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PAPER

Salalen aluminium complexes and their exploitation for the ring opening polymerisation of *rac*-lactide†

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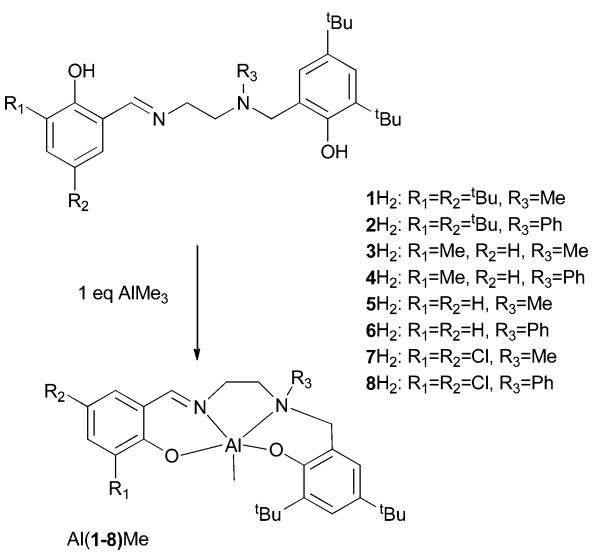
In this paper we report the first use of Al(III) salalen complexes for the ring opening polymerisation of *rac*-lactide. Polylactides with narrow polydispersities (PDIs range from 1.04–1.65) and moderate degrees of stereoselectivity were formed. Eight salalen Al(III) complexes have been prepared and fully characterised by solution-state NMR spectroscopy and, where appropriate, single crystal X-ray diffraction. With ligand $\mathbf{3}H_2$ either a monomeric or dimeric Al(III) species was formed, the dimeric species was favoured at low concentrations. The complexes were tested for the ring opening polymerisation of *rac*-lactide in toluene at 80 or 100 °C. Interestingly, various tacticities of polymer were formed, which were dependent upon the nature of the group bound to the amine nitrogen centre.

Introduction

In the last decade there has been an explosion of interest in the field of single-site catalysts for the ring opening polymerisation (ROP) of *rac*-lactide (*rac*-LA) to afford polylactide (PLA).[1] The polymer itself is not only sourced from sustainable materials but is biodegradable.[2] In addition the polymer properties can be tuned by judicious choice of the catalyst, which can invoke stereoselectivity in the resultant polymerisation. For example, stereoblock isotactic PLA has a melting point of *ca.* 230 °C whereas poly-L-lactide has a melting point of *ca.* 180 °C.[3] There have been many impressive advances in catalysts within the area and metals such as those in Groups 1-4,[4,5] Zn(II),[6] and pertinent to this study Al(III) have all been utilised.[7–10] For example, Gibson has shown that minor alterations to the ligand can have significant affects on the stereochemistry of the resulting polymer.[8] The use of Al(III) for the ROP of *rac*-LA is well established.[7–10] One of the earliest such reports is that of Spassky and co-workers who used a complex based on a chiral Schiff base ligand of *R*-(+)-1,1′-binaphthyl-2,2′-diamine.[9] This was active for the production of isotactically enriched PLA. The vast majority of Al(III) initiators for the production of PLA are based on either salan or salen ligands,[8–10] we have recently demonstrated that Group 4 salalen complexes are active for the polymerisation of *rac*-lactide under both solution and melt conditions.[5] The results herein represent the first example of the use of salalen ligands with Al(III) for the polymerisation of *rac*-LA. Catalytic reactions involving aluminium salalen complexes are rare and notable examples are by Katsuki *et al.* who have shown that they are active for the oxidation of sulfides and the hydrophosphonylation of aldehydes.[11,12] However, due to their facile nature of the preparation and degree of synthetic variability the use of salalen ligands is proving more popular.[13]

Results and discussion

In this publication a series of Al(III) salalen complexes have been prepared and tested for the ROP of *rac*-LA. The ligands and complexes used in this study are shown in Scheme 1.† The steric effects of the group on the amine, and the impact of changing the substituents (both electronic and sterics) on the salen phenoxide fragment have been investigated. The complexes were



Scheme 1 Ligands and complexes prepared in this study.

