L- and rac-lactide polymerisation using scandium and aluminium permethylindenyl complexes

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The synthesis and characterisation of constrained geometry scandium and aluminium permethylindenyl complexes \( \text{Me}_2\text{SB}((\text{N},\text{I}^\ast)\text{Sc}((\text{THF})) (R = \text{Pr}, \text{Bu} (2) \text{and Ph} (3), \text{Me}_2\text{SB}((\text{N},\text{I}^\ast)\text{Sc}((\text{O}-2,6-\text{Pr}-\text{C}_6\text{H}_3)) (\text{THF}) (4), \text{Me}_2\text{SB}((\text{N},\text{I}^\ast)\text{Sc}((\text{O}-2,4-\text{Bu}-\text{C}_6\text{H}_3)) (\text{THF}) (5) \text{Me}_2\text{SB}((\text{R},\text{I}^\ast)\text{Sc}((\text{O}-2,6-\text{Pr}-\text{C}_6\text{H}_3)) (\text{THF}) (6), \text{Me}_2\text{SB}((\text{Pr},\text{I}^\ast)\text{Sc}((\text{O}-2,6-\text{Pr}-\text{C}_6\text{H}_3)) (\text{THF}) (7), \text{Me}_2\text{SB}((\text{Bu},\text{I}^\ast)\text{Al}((\text{O}-2,6-\text{Me}-\text{C}_6\text{H}_3)) (\text{THF}) (8) \text{and Me}_2\text{SB}((\text{Bu},\text{I}^\ast)\text{Al}((\text{O}-2,4-\text{Bu}-\text{C}_6\text{H}_3)) (\text{THF}) (9)) \) are reported. All complexes were characterised by NMR spectroscopy. Ring-opening polymerisation of L- and rac-lactide using all complexes with the exception of 6 show first-order dependence on monomer concentration and produced polylactide with unimodal molecular weight distribution. First-order dependence on catalyst concentration was determined from L-lactide polymerisation using 4 and 9. Moderately heterotactic polylactide (\( \rho = 0.53–0.68 \)) was achieved from rac-lactide polymerisation using 4, 5, 7 and 9. The effects of the metal centre (Sc and Al), the amido substituent (Pr, Bu, Ph and the aryloxide initiating group (O-2,6-Me-C\(_6\)H\(_3\), O-2,6-Pr-C\(_6\)H\(_3\) and O-2,4-Bu-C\(_6\)H\(_3\)) on the catalytic activity are discussed.

Introduction

Poly(lactide) (PLA) has diverse usage due to its biodegradability, biocompatibility and production from renewable feedstocks such as corn starch and sugar cane.\(^1\) Two stereocentres per lactide (LA) molecule result in L-LA (S,S-LA), d-LA (R,R-LA) and meso-LA (R,S-LA). A racemic mixture of L-LA and d-LA is referred to as rac-LA. Ring-opening polymerisation (ROP) of lactide initiated by single-site metal catalysts via a coordination-insertion mechanism can form well-controlled polymers in terms of molecular weight, molecular weight distribution and microstructure.\(^2\) Single-site initiators are based on Lewis acidic metal centre surrounded by ancillary ligand(s), and an initiating nucleophile which is commonly an alkoxide group.\(^2\) Constrained geometry complexes (CGCs) were originally developed in the academic literature by Bercaw et al. for scandium centres with a dicaticonic ligand and a dimethylsilyl ansa-bridge (SiMe\(_2\)) linking a cyclopentadienyl ring and an amido ligand.\(^3\) Afterwards, Okuda et al. reported titanium and ferro-cene CGCs containing a bridged amido-cyclopentadienyl \( \{\text{C}_5h_4(\text{Bu})^+\} \) ligand.\(^4\) Since then, several synthesis and applications of CGCs containing different substituted cyclopentadienyl, indenyl and fluorenyl groups, coordinating heteroatoms, ansa-linkages and metal centres were reported in the literature,\(^5\) particularly Group 4 CGCs for olefin polymerisations.\(^6\) The enhanced ability of Group 4 CGCs for ethylene polymerisation and (co)polymerisation of ethylene and \( \alpha \)-olefins is ascribed to a smaller Cp centroid–M bond angle than the typical Cp centroid–M–Cp centroid in metalloocene systems and a reduced tendency to undergo chain transfer reactions, resulting in high molecular weight polymers.\(^3a\),\(^7\) More electron deficient metal centres (an amido moiety formerly donates two electrons less than a cyclopentadienyl-based ligand) also promote olefin insertion into the metal–carbon bond and increase reactivity.\(^3a\),\(^7\) Due to the higher thermal stability than related metalloccenes, higher polymerisation temperatures are permitted by alkyl or dialkyl CGCs.\(^8\) The indenyl ligand (C\(_5h_7^-, \text{Ind}, I\) has been studied as an alternative to the cyclopentadienyl ligand (C\(_5h_5^-, \text{Cp}\)).\(^6\),\(^a\),\(^b\),\(^9\) The indenyl ring slippage from \( \eta^5 \) to \( \eta^1 \)-hapticity was observed when the formal number of metal electrons increased by two, resulting in a higher activity of ligand substitution reactions of electronically unsaturated complexes compared to their analogous Cp complexes.\(^10\) Permethylation of the indenyl ring has been proposed to increase steric congestion around the metal centre compared to the indenyl ligand, and afford kinetic stability to the
Results and discussion

