $[C_{33}H_{50}FeN_2O_2]^+$ = 562.3222, found m/z = 562.3257.

Elemental analysis: Calcd for $C_{33}H_{50}ClFeN_2O_2$ (found): C, 66.27 (66.13); H, 8.43 (8.49); N, 4.68 (4.57).

MALDI-ToF: Calcd m/z [Fe(**1**)Cl]$^+$ (found) 597.291 (597.287).

Fe(2)Cl. The complex was prepared following the general complexation procedure under air.

Yield: 0.149 g, 31%.

ESI-MS (AcCN): Calcd m/z $[C_{25}H_{34}FeN_2O_2]^+$ = 450.1970, found = 450.2044.

Elemental analysis: Calcd for $C_{25}H_{34}ClFeN_2O_2$ (found): C, 61.80 (61.87); H, 7.05 (7.16); N, 5.77 (5.63).

Fe(3)Cl. The complex was prepared following the general complexation procedure under argon.

Yield: 0.526 g, 95%.

ESI-MS (AcCN): Calcd m/z $[C_{25}H_{32}Cl_2FeN_2O_2]^+$ = 518.1190, found = 518.1206.

Elemental analysis: Calcd for $C_{25}H_{32}Cl_3FeN_2O_2$ (found): C, 54.13 (54.39); H, 5.81 (6.10); N, 5.05 (5.25).

Fe(4)Cl. The complex was prepared following the general complexation procedure under argon and recrystallised using diethylether.

Yield: 0.310 g, 60 %.

ESI-MS (AcCN): Calcd m/z $[C_{27}H_{38}FeN_2O_2]^+$ = 478.2283, found = 478.2284.

Elemental analysis: Calcd for $C_{27}H_{38}ClFeN_2O_2$ (found): C, 63.10 (58.67); H, 7.45 (8.30); N, 5.45 (4.27).

MALDI-ToF: Calcd m/z [Fe(**4**)Cl]$^+$ (found) 478.228 (478.355).

Fe(5)Cl. The complex was prepared following the general complexation procedure under argon and recrystallised using dichloromethane / hexane.

Yield: 0.237 g, 37 %.

ESI-MS (AcCN): Calcd m/z $[C_{37}H_{50}FeN_2O_2]^+$ = 610.3222, found = 610.3251.

Elemental analysis: Calcd for $C_{37}H_{50}ClFeN_2O_2$ (found): C, 68.78 (68.86); H, 7.80 (7.96); N, 4.34 (4.46).

Fe(6)Cl. The complex was prepared following the general complexation procedure under air and recrystallised using dichloromethane / hexane.

Yield: 0.291 g, 46%.

ESI-MS (AcCN): Calcd m/z $[C_{36}H_{54}FeN_2O_2]^+$ = 602.3535, found = 602.3542.

Elemental analysis: Calcd for $C_{36}H_{54}ClFeN_2O_2$ (found): C, 67.76 (67.89); H, 8.53 (8.67); N, 4.39 (4.49).

MALDI-ToF: Calcd m/z [Fe(**6**)Cl]$^+$ (found) 637.322 (637.470).

Fe(7)Cl. The complex was prepared following the general complexation procedure under argon.

Yield: 0.225 g, 42%.

ESI-MS (AcCN): Calcd m/z $[C_{29}H_{40}FeN_2O_2]^+$ = 504.2439, found = 504.2417.

Elemental analysis: Calcd for $C_{29}H_{40}ClFeN_2O_2$ (found): C, 64.51 (64.73); H, 7.47 (7.59); N, 5.19 (5.32).

Acknowledgments

We would like to thank the University of Bath and the EPRSC (EP/P016405/1) for funding. We also thank Dr Antoine Buchard is for fruitful discussions. Isabel Thomlinson is acknowledged for preparation of the graphical abstract. CCAF are also acknowledged for the use of their analytical facilities.

Keywords: Iron • lactide • ring opening polymerization •homogeneous catalysis•

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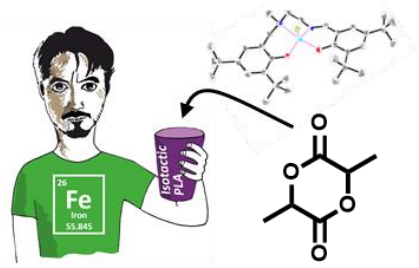
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Iron (III) salalen complexes are used for the isoselective, controlled ring opening polymerisation of *rac*-lactide.



Key Topic* Iron, lactide

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