A study of ligand substituent effects on the rate and stereoselectivity of lactide polymerization using aluminum salen-type initiators.


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Abstract

A series of aluminum salen-type complexes (salen = N,N’-bis(salicylaldimine)-1,2-ethylenediamine) bearing ligands that differ in their steric and electronic properties have been synthesized and investigated for the polymerization of rac-lactide. X-ray crystal structures on key precatalysts reveal metal coordination geometries intermediate between trigonal bipyramidal and square-based pyramidal. Both the phenoxy substituents and the backbone linker were found to have a significant influence over the polymerization. Electron-withdrawing groups attached to the phenoxy donor generally gave an increased polymerization rate, while large ortho substituents were generally found to slow down the polymerization. The vast majority of the initiators afforded PLA with an isotactic bias; only one exhibited a bias towards heteroselectivity. Isoselectivity generally increases with increased flexibility of the backbone linker which is presumed to be better able to accommodate any potential steric clashes between the propagating polymer chain, the inserting monomer unit, and the substituents on the phenoxy donor.
Introduction

In recent years Al(salen) complexes have been widely investigated for their ability to initiate the stereocontrolled polymerization of lactide\textsuperscript{1-17} to give a material, polylactide (PLA), which has a range of biomedical, pharmaceutical, and agricultural applications.\textsuperscript{18-21} A convenient synthetic route to PLA is the ring-opening polymerization (ROP) of lactide (LA), the cyclic diester of lactic acid, which is derivable from renewable resources such as corn starch, sugars and dairy produce. Metal alkoxides, for example those of Al, Zn, Mg, Y, Ln, Sn(II), Sn(IV), Fe(II) and Fe(III), are typically used to catalyze the ROP of LA and related cyclic esters. Several reviews describing the mechanism of ROP, and the types of initiators and catalysts have been published recently.\textsuperscript{22-27}

Following initial findings that simple (salen)Al complexes such as I-III (Figure 1) could initiate a relatively controlled polymerization of rac-lactide to moderately isotactic PLA,\textsuperscript{1,2} interest developed in the potential of such initiators to mediate the stereoselective polymerization of rac-lactide by exploiting chiral ligand backbones. Thus, the enantiomerically pure chiral aluminum complex, (R)-IV, was shown to selectively consume D-LA from a racemic mix ($k_D/k_L = 20$) to give optically active isotactic poly(D-LA).\textsuperscript{9} The related derivative, (R)-V, was exploited to obtain syndiotactic PLA from meso-LA with an enantiotopic selectivity of 96 \%.\textsuperscript{10,11} Using the optically inactive racemate, (rac)-VI,\textsuperscript{12,13} a tapered stereoblock copolymer was obtained from rac-lactide. A polymer exchange mechanism was proposed where each enantiomer of (rac)-VI preferentially polymerizes one enantiomer of rac-LA, but the growing chains undergo exchange at aluminum centers of opposite chirality to produce blocks composed of the other enantiomer of LA with averaged block length of 11 monomer units.\textsuperscript{12} More recently the cyclohexane derivatives, (R)-VII and (rac)-VIII, have been shown to polymerize rac-LA with high isoselectivity and excellent control in both solvent-based and solvent-free polymerizations.\textsuperscript{14,15}

An interesting and potentially useful aspect of (salen)Al systems is their apparent ability to mediate iso-selective polymerizations of rac-lactide using an achiral ligand system such as those contained in IX and X.\textsuperscript{6} The iso-selectivity is enhanced for initiators bearing more flexible C\textsubscript{3} linkers, while introducing large ortho-phenoxy substituents was also found to increase the isotacticity. Further
tacticity enhancements have been reported for the dimethyl substituted derivative XI.\(^7\) The mechanism of stereoselective polymerization using these achiral ligand-based complexes is postulated to operate via a chain end control process,\(^6\) whereas an enantiomorphic-site control mechanism is proposed for the chiral salen-based complexes.\(^10\) However, recent studies have highlighted some complexities in ascribing the mechanism to chain-end control or enantiomorphic-site control.\(^16\) The chirality of the ligand bonded to the metal, the chirality of the end group of the growing polymer chain and the solvent all seem to play a complex and rather unpredictable role in influencing the stereo-preference in a racemic monomer mixture.