Synthesis of constrained geometry scandium complexes

Reactions of $\text{Me}_2\text{SB}(\text{RN},\text{I}^\ast)\text{ScCl(THF)}$ (R = $\text{Pr}$, $\text{Bu}$, $\text{iBu}$ and Ph) and ScCl₃·THF in a 1:1 molar ratio were carried out in benzene at room temperature (Scheme 1a). $\text{Me}_2\text{SB}((\text{RN},\text{I}^\ast)\text{ScCl(THF)}$ (1), $\text{Me}_2\text{SB}((\text{RN},\text{I}^\ast)\text{ScCl(THF)}$ (2) and $\text{Me}_2\text{SB}((\text{PhN},\text{I}^\ast)\text{ScCl(THF)}$ (3) were isolated as yellow solids in 35, 6 and 41% yield, respectively. A series of aryloxide complexes $\text{Me}_2\text{SB}((\text{PhN},\text{I}^\ast)\text{ScCl(THF)}$ (4), $\text{Me}_2\text{SB}((\text{PhN},\text{I}^\ast)\text{ScCl(THF)}$ (5), $\text{Me}_2\text{SB}((\text{PhN},\text{I}^\ast)\text{ScCl(THF)}$ (6) and $\text{Me}_2\text{SB}((\text{PhN},\text{I}^\ast)\text{ScCl(THF)}$ (7) were synthesised from reactions between complexes 1–3 and appropriate potassium aryloxide salts (Scheme 1b). Complexes 4, 5 and 7 were isolated in 44, 34 and 41% yields, respectively. The $^1$H NMR spectra of 1–7 (see ESIT†) show five singlets corresponding to the indenyl methyl protons at 1.50–3.00 ppm and two singlets corresponding to the silylmethyl groups between 0.50–1.20 ppm. Resonances of methylene protons of a THF molecule coordinated to the metal centre were also observed. The X-ray crystal structures of complexes 2–4 and 6 have been determined and are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

Single crystals suitable of X-ray diffraction studies of 2 and 3 were grown at room temperature of saturated benzene solution and pentane solution, respectively, and found to crystallise in the space group $P1$ and $C2/c$. The solid-state structures of 2 and 3 are dimeric, consisting of two chloride-bridged scandium centres. Each scandium centre has a distorted square pyramidal geometry, evidenced by the $\tau_5$ values of 0.22 and 0.02 for 2 and 3, respectively, with $\eta^1$-coordination with the $\text{C}_5\text{Me}_5$ ring. The oxygen of the THF ligand and nitrogen of the amido group also coordinate to the metal centre. The Sc (1)–1$^\ast$ cent bond length of 3 (2.1845(1) Å) is slightly longer than 2 (2.1836(1) Å) due to the increased steric bulk of the phenyl group on the amido ligand compared with the $n$-butyl group. The two $\text{C}_5\text{Me}_5$ rings on 2 have a trans arrangement while those on 3 have a cis arrangement. Therefore, the plane containing scandium and chlorine atoms of 2 is planar while that of 3 is puckered with an interplanar angle of 24.3° (Fig. S61†) in order to reduce steric repulsion between the $\text{C}_5\text{Me}_5$ rings.

The average Sc–Cl bond lengths of 2 and 3 (2.5987 and 2.5894 Å) are comparable to those observed from reported complexes.16 Compared to 3, an analogous Cp-based scandium CGC $[\text{Me}_2\text{SB}(\text{PhN},\text{C}_5\text{Me}_5)\text{Sc}[\text{μ-Cl}(\text{THF})]$ was reported by Hou et al., has comparable Sc–Cl (2.545 Å), Sc–Cp$_{\text{cent}}$ (2.171 Å), Sc–N (2.142 Å) and Sc–O (2.224 Å) bond lengths.16k The crystal structure of $[\text{Cp}_2\text{Sc}[\text{μ-Cl}]$_2 was reported with a Sc–Cl distance of 2.575 Å.16d Another THF-free complex $[\text{Sc}(\text{N}_2\text{N}^\ast\text{Cl},\text{Me})\text{Sc}[\text{μ-Cl}]$, where $\text{N}_2\text{N}^\ast\text{Cl},\text{Me} = \text{MeN}[(\text{CH}_2)_2\text{NSiMe}_2]_2$ was reported with a Sc–Cl bond length of 2.5683 Å,16e $[\text{Sc}(\text{C}_8\text{H}_8)[\text{μ-Cl}(\text{THF})]$ was reported with $[\text{Sc}(\text{C}_8\text{H}_8)[\text{4-SiMe}_2]_2[\text{μ-Cl}]$ and $[\text{Sc}(\text{C}_8\text{H}_8)[\text{4-SiMe}_2]_2[\text{μ-Cl}]$ and $[\text{Sc}(\text{C}_8\text{H}_8)[\text{4-SiMe}_2]_2[\text{μ-Cl}]$.16d were reported with Sc–Cl bond distances of 2.5972 and 2.5155 Å, respectively. A scandium chloride complex containing $\text{C}_5\text{Me}_5\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph}$ ligand has a tetrameric structure with the average Sc–Cl bond
The crystal structures of 2 and 3 also show similar Sc(1)–I\(^{*}\)cent bond lengths to those of cyclopentadienyl based scandium chloride complexes (2.12–2.18 Å).\(^{16}\) In contrast to the dimeric structure of 2 and 3, their titanium analogues were described as monomeric with no THF ligand coordinated to the metal centre.\(^{12}\) The Ti–C\(_{\text{Cp}}\)cent (2.03 Å) and Ti–N (1.89–1.94 Å) bond lengths of Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))TiCl\(_2\) (R = \(t\)-Bu, \(i\)-Pr and 4-\(t\)-Bu-C\(_6\)H\(_4\)) are smaller than those of 2 and 3.