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simply prepared by the reaction of 1 equivalent of $AlMe_3$ with 1 equivalent of the salalen ligand in toluene. Complexes based on ligands $\mathbf{2}H_2$, $\mathbf{3}H_2$, $\mathbf{7}H_2$ and $\mathbf{8}H_2$ were characterised by single crystal X-ray diffraction, Fig. 1.† The production of crystals of suitable quality for diffraction studies was challenging as these complexes were highly soluable in common organic solvents.

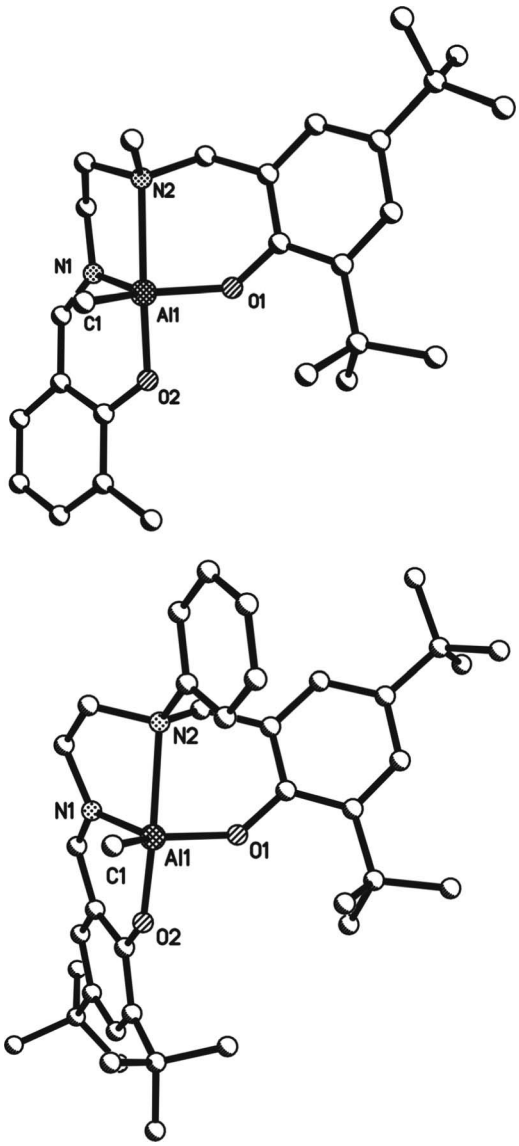

Fig. 1 **Top**: Molecular structure of Al(**3**)Me. Selected bond lengths (Å) and angles (°) are Al(1)–O(1) 1.757(2), Al(1)–O(2) 1.827(2), Al(1)–C(1) 1.960(3), Al(1)–N(1) 1.979(3), Al(1)–N(2) 2.266(3). O(2)–Al(1)–O(1) 90.48(11), O(2)–Al(1)–C(1) 99.65(14), O(1)–Al(1)–C(1) 124.68(14), O(2)–Al(1)–N(1) 89.51(12), O(1)–Al(1)–N(1) 120.70(12), O(2)–Al(1)–N(2) 165.45(12). **Bottom**: Molecular structure of Al(**2**)Me. Selected bond lengths (Å) and angles (°) are Al(1)–O(1) 1.7701(17), Al(1)–O(2) 1.8193(18), Al(1)–C(1) 1.957(3), Al(1)–N(1) 1.958(2), Al(1)–N(2) 2.315(2). O(2)–Al(1)–O(1) 93.74(8), O(2)–Al(1)–C(1) 97.56(10), O(1)–Al(1)–C(1) 126.88(11), O(2)–Al(1)–N(1) 90.12(8), O(1)–Al(1)–N(1) 116.83(9), O(2)–Al(1)–N(2) 165.36(8).

The crystals were formed by slowly cooling a saturated solution of the complexes in hexane to – 20 °C. For the crystallographically characterised complexes the Al(III) centre was seen to be in a highly distorted trigonal pyramidal geometry with C(1)–Al(1)–N(1) 113.68(13)°, C(1)–Al(1)–O(1) 124.68(14)° and O(2)–Al(1)–N(2) 165.45(12)°, for Al(**3**)Me, Fig. 1, with the τ values for these complexes ranging from 0.56–0.80. This also suggests a bias towards the trigonal bipyramidal geometry.[14] The phenoxide *trans* to the imine has the shortest Al-O bond distance and as expected the Al-N_{imine} distance is considerably shorter than that of the Al-N_{amine}. To the best of our knowledge these are the first examples of crystallographically characterised Al-alkyl salalen complexes. The only previous Al(III)-salalen complex characterised in the solid-state is the chiral Al-Cl system of Katsuki, in which an analogue of Jacobsen's ligand was employed.[12] It should also be noted that, to date, all Al(III) complexes of salan or salen ligands in the Cambridge Crystallographic data base are symmetric in their phenoxide subsituents.[15] There is a necessity for novel ligand systems, for Al(III), that can be easily prepared and derivatised.