With regard to the productivities of (salen)Al systems, in the rather limited number of studies to date it has been found that the rate of polymerization is enhanced by appending electron-withdrawing substituents to the phenoxide donor,\(^4\) and interestingly, improved control was also apparent, with little trans-esterification (backbiting) of the polymer chain. Enhanced activities have also been observed using a salicylketimine derivative containing neither bulky nor electron-withdrawing substituents on the phenoxide donor.\(^5\)

*** Figure 1 ***

While Al(salen) complexes are attractive as initiators due to their ease of preparation and the stability afforded by the tetradentate ligand, it is clear from studies to date that significant gaps remain in our knowledge of the fundamental factors influencing activity and selectivity. We therefore initiated a systematic investigation into the lactide polymerization behavior of a family of Al(salen) initiator systems, in which the phenoxy substituents and the length and nature of the diimino linking units are varied, with a view to obtaining an improved understanding of the influence of salen-type ligands on the rate and stereoselectivity of rac-lactide polymerization.
Results

Pro-Initiator synthesis

The salicylaldimine pro-ligands employed in this study were prepared via condensation of two equivalents of commercially available salicylaldehydes (α-hydroxybenzaldehydes) with an α,ω-diamine according to standard literature procedures. The salicylaldimines were then reacted with one equivalent of trimethylaluminum at 110 °C for 18 hours to afford the (salen)Al(CH₃) complexes in moderate to high yields according to Figure 2 (attempts to synthesise the R¹=R²=H and R¹=R²=Cl members of Group F led to intractable product mixtures). The complexes synthesized (1–24) are collected in Figure 3 and span ethylene (C₂) and propylene (C₃) backbones of varying degrees of rigidity (Groups A-F) along with two additional families containing arylene linkers (Groups G and H). To the best of our knowledge only complexes 1, 2, 4 and 10 have been reported previously.²⁸-³⁰

*** Figures 2 and 3 ***

The 1,2-ethylenediamino-based complexes 1–7 were all obtained as yellow crystalline materials following recrystallization either directly from the reaction medium for the less soluble examples (e.g. 3) or from MeCN (full experimental details for complexes 1-24 are provided in the Supporting Information). The presence of the methyl substituents on the backbone of 5–7 renders these complexes significantly more soluble than their non-substituted counterparts, and hence recrystallized yields of these were generally lower than for 1–4, (e.g. 37%, 6; 45%, 7). The difference in solubility is particularly apparent for the dichlorophenoxy derivatives 3 and 6: the former being insoluble in hot toluene while complex 6 is soluble in room temperature toluene solution. This observation suggests that the low solubility of other metal salen complexes, a problem commonly encountered with such species, may be rectified by introducing alkyl groups onto the diimino linker.

The ^1H NMR spectra of complexes 1–4 all feature complex second order multiplets in the region δ 2.0-4.0 for the protons of the ethylene backbone consistent with diastereotopic methylene proton
environments. The observation of just one imine environment in their $^1$H and $^{13}$C NMR spectra is consistent with fluxional behavior. For complexes 5–7, the unsymmetrical nature of the 1,1-dimethyl-1,2-ethylenediamino backboneexpectedly affords inequivalent phenoxide rings and two imine proton resonances.

Syntheses of the C$_3$ linked diamino-based complexes (8–18) also proceed in straightforward fashion. The spectroscopic data obtained on these compounds are largely unremarkable and consistent with the proposed formulations. In the $^1$H NMR spectra of complexes 8–10, 11–14, and 15–17, the unsubstituted backbone methylene protons again display second order coupling effects, typically giving rise to symmetrical doublets of multiplets (9, 10) or doublets of doublets (11–17) as expected for diastereotopic proton environments.

The $^1$H NMR spectra of the diaryl-linked backbone species 19–21 show two $^1$H imine singlet resonances consistent with a locked conformation; accordingly the spectrum of 21 also features four singlets for the t-butyl substituents. The $^1$H NMR spectra of complexes 22–24 are more complex, arising from the mobility of the ethylene linking unit, with broadened signals being observed for the ethylene bridge and the protons of the backbone arylene units.