Solid-state structures of Me\(_2\)SB(\(n\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF) (4) and Me\(_2\)SB(\(t\)-Bu          N,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF) (6) are monomeric with a distorted tetrahedral geometry at the scandium centre, indicated by the \(\tau_4\) parameters of 0.89 and 0.86 for 4 and 6,\(^{17}\) respectively. The bond distances of Sc(1)–O(1) and Sc(1)–N(1) of 4 (1.9344(10) and 2.0458(12) Å) are slightly longer than those of 6 (1.9298(1) and 2.0265(1) Å). The bond lengths of Sc(1)–I\(^{*}\)cent, Sc(1)–O(1), Sc(1)–O(2) and Sc(1)–N(1) of 4 and 6 are comparable to those previously reported from Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF)\(^{14}\) (Table 1). As a consequence of the less sterically demanding \(n\)-Bu group on the amido ligand of 6 compared to the \(i\)-Pr group on 4 or \(t\)-Bu group on Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF), the aryloxide group is more oriented towards the amido ligand on 6 than 4 or Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF). Hence, the Sc(1)–O(1)–COAr angle of 169.94(1) in 6 is considerably smaller than that of 176.91(9)° in 4 and 175.63(9)° in Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF).

### Table 1

Selected bond lengths (Å) and angles (°) for Me\(_2\)SB(\(n\)-BuN,I\(^{*}\))Sc(Cl)(THF) (2) and Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(Cl)(THF) (3), Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF) (4), Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF) (6) and Me\(_2\)SB(\(n\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF)\(^{14}\) (E.S.D.s are given in parentheses)

| Complex                  | 2               | 3               | 4               | 6               | Ref\(^{b}\) |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------|
| Sc(1)–I\(^{*}\)cent      | 2.1836(1)       | 2.1845(1)       | 2.1704(1)       | 2.1735(1)       | 2.1718(1) |
| Sc(1)–Cl(1)              | 2.5700(5)       | 2.5732(5)       | —               | —               | —         |
| Sc(1)–Cl(1\(^{'\})      | 2.6273(5)       | —               | —               | —               | —         |
| Sc(1)–O(1)               | 2.2257(12)      | 2.2174(12)      | 1.9344(10)      | 1.9298(1)       | 1.9450(9) |
| Sc(1)–O(2)               | —               | 2.1705(10)      | 2.1820(1)       | 2.1820(1)       | 2.1868(9) |
| Sc(1)–N(1)               | 2.0412(14)      | 2.0909(14)      | 2.0458(12)      | 2.0265(1)       | 2.0593(11) |
| Sc(1)–O(1)–C\(_{21}\)    | 102.77          | 102.50          | 103.82(1)       | 103.63          | 103.99(1) |
| Sc(1)–O(1)–C\(_{22}\)    | 105.173(15)     | 102.264(15)     | —               | —               | —         |
| Sc(1)–O(1)–C\(_{\text{OM}}\) | —               | —               | 176.91(9)       | 169.94(1)       | 175.63(9) |

\(^a\) Me\(_2\)SB(\(t\)-BuN,I\(^{*}\))Sc(O-2,6-\(i\)-Pr-C\(_6\)H\(_3\))(THF).\(^{14}\) \(^b\) Sc(1)–O(1)–C(21) for 4 and Sc(1)–O(1)–C(22) for 6.
Synthesis of constrained geometry aluminium complexes

Me₂SB([BuN, I*]Al(Cl)(THF) (8) was prepared in 49% yield via the salt elimination reaction of Me₂SB([BuN, I*]Li2(THF) and AlCl₃·THF in benzene at room temperature (Scheme 2a). The aryloxide complexes, Me₂SB([BuN, I*]Al(O-2,6-Me-C₆H₃)(THF) (9) and Me₂SB([BuN, I*]Al(O-2,4'-Bu-C₆H₃)(THF) (10), were synthesised by reactions of 8 and K(O-2,6-Me-C₆H₃) or K(O-2,4'-Bu-C₆H₃) in benzene at room temperature (Scheme 2b), and were isolated in 41 and 24% yield, respectively. Reaction of 8 with K(O-2,6-iPr-C₆H₃) to form Me₂SB([BuN, I*]Al(O-2,6'-iPr-C₆H₃)(THF) was carried out. However, several attempts to isolate clean product of Me₂SB([BuN, I*]Al(O-2,6'-Pr-C₆H₃)(THF) were unsuccessful. The ¹H NMR spectra of 8–10 (Fig. S18, S20 and S22†) show two sets of resonances corresponding to a mixture of two isomers.

Diffraction-quality crystals were grown from a concentrated benzene solution of 8 and 9 and a pentane solution of 10 at room temperature. X-ray crystal structures of 8 and 9 (Fig. 2) were obtained for one isomer, while for complex 10 (Fig. 3), both isomers were obtained (Fig. S22†). In contrast to the scandium constrained geometry complexes (1–7), 8–10 display σ-instead of π-bonding interactions between the metal centre and C₉Me₆ ring due to the absence of accepting d-orbitals on the aluminium centre. The hapticity of one between the C₉Me₆ ring and the metal centre is consistent with the known Group 1318 and 1519 cyclopentadienyl constrained geometry complexes reported in literature. Cowley et al. synthesised and crystallographically characterised complexes Me₂SB([BuN,C₅Me₄]M(CH₃)(THF) (M = Al and Ga).18b The C₅Me₄ ring possesses a...
localised diene structure, and the σ-attachment occurs at the metal centre at an α position with respect to the SiMe₂ group affording a five-membered ring M–C–C–Si–N ring. The solid-state structures of 8–10 show σ-bonds between the aluminium centre and the carbon on the C₉Me₆ ring adjacent to SiMe₂ group, and the nitrogen of the tBuN moiety linked between the metal centre and the SiMe₂ group. The four-membered ring of Al–C–Si–N is perpendicular to the C₉Me₆ ring. Distorted tetrahedral geometry at the aluminium centre was observed, confirmed by the τ values of 0.81, 0.76 and 0.72 for 8, 9 and 10, respectively. The presence of the four-membered ring species was reported by Rieger et al. for the solid-state structure of aluminium constrained geometry cyclopentadienyl complex containing the lutidinyl moiety.