The complexes have C_1 symmetry and all adopt a β-*cis* configuration in the solid-state. Upon complexation the tertiary amine becomes chiral and due to the chelation of the ligand the metal centre is also chiral; the *S* configuration at N(2) induces the Λ form in the complex where the *R* configuration corresponds to the Δ form. The complexes crystallise in centrosymmetric space groups so both forms are present.† The ^{1}H NMR spectra for these complexes are in agreement with the solid-state structures being maintained in solution, with resonances at *ca.* – 0.5 ppm for the methyl group and at *ca.* 7.4 ppm for the imine proton, also the CH_2 groups are now diastereotopic indicating that the ligand is "*locked*" in position once coordinated to Al(III).†

If the reaction was performed at a lower concentration in toluene a second product was observed, Fig. 2. Again this is a C_1 symmetric complex, however the Al(III) centres are now tetrahedral in geometry. In this case the salalen $\mathbf{3}H_2$ has reacted with two equivalents of $AlMe_3$ forming $Al_2(\mathbf{3})(Me)_4$. Under these lower dilution conditions both the 1 : 1 and 1 : 2 species were produced as evidenced by the ^{1}H NMR spectrum and it proved troublesome to separate the different forms. However, the 1 : 1 complexes could be isolated in high purities under more concentrated conditions.†

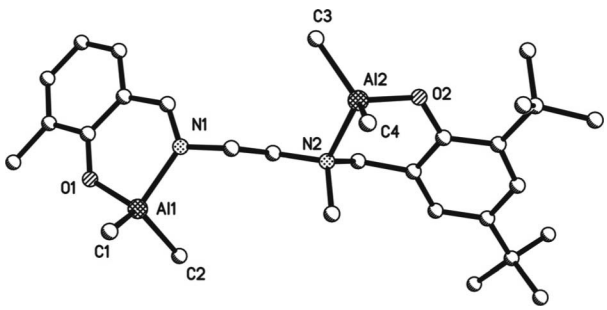

Fig. 2 Molecular structure of $Al_2(\mathbf{3})Me_4$. Selected bond lengths (Å) and angles (°) are Al(1)–O(1) 1.7750(13), Al(1)–C(2) 1.952(2), Al(1)–N(1) 1.9613(15), Al(1)–C(1) 1.9624(19), Al(2)–O(2) 1.7638(13), Al(2)–C(3) 1.950(2), Al(2)–C(4) 1.957(2), Al(2)–N(2) 2.0577(15). O(1)–Al(1)–C(2) 114.01(8), O(1)–Al(1)–N(1) 95.00(6), C(2)–Al(1)–N(1) 105.89(8), O(1)–Al(1)–C(1) 111.74(7), C(2)–Al(1)–C(1) 118.11(9), N(1)–Al(1)–C(1) 109.22(8).

The complexes were tested for the ROP of *rac*-LA in solution at either 80 or 100 °C for 24 or 72 h with the addition of 1 equivalent of benzyl alcohol (BnOH) to generate the alkoxide *in situ*, the results of which are shown in Table 1.