In contrast to the analogous dimeric scandium complexes (2 and 3), 8 was obtained as a monomer with smaller M(1)–Cl (1 bond length of 2.1375(7) Å than those in 2 and 3 (2.5700–2.5732 Å). A similar trend was observed for the aryl-oxide complexes 9 and 10 with the shorter M(1)–O, M(1)–O (2) and M(1)–N(1) distances comparing to those of 4 and 6. The C(1)–Al(1)–O(1) and Al(1)–O(1)–C₉Me₆ angles of 9 (124.98(6) and 143.72(14)°) are considerably smaller than those of 10 (133.04(13) and 147.2(2)°) as a result of the less sterically-hindered aryl-oxide group on 9.

X-ray crystal structures of 10 show two components of the complex in which the C₉Me₆ ring featuring in two different positions (Fig. 3, Table S6†). The C₉Me₆ ring in isomer 1 and isomer 2 are labelled as C(1)–C(9) and C(1c)–C(9c), respectively. The direction of the six-membered ring on the C₉Me₆ ring of isomer 1 is at the front side of the five-membered ring, while that of isomer 2 is at the backside of the five-membered ring. Bond lengths and angles of the two isomers of 10 are shown in Table 2. The significant differences between the C(1)–Al(1)–O(1) and C(1)–Al(1)–O(2) angles in isomer 1 and those in isomer 2 were observed, and reflect a different conformation of the C₉Me₆ ring found in the solid state structures of 10. The ratio of these two components from the crystal structure of 10 (59 : 41) is consistent with those from the solution ¹H NMR spectrum (55 : 45) (Fig. S22†). Two isomers found in the ¹H NMR spectra of 8 and 9 (Fig. S18 and S20†) are also proposed to be attributed to the different C₉Me₆ ring position.

Table 2 Selected bond lengths (Å) and angles (°) for Me₂SB[(tBuN)₃]AlCl(THF) (8), Me₂SB[(tBuN)₃]Al(O-2,6-Me-C₆H₃)(THF) (9) and isomer 1 and 2 of Me₂SB[(tBuN)₃]Al(O-2,4-tBu-C₆H₃)(THF) (10) (E.S.D.s are given in parentheses)

| Complex                  | 8         | 9         | 10 (Isomer 1) | 10 (Isomer 2) |
|--------------------------|-----------|-----------|---------------|---------------|
| Al(1)–Cl(1)              | 2.1375(7) | —         | 1.7150(15)    | 1.712(3)      |
| Al(1)–O(1)               | 1.8600(13)| —         | 1.891(15)     | 1.880(2)      |
| Al(1)–O(2)               | 1.8047(15)| —         | 1.8211(18)    | 1.815(2)      |
| Al(1)–N(1)               | 2.0257(18)| —         | 2.027(2)      | 2.051(4)      |
| Al(1)–C(1)               | 1.1078(7) | 112.96(8) | 133.04(13)    | 111.5(2)      |
| C(1)–Al(1)–O(1)          | —         | 1.1506(8) | 101.68(15)    | 129.1(3)      |
| C(1)–Al(1)–O(2)          | —         | 88.36(8)  | 89.13(14)     | 86.8(3)       |
| Si(1)–C(1)–Al(1)         | 82.08(7)  | 82.67(8)  | 81.13(16)     | 80.4(3)       |
| C(1)–Si(1)–N(1)          | 94.17(7)  | 94.34(8)  | 94.87(14)     | 90.0(2)       |
| Al(1)–O(1)–C₉Me₆         | —         | 143.72(14)| 147.2(2)      | 147.2(2)      |
cases, evidenced by linear plots of ln([L-LA]0/[L-LA]) dependence on monomer concentration was observed in all initiation step. For lactide insertion into the metal crowding around the metal centre and an increased rate of 7 exhibited greater polymerisation rate than 4 (see ESI†). Calculated \( M_n \) for PLA synthesised by using 1–3 = conv.(%) \times 400 \times 144.1 + 108.1, calculated \( M_n \) for PLA synthesised with 4 and 7 = conv.(%) \times [LA]_0 \times 144.1 + 178.1 and calculated \( M_n \) for PLA synthesised by using 5 = conv.(%) \times [LA]_0 \times 144.1 + 206.2.