Table 1 Polymerisation data for the solution ROP of *rac*-lactide

Entry	*T*/°C	Time/h	Initiator	Con.[a]	M_n[b]	M_n^{calc}	PDI[b]	P_r[c]
1	80	72	Al(1)Me	73	11900	10600	1.05	0.39
2	80	24	Al(2)Me	96	11925	13950	1.11	0.43
3	80	72	Al(2)Me	97	8100	14100	1.08	0.43
4	100	72	Al(2)Me	96	11900	13950	1.11	0.43
5	100	24	Al(2)Me	99	12050	14350	1.27	0.46
6	80	72	Al(3)Me	26	7400	3850	1.04	0.75
7	100	24	Al(3)Me	54	4800	7900	1.06	nd
8	80	24	Al(4)Me	96	10425	13950	1.65	0.42
9	100	24	Al(4)Me	98	7420	14200	1.62	0.41
10	80	72	Al(5)Me	86	6620	12500	1.07	0.74
11	100	24	Al(5)Me	99	7700	14350	1.09	0.66
12	80	24	Al(6)Me	98	9050	14200	1.39	0.45
13	100	24	Al(6)Me	98	14650	14200	1.53	0.46
14	80	24	Al(7)Me	96	8600	13950	1.10	0.63
15	100	24	Al(7)Me	97	7600	14100	1.23	0.59
16	80	24	Al(8)Me	69	7950	10050	1.08	0.48
17	80	72	Al(8)Me	98	12500	14200	1.12	0.40
18	100	24	Al(8)Me	98	11000	14200	1.26	0.50

Conditions [LA] : [Initiator] : [BnOH] = 100 : 1 : 1, temperature and time as given in the table.[a] as determined *via* ^{1}H NMR, [b] Determined from GPC (in THF) referenced to polystyrene. It is noted that a correction factor to account for the differences in the hydrodynamic volume of PLA and polystyrene can be applied (typically × by 0.58) this has not been applied in this case. [c] Calculated from the ^{1}H homonuclear decoupled NMR ($CDCl_3$) analysis. The calculated molecular weights were determined by the following (144 × conversion) + 108 {where 108 is the mass of the end groups (H/OCH_2Ph)}.

All complexes were shown to be active for the polymerisation of *rac*-LA with the addition of 1 equivalent of BnOH. Relatively narrow polydispersity indices were observed, except with the polymers formed with complex Al(**4**)Me. MALDI-ToF mass spectrometry analysis of the polymers prepared with Al(**3**)Me indicate the presence of the benzyl alcohol end group (entries 6 and 7), which would be expected from the coordination insertion mechanism. Interestingly, the repeat unit of the polymer was seen to be 144 mass units. This is indicative of only a small degree of transesterification taking place. The initiators were also able to offer a degree of stereocontrol in the polymerisations. Complexes based on ligands **2**H_2, **4**H_2, **6**H_2 and **8**H_2 (entries 2-5, 8, 9, 12, 13 and 17) have a slight isotactic bias, whilst those based on **3**H_2, **5**H_2 and **7**H_2 (entries 6, 7, 10, 11, 14 and 15) afforded PLA with a moderate heterotactic bias, especially the polymer produced from Al(**5**)Me. Unlike previous work with Al(III) salan complexes where changing the subsituents on the aromatic rings played a significant role in the stereoselectivity,[6b] it would appear in this case the group on the amine nitrogen R_3 is more important. In this current work {except for Al(**1**)Me} when R_3 = Ph slightly isotactic PLA was observed, *but* when this group was changed to Me polylactide with an heterotactic bias was formed.

Conclusions

In conclusion we have shown for the first time that Al-salalen complexes are active for the ROP of *rac*-LA with narrow molecular weight distributions. We have also shown that there is a correlation between the group on the amine nitrogen and the tacticity of the resultant polymer.

Experimental

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. *rac*-LA (Aldrich) was recrystallised from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 250, 300 or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analyses were performed by Mr A. K. Carver at the Department of Chemistry, University of Bath. The ligands were prepared according to standard literature procedures and the purity confirmed *via* ^{1}H/^{13}C{^{1}H} NMR and HR-MS prior to use.[5]

Typical polymerisation procedure

For solution polymerisations a monomer:initiator ratio of 100 : 1 was used. In all cases toluene (10 ml) was added to a Schlenk followed by the initiator and 1 eq of BnOH, the lactide (0.72 g) was added and the flask heated for the desired time at the desired temperature. The reaction was quenched by the addition of methanol (20 ml). ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra.

Complex preparation

A representative procedure for the preparation of Al(**3**)Me is given, see supporting information for further details for all other complexes:

3H_2 (0.502 g, 1.22 mmol) was dissolved in toluene (20 cm^3) to which $AlMe_3$ (0.6 ml of a 2.0 M solution in hexane, 1.22 mmol) was added and stirred for 2 h. After which time the solvent was removed *in- vacuo* and the product was recrystallised in hexane.

Table 2 X-Ray crystallographic data

Compound reference	Al(**2**)(Me)	Al(**3**)(Me)	Al_2(**3**)$(Me)_2$	Al(**7**)(Me)	Al(**8**)(Me)
Chemical formula	$C_{39}H_{55}AlN_2O_2$	$C_{27}H_{39}AlN_2O_2$	$C_{30}H_{48}Al_2N_2O_2$	$C_{26}H_{35}AlCl_2N_2O_2$	$C_{31}H_{37}AlCl_2N_2O_2$
Formula mass	610.83	450.58	522.66	505.44	567.51
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	10.0400(5)	9.7286(7)	10.5560(9)	9.708(4)	15.0450(3)
b/Å	22.8750(14)	12.5296(10)	10.7180(11)	9.824(4)	11.7530(3)
c/Å	31.7450(18)	13.0282(10)	14.6300(13)	15.270(4)	17.2050(5)
α (°)	90	110.181(4)	75.586(5)	82.591(15)	90
β (°)	90	109.510(4)	72.438(5)	75.027(16)	100.5930(10)
γ (°)	90	103.090(5)	78.516(6)	72.308(17)	90
Unit cell volume/Å^3	7290.7(7)	1295.98(17)	1514.6(2)	1338.3(9)	2990.41(13)
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	*Pcab*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
No. of formula units per unit cell, Z	8	2	2	2	4
Absorption coefficient, μ/mm^{-1}	0.090	0.103	0.124	0.300	0.277
No. of reflections measured	58588	10691	28305	15193	35301
No. of independent reflections	6295	4417	6868	4732	5671
R_{int}	0.1130	0.0835	0.0569	0.0781	0.1508
Final R_1 values ($I > 2\sigma(I)$)	0.0583	0.0615	0.0462	0.0502	0.0645
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1168	0.1466	0.1065	0.1101	0.1334
Final R_1 values (all data)	0.1157	0.1144	0.0721	0.0973	0.1224
Final $wR(F^2)$ values (all data)	0.1393	0.1797	0.1221	0.1316	0.1609
Goodness of fit on F^2	1.041	1.021	1.048	1.008	1.055

After 5 days at –20 °C a crop of crystals were obtained which were filtered and dried. ^{1}H NMR (C_6D_6) - 0.42 (3H, s, CH_3), 1.46 (9H, s, $C(CH_3)_3$), 1.65–1.76 (1H, m, CH_2), 1.79 (9H, s, $C(CH_3)_3$), 1.80 (3H, s, CH_3), 2.10–2.23 (1H, m, CH_2), 2.43–2.52 (1H, m, CH_2), 2.53 (3H, s, CH_3), 2.59 (1H, d J = 12.0 Hz, CH_2), 2.66–2.79 (1H, m, CH_2), 3.56 (1H, d J = 12.0 Hz, CH_2), 6.56 (1H, t J = 7.5 Hz, Ar-H), 6.76 (1H, dd J = 7.5 Hz, J = 1.0 Hz, Ar-H), 6.92 (1H, d J = 2.5 Hz, Ar-H), 7.23 (1H, d J = 7.0 Hz, Ar-H), 7.35 (1H, s, CH), 7.60 (1H, d J = 2.5 Hz, Ar-H). ^{13}C{^{1}H} (C_6D_6) - 10.0, (Al-CH_3), 16.5 (CH_3), 30.1, 32.3 ($C(CH_3)_3$), 34.4, 35.5 ($C(CH_3)_3$), 44.1 (CH_3), 51.2, 54.4, 59.2 (CH_2), 115.3 (Ar-CH), 117.2, 122.1 (Ar-C), 123.8, 124.0 (Ar-CH), 131.2 (Ar-C), 131.4, 137.1 (Ar-CH) 138.2, 138.7 (Ar-C), 156.9, 167.2 (Ar-O), 172.7 (CH). Anal: Calc for $C_{27}H_{39}N_2O_2Al$ C, 71.97, H 8.72, N 6.22. Found C 71.6, H 8.65, N 6.08.

X-Ray crystallography

Crystallographic data are summarised in Table 2. All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97.[16] Hydrogen atoms were included in idealised position. Refinement was straightforward with the following noteworthy points–for Al(**8**)Me one ^{t}Bu group was disordered over two positions in a 60 : 40 ratio the minor component was left isotropic, due to crystal quality the R_{int} for this structure was higher than desirable.

Acknowledgements

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