### Table 3: Selected polymerisation data using complexes 1–5 and 7

| Entry | Complex | LA \([\text{LA}]_0 : [\text{Sc}]_0 : [\text{BnOH}]_0\) | \( T (^\circ \text{C})\) | \( t (h)\) | Conv.(%) | \( k_{\text{obs}} (h^{-1})\) | \( M_n (\text{GPC}) (g \text{ mol}^{-1})\) | \( M_n (\text{Calc}) (g \text{ mol}^{-1})\) | \( M_n / M_n\) | \( P_i\) |
|-------|---------|-----------------------------------------------|-----------------|--------|---------|----------------|----------------|----------------|----------------|------|
| 1     | 1       | \( \text{L-} \) 400 : 1 : 1 | 70              | 2      | 90      | 1.21 ± 0.03 | 42290          | 51 984         | 1.17            | 0.00 |
| 2     | 2       | \( \text{L-} \) 400 : 1 : 1 | 70              | 3      | 91      | 0.89 ± 0.02 | 44 920          | 52 560         | 1.17            | 0.00 |
| 3     | 3       | \( \text{L-} \) 400 : 1 : 1 | 70              | 4.5    | 90      | 0.57 ± 0.02 | 39 810          | 51 984         | 1.16            | 0.00 |
| 4     | 4       | \( \text{L-} \) 600 : 1 | 70              | 2.25   | 87      | 1.18 ± 0.05 | 69 700          | 99 319         | 1.16            | 0.00 |
| 5     | 5       | \( \text{L-} \) 800 : 1 | 70              | 3      | 86      | 0.81 ± 0.01 | 103 670        | 150 618        | 1.14            | 0.00 |
| 6     | 6       | \( \text{L-} \) 1000 : 1 | 70              | 3.5    | 85      | 0.66 ± 0.02 | 91 500          | 122 663        | 1.13            | 0.00 |
| 7     | 7       | \( \text{L-} \) 1200 : 1 | 70              | 5      | 87      | 0.46 ± 0.01 | 103 670        | 150 618        | 1.14            | 0.00 |
| 8     | 8       | \( \text{L-} \) 1000 : 1 | 60              | 8      | 91      | 0.34 ± 0.01 | 105 980        | 130 309        | 1.09            | 0.00 |
| 9     | 9       | \( \text{L-} \) 1000 : 1 | 100             | 1.25   | 90      | 2.68 ± 0.09 | 75 280          | 129 868        | 1.19            | 0.00 |
| 10    | 10      | \( \text{L-} \) 1000 : 1 | 80              | 2.5    | 92      | 1.35 ± 0.04 | 85 090          | 132 750        | 1.18            | 0.00 |
| 11    | 11      | \( \text{rac-} \) 1000 : 1 | 70              | 2.5    | 93      | 1.27 ± 0.04 | 83 100          | 134 191        | 1.21            | 0.59 |
| 12    | 12      | \( \text{rac-} \) 1000 : 1 | 70              | 0.5    | 91      | 6.32 ± 0.37 | 77 560          | 131 337        | 1.18            | 0.00 |
| 13    | 13      | \( \text{rac-} \) 1000 : 1 | 70              | 0.5    | 91      | 7.40 ± 0.50 | 64 540          | 131 337        | 1.23            | 0.68 |
| 14    | 14      | \( \text{rac-} \) 1000 : 1 | 70              | 4      | 84      | 0.48 ± 0.01 | 69 570          | 121 222        | 1.15            | 0.00 |
| 15    | 15      | \( \text{rac-} \) 1000 : 1 | 70              | 3.5    | 86      | 0.58 ± 0.01 | 64 820          | 124 104        | 1.17            | 0.63 |

*Conditions for ROP using 1–3: \([\text{LA}]_0 : [\text{Sc}]_0 : [\text{BnOH}]_0 = 400 : 1 : 1\), \([\text{LA}]_0 = 0.5 \text{ M}, 7.0 \text{ mL toluene and conditions for ROP using 4, 5 and 7:} \([\text{LA}]_0 : [\text{Sc}]_0\) as stated, \([\text{LA}]_0 = 0.5 \text{ M}, 7.0 \text{ mL toluene.})*

The polymer tacticity measured by homonuclear decoupled \(^1\text{H}\{^1\text{H}\} \text{NMR spectroscopy showed that 4, 5 and} 7 produced slightly heterotactic polylactide with \( P_i \) values of 0.59–0.68, suggesting the initiators favour racemic enchainment with chain-end control, where the next monomer to insert has an opposing stereocentre from the last monomer. This suggests that the substituent on the amido group has marginal influence on the stereoselectivity. Isotactic pure poly(lactide) was formed without epimerisation during polymerisation of l-lactide with 4, 5 and 7, confirmed by a single resonance in the methine region of the \(^1\text{H}\{^1\text{H}\} \text{NMR spectra (see ESI†).})*

Detailed kinetic studies were performed using 4. Polymersisation of l-lactide with 4 using different catalyst loading was carried out at 70 °C in toluene. Concentration of l-lactide was maintained at 0.5 M while that of 4 was varied giving the monomer to catalyst ratio of 600, 800, 1000 and 1200. The polymerisation data are summarised in Table 3 (entries 4–7). First-order dependence on l-lactide was observed from all conditions evidenced by linear plots of ln([l-LA]_0/[l-LA]) vs. time with an induction period of 0.5 h (Fig. 5). The gradient of 0.89 is indicative of first-order dependence on the concentration of 4 (Fig. 6). The propagation rate constant (\( k_p \)) of 1120 ± 29 M⁻¹ h⁻¹ was calculated from plot of \( k_{\text{obs}} \) vs. \([4]_0\) (Fig. 7). The overall rate law was determined as \(-d[l-LA]/dt = k_p[l-LA][4]\).

The \(^1\text{H}\) NMR spectra of oligomers synthesised by 4 and 5 (Fig. S52 and S53†) show signals corresponding to O-2,6′-Pr-C₆H₃ and O-2,4′-Bu-C₆H₃ end-groups, suggesting that the ROP of lactide proceeds via a coordination–insertion mechanism (Scheme S1†). The presence of polylactide with \(^1\text{HN}\) and OH end-groups was observed from MALDI-ToF mass spectra of...
The order of reaction with respect to $\frac{[L-LA]}{[Sc]}_0$ is equal to 0.89 ± 0.02. (Fig. S57 and S58†), suggesting the role of the amido ligand as an initiator. Peaks corresponding to cyclic polylactide and a repeating unit of $\Delta(m/z) = 72.0$ Da between peak envelopes were also observed, indicating an occurrence of intra- and intermolecular transesterification reactions, respectively. Therefore, the considerably lower than calculated $M_n$(GPC) values could be attributed to double-site initiator from the amido and aryloxide ligands.

Complexes 4, 5 and 7 show better activity for $\Lambda$-lactide polymerisation with high monomer loading (600–1200) compared to other metallocene catalysts in the literature.1,13,24 Zirconocene bis(ester enolate) complex (Ph$_5$C(Cp,Flu)Zr[OC(O)Pr]CMe$_2$) reported by Chen et al. polymerised 200 equivalents of $\Lambda$-lactide (toluene, 80 °C) up to 85% within 5 h.24 Other zirconocene complexes (rac-C$_8$H$_8$(Ind)$_2$Zr[OC(O)Pr]CMe$_2$ and Cp$_2$Zr[OC(O)Pr]CMe$_2$) from the same research group were reported to be poorly active under the same conditions.24 A series of Cp and Ind-based group 4 complexes reported by O’Hare et al. were found to be active in $\Lambda$-lactide polymerisation.2,24 (Ind)$_2$ZrMe(Cl) reported by Hare et al. was the fastest catalyst with the $k_{obs}$ values of 0.317 and 0.293 h$^{-1}$ for polymerisation of $\Lambda$- and rac-$\Lambda$-lactide (50 equivalents) at 100 °C in chloroform-d$_4$, respectively. Me$_2$SB(Cp,1*)ZrCl(O-2,6-Me-C$_6$H$_3$)$_2$ presented a second-order dependence on $\Lambda$-lactide concentration ($k_{obs} = 3.23$ M$^{-1}$ h$^{-1}$) for the polymerisation with $\Lambda$-[L-LA]$_0$/[Zr]$_0$/[BnOH]$_0$ ratio of 50 : 1 : 2 in chloroform-d$_4$ at 80 °C.1,13 Okuda et al. reported the yttrocene complex Li[(Me$_2$Si(Cp,NC$_2$H$_4$OMe)$_2$)Y] as the fastest catalyst for $\Lambda$-lactide polymerisation using scandium aryloxide complex supported by a pentadentate (N$_2$O$_3$) salen-type ligand in THF at room temperature (71% conversion, 2 h).25 Scandium alkoxide complexes containing a phosphasalen ligand were found to be inactive for rac-$\Lambda$-lactide polymerisation attributed to the formation of an unreactive single-lactide insertion product.26

The effect of temperature on $\Lambda$-lactide polymerisation activity using 4 was studied with polymerisation temperature varied from 60–100 °C (Table 3, and Fig. 8). The enthalpy of activation $(\Delta H^\ddagger)$ of 53 kJ mol$^{-1}$ and entropy of activation $(\Delta S^\ddagger)$ of ~95 J mol$^{-1}$ K$^{-1}$ were calculated from an Eyring plot of ln($k_{obs}/T$) vs. 1/T (Fig. S76†). These values are comparable to those reported, and suggest the ordered transition state in a coordination–insertion mechanism.1,13 As expected, the polymerisation activity increased at higher temperatures. $M_n$/$M_n$ values and discrepancy between $M_n$(GPC) values and those calculated were observed to increase with increased temperature, attributed to transesterification reactions. 

**Polymerisation of $\Lambda$- and rac-$\Lambda$-lactide using aluminium complexes**

Me$_2$SB(η$^8$BuN,1*)Al(Cl)(THF) (8) was found to be less active than the analogous scandium chloride complexes (1–3) for $\Lambda$-lactide polymerisation in the presence of benzyl alcohol even at higher polymerisation temperature (100 °C) and lower ratio of
reached 55% after 7.5 h which first-order dependence on 80% conversion. The experimental Fig. S84
angle:
time of polymerisation (Fig. S85 and S100
(11 636 g mol
is higher than that calculated for one chain per metal centre
70 °C, blue circle: \( k_{\text{obs}} = 0.66 \pm 0.02 \) h\(^{-1}\), \( R^2 = 0.989 \). 80 °C, yellow triangle: \( k_{\text{obs}} = 1.35 \pm 0.04 \) h\(^{-1}\), \( R^2 = 0.996 \). 100 °C, green down triangle: \( k_{\text{obs}} = 2.68 \pm 0.09 \) h\(^{-1}\), \( R^2 = 0.989 \). Conditions: \([\text{L-LA}]_0 = 0.5 \text{ M}, [\text{L-LA}]_0 : [\text{BnOH}]_0 = 1000, 7.0 \text{ mL toluene.}\)

\([\text{L-LA}]_0 : [\text{Al}]_0 : [\text{BnOH}]_0 = (100 : 1 : 1)\). \( \text{l-Lactide} \) conversion reached 55% after 7.5 h which first-order dependence on \( \text{l-lactide} \) concentration was observed (\( k_{\text{obs}} = 0.11 \) h\(^{-1}\), Fig. S84\)). The polymerisations were quenched after 23 h with 80% conversion. The experimental \( M_n \) value (17 600 g mol\(^{-1}\)) is higher than that calculated for one chain per metal centre (11 636 g mol\(^{-1}\)) with moderate \( M_n/M_M \) value of 1.37. \( \text{OCH}_2\text{Ph} \) terminated polylactide was observed from the \( ^1\text{H} \) NMR (Fig. S54\(^\dagger\)) and MALDI-ToF mass spectra (Fig. S59\(^\dagger\)). \( \text{Me}_2\text{SB}[^{11}\text{B}]\text{N,I}^*\text{Al}[\text{O}-2,6-\text{Me}-\text{C}_6\text{H}_3](\text{THF}) \) (9) and \( \text{Me}_2\text{SB}[^{11}\text{B}]\text{N,I}^*\text{Al}[\text{O}-2,4-\text{Bu}-\text{C}_6\text{H}_3](\text{THF}) \) (10) show comparable activity for polymerisation of \( \text{l-lactide} \) at 100 °C in toluene with more than 80% conversion reached after 9 h (Table 4, entries 3 and 10). Kinetic studies show the first-order dependence on \( \text{l-lactide} \) concentration, supported by linear plots of ln(\([\text{L-LA}]_0 / [\text{L-LA}]_0 \)) vs. time of polymerisation (Fig. S83 and S100\(^\dagger\)) with \( k_{\text{obs}} \) values of 0.24 and 0.19 h\(^{-1}\) for the polymerisation with 9 and 10, respectively. Isotactic poly\(\text{l-lactide} \) was produced with an absence of epimerisation occurring during polymerisation as evidenced by a singlet in the methine region of the homonuclear decoupled \( ^1\text{H}(^1\text{H}) \) NMR spectrum (Fig. S42 and S50\(^\dagger\)).

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Fig. 8 Plots of ln([L-LA]/[L-LA]) vs. time of polymerisation. ROP of \( \text{l-lactide} \) using 4. 60 °C, red square: \( k_{\text{obs}} = 0.34 \pm 0.01 \) h\(^{-1}\), \( R^2 = 0.995 \). 70 °C, blue circle: \( k_{\text{obs}} = 0.66 \pm 0.02 \) h\(^{-1}\), \( R^2 = 0.989 \). 80 °C, yellow triangle: \( k_{\text{obs}} = 1.35 \pm 0.04 \) h\(^{-1}\), \( R^2 = 0.996 \). 100 °C, green down triangle: \( k_{\text{obs}} = 2.68 \pm 0.09 \) h\(^{-1}\), \( R^2 = 0.989 \). Conditions: \([\text{L-LA}]_0 = 0.5 \text{ M}, [\text{L-LA}]_0 : [\text{Al}]_0 = 1000, 7.0 \text{ mL toluene.}\)

Heterotactic polylactide (\( P_t = 0.57 \)) was produced after 280 h with \([\text{rac-LA}]_0 : [\text{Al}]_0 = 50 \text{ in toluene at 70 °C. Aluminium methyl complexes supported by tetradentate phenoxy-amine ligand.}\(^{30b}\) Heterotactic polylactide (\( P_t = 0.57 \)) was produced after 280 h with \([\text{rac-LA}]_0 : [\text{Al}]_0 = 50 \text{ in toluene at 70 °C. Aluminium methyl complexes supported by asymmetric [ONNO]\(^*\)type Salan ligand reported by Hormnirun \( et\) \( et\) \( al\). polymerised 100 equivalents of \( \text{rac-LA} \) with benzyl alcohol in toluene at 70 °C (more than 80% conversion after 300 h).\(^{30e}\) Heterotactic polylactides were formed with \( P_t \) values of 0.64–0.74.

All polymerisations produced polymers with monomodal molecular weight distribution and moderate \( M_w/M_M \) values (1.29–1.44, Table 4). Experimental \( M_n \) values are also consistent with those calculated for one chain per metal centre, suggesting a well-controlled and living manner of polymerisation can be attained under harsh experimental conditions.

Table 4 Selected polymerisation data using complexes 9 and 10\(^\dagger\)

| Entry | complex | LA  | \([\text{LA}]_0 : [\text{Al}]_0 \) | \( T \) (°C) | \( t \) (h) | Conv.\(^b\) (%) | \( k_{\text{obs}} \) (h\(^{-1}\)) | \( M_n(GPC)\) (g mol\(^{-1}\)) | \( M_n(\text{calcld})\) (g mol\(^{-1}\)) | \( M_w/M_M \) |
|-------|---------|-----|----------------|-------------|----------|---------------|------------------|-------------------------|-------------------------------|-------------------|
| 1     | 9       | L-  | 100            | 70          | 55       | 82            | 0.04 ± 0.01      | 11 600                  | 11 938                       | 1.44              |
| 2     | 9       | L-  | 100            | 80          | 47       | 89            | 0.05 ± 0.01      | 15 290                  | 12 947                       | 1.41              |
| 3     | 9       | L-  | 100            | 90          | 23       | 90            | 0.11 ± 0.01      | 14 520                  | 13 091                       | 1.37              |
| 4     | 9       | L-  | 100            | 100         | 9        | 86            | 0.24 ± 0.01      | 12 420                  | 12 515                       | 1.35              |
| 5     | 9       | L-  | 200            | 100         | 10       | 81            | 0.20 ± 0.01      | 21 230                  | 23 466                       | 1.27              |
| 6     | 9       | L-  | 300            | 100         | 11       | 79            | 0.17 ± 0.01      | 25 310                  | 34 274                       | 1.33              |
| 7     | 9       | L-  | 500            | 100         | 24       | 85            | 0.08 ± 0.01      | 46 040                  | 61 364                       | 1.33              |
| 8     | 9       | L-  | 700            | 100         | 24       | 77            | 0.06 ± 0.01      | 53 110                  | 77 792                       | 1.31              |
| 9     | 9       | L-  | 1000           | 100         | 27       | 76            | 0.05 ± 0.01      | 74 390                  | 109 638                      | 1.16              |
| 10    | 10      | rac-| 100            | 100         | 8        | 87            | 0.30 ± 0.01      | 12 070                  | 12 659                       | 1.29              |
| 11    | 10      | L-  | 100            | 100         | 10       | 82            | 0.19 ± 0.01      | 13 310                  | 12 022                       | 1.37              |

\[^a\] Conditions: \([\text{LA}]_0 = 0.5 \text{ M}, 4.0 \text{ mL toluene.}\] \[^b\] Measured by \(^1\text{H} \) NMR spectroscopic analyses. \[^c\] Determined by GPC in THF against PS standards using the appropriate Mark-Houwink corrections.\(^{2,3}\) \[^d\] Calculated \( M_n \) for PLA synthesised by using 9 = conv. (%) × 100 × 144.1 + 122.2 and calculated \( M_n \) for PLA synthesised by using 10 = conv. (%) × 100 × 144.1 + 206.2.
including high temperature and long polymerisation time. The polymerisation of \( L \)-lactide with 9 using various monomer to catalyst ratios was carried out at 100 °C in toluene to determine the kinetic order dependence on catalyst concentrations. The concentration of \( L \)-lactide remains at 0.5 M, while the concentration of 9 was varied, providing the ratio of \([L-LA]_0 : [9]_0 = 200, 300, 500, 700 \) and 1000. The polymerisation data are summarised in Table 4 (entries 5–9). Plots of first-order dependence on \( L \)-lactide concentration are shown in Fig. 10. The gradient of 0.79 from the plot of \(-\ln(k_{obs})\) vs. \(-\ln[9]_0\) is indicative of the first-order dependence on catalyst concentration (Fig. S97†).

The propagation rate constant \( k_p \) of 70 ± 11 M\(^{-1}\) h\(^{-1}\) was calculated from the plot between \( k_{obs} \) vs. \([9]_0\) (Fig. S98†). The overall rate law was determined as \(-d[L-LA]/dt = k_p[L-LA][9]\). At a \([L-LA]_0 : [Al]_0\) ratio of 200 and 300, \( M_n(GPC)\) values are similar to those calculated. However, polylactide obtained from high monomer loading \([L-LA]_0 : [Al]_0 = 500, 700 \) and 1000 show molecular weights lower than those predicted with moderate \( M_n/M_w\) values (1.16–1.33). The MALDI-ToF mass spectrum of polymer synthesised by 9 (Fig. S60†) shows peaks corresponding to polylactide with O-2,6-Me-C\(_6\)H\(_3\) and OH end-groups. Other peaks are assigned to polylactide terminated with \( \text{MeNH} \) and OH end-groups. Double-site initiator from the amido and aryl oxide ligands, which was previously observed from ROP initiated by 4, results in the mismatch between the \( M_n(GPC)\) values and those calculated for one polymer chain per metal centre.

Conclusions

A series of new scandium (1–7) and aluminium (8–10) constrained geometry permethylindenyl complexes were reported. Scandium complexes (1–5 and 7) are highly active catalysts for lactide polymerisation whereas aluminium complexes (8–10) show moderate activity. First-order dependence on lactide concentration was observed in all polymerisations. First-order dependence on catalyst concentration was measured from polymerisation of \( L \)-lactide using 4 and 9 with \( k_p \) values of 1120 ± 29 and 70 ± 11 M\(^{-1}\) h\(^{-1}\), respectively. Polymers with \( M_n(GPC)\) values lower than those calculated for one polymer chain per metal centre were observed, attributed to the double-site nature of scandium and aluminium complexes using these amido and aryl oxide ligands.

Complexes with a more electron donating substituent on the amido ligand (\( \text{Pr} > ^8\text{Bu} > \text{Ph} \)) show greater polymerisation activity as observed from \( L \)-lactide polymerisation using 1–3 with one equivalent of benzyl alcohol and \( L \)-and \( rac \)-lactide polymerisation using 4, 5 and 7. The effect of the less sterically demanding aryl oxide substituent was observed with the scandium system as 5 (O-2,4-\(^8\text{Bu}-\text{C}_6\text{H}_3\) shows higher activity than 4 (O-2,6-\( \text{Pr}-\text{C}_6\text{H}_3\)). Complexes 1–5 and 7–10 produced isotactic poly-\( L \)-lactide without epimerisation occurring during polymerisation. Moderate heterotactically enriched polylactide \( (P_r = 0.53–0.68)\) was obtained from polymerisation of \( rac \)-lactide using 4, 5, 7 and 9, suggesting minor influence of the metal centre, the amido substituent and the aryl oxide group on the stereoselectivity.

Experimental section

General polymerisation procedure

To a stock solution of 1–3 and 8 (31.25 \( \mu \)mol) in toluene (5.00 mL), benzyl alcohol (31.25 \( \mu \)mol) was added. \( L \)-Lactide (2.50 mmol) was added into an ampoule and dissolved in 4.0 mL of toluene. The catalyst stock solution (1.0 mL) was added to the solution of lactide in the ampoule, corresponding to an initial lactide concentration of 0.5 M and a
The polymerisation ampoule was then stirred at the preheated oil bath at desired temperature.

A stock solution of 4, 5, 7, 9, 10 (17.50 μmol) in benzene (2.50 mL) was prepared. The stock solution of catalyst (3.50 μmol, 0.50 mL) was added into a toluene solution of lactide (0.50 g, 3.50 mmol, 6.50 mL) in the ampoule, corresponding to an initial lactide concentration of 0.5 M and a monomer-to-catalyst ratio of 1000:1. The polymerisation ampoule was then stirred at the preheated oil bath at desired temperature.

Aliquots (ca. 0.1 mL) were taken at appropriate time intervals and quenched with THF (ca. 0.3 mL). The volatiles were evaporated to give PLA. The monomer to polymer% conversion was determined using $^1$H NMR spectroscopy and measured by integration of the CHMe resonances of the unreacted monomer and PLA. After the chosen time, the reaction was quenched with THF. The polymer was isolated by addition of pentane to a concentrated solution of PLA to yield a precipitate which was washed with pentane and dried under vacuum at 30 °C.

**Conflicts of interest**

There are no conflicts to declare.

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