**X-ray crystallography**

With a view to assessing whether any underlying geometrical effect imposed by the tetradentate ligand might account for the polymerization activities and selectivities, crystal structure determinations were carried out on selected complexes from Groups B, D, E, G and H; a number of examples from Group A were available from the literature.  The molecular structures of the representative complexes 6, 17, 20 and 24 are shown in Figures 4–7; selected bond lengths and angles are given in the Figure captions. The structures of complexes 7, 11, 13 and 19 are collected in the Supporting Information. The solid state analyses of all eight structures revealed five-coordinate trigonal bipyramidal (TBP) geometries at the aluminum centers, though at varying places in the continuum from ideal square-based pyramidal [$\tau = 0$] to ideal trigonal bipyramidal [$\tau = 1$] as described using the $\tau$ parameter.
introduced by Addison et al.33 (see Table 1). To a first approximation, it might be expected that there would be a correlation between $\tau$ and the bite angle of the central $N,N'$ chelate (the $O,N$ chelate rings at each end of the ligands are the same in each complex, and the fifth donor is methyl in each case); since the $N,N'$ chelate in each complex links an equatorial donor to an axial donor, a bite angle of less than 90° would be expected to reduce the trans-axial angle $\beta$, and thus reduce $\tau$. However, such a correlation is only present at the extreme ends of the $\tau$ range; complexes 6 and 7 have the smallest values of $\tau$ (ca. 0.5) and the smallest $N,N'$ bite angles [ca. 77°], and complex 19 has the largest $\tau$ (0.91) and the largest $N,N'$ bite angle [87.33(12)°]. In between the correlation is lost; complexes 20 and 24 have $\tau \sim 0.67$ with $N,N'$ bite angles of ca. 86°, whilst complexes 11, 13 and 17 have a larger $\tau$ of ca. 0.75 but smaller $N,N'$ bite angles of ca. 84°. It is thus clear that the flexibility of the linkage between the two nitrogen centers, and thus their ability to adopt a bite angle of approaching 90°, is not the sole factor effecting the geometry at the metal center. Indeed, comparing complexes 19 and 20, which differ only in the 2,4-substituents of the salicylaldimine rings (hydrogen in 19, chlorine in 20), reveals bite angles that differ by ca. 2°, $\beta$ angles that vary by ca. 6° and $\tau$ values of 0.91 and ca. 0.68 respectively. It is apparent, therefore, that electronic effects also have a vital role. Interestingly, changing the 2,4-substituents on the salicylaldimine from chlorine to $t$-butyl has almost no effect; comparing complex 6 (chlorine) to complex 7 ($t$-butyl) reveals almost no change in the $N,N'$ bite angles, $\beta$ angles or the $\tau$ values. For complexes 11 (hydrogen) and 13 ($t$-butyl) the $N,N'$ bite angles are almost identical (different by only ca. 0.1°), the $\beta$ angles vary by ca. 4°, and the $\tau$ values are 0.79 and 0.72 respectively. Clearly, therefore, the geometry at the aluminum centers is a result of a subtle interweaving of disparate factors, and more work will be required if these relationships are to be fully understood.

*** Figures 4-7 ***

*** Table 1 ***
**Polymerization studies**

Polymerizations were carried out by treatment of the methyl precursor complexes 1–24 with a stoichiometric equivalent of benzyl alcohol in toluene. $^1$H NMR validation studies confirmed that the alkoxide initiating species is generated cleanly and swiftly by this procedure. The temperature of the initiator solution was then raised to 70 °C and rac-LA was added. For comparative purposes, the molar ratio of rac-LA to initiator was fixed at 50:1 ([LA]₀ = 0.416 M; [Al]₀ = 8.33 mM; $M_n$ (theory) = 7,200). Polymerizations were typically allowed to proceed to high (> 90%) conversion, with the exception of some of the slower systems, before termination by addition of a small amount of methanol. In each case, aliquots were removed throughout the polymerization and monomer conversion and molecular weights were determined by $^1$H NMR spectroscopy and GPC, respectively. Molecular weight, rate and tacticity data are collected for systems containing C₂ and C₃ alkylene linkers and the phenylene-containing linkers in Figures 8 and 9, respectively.

i) C₂ and C₃ alkylene backbones

For initiators derived from Group A complexes containing a C₂ (ethylene) backbone, a comparison of the data for compounds 1 and 4 reveals a dramatic effect on rate upon incorporating bulky substituents at the ortho positions of the phenoxo donors. Thus, the initiator derived from 4 polymerizes rac-lactide at a rate ca. 50 times slower than for 1, which has protons in the equivalent positions. An enhancement of the polymerization rate due to an electronic effect is also observed. For example, comparing 1 with 3 reveals a tripling of the rate for the chloro substituted ligand, despite the increased steric hindrance of the ortho chloro groups which, to a first approximation, may be viewed as being sterically similar to methyl substituents. A smaller, though significant rate enhancement is seen upon introducing a chloro substituent into the para position (*cf.* 1 vs 2). The kinetic behavior of this group of catalysts is significantly different to the other groups (B-H) – *vide infra.* Higher $M_n$ values than
predicted are found at the beginning of the polymerizations (Fig S19), likely related to an induction effect which is apparent in plots of ln([LA]/[LA]₀) vs time (Fig S29). Such induction periods have also been observed for other initiator systems, but they do not occur for the other groups of initiators described here.

*** Figure 8 ***

All of the polylactide products the the Group A initiators show a bias towards isotacticity with the t-butyl derivative 4 giving the highest value (83%) within this grouping. Interestingly, the 2,6-dichloro derivative (3) afforded the lowest bias towards isotacticity (56%) despite the presence of quite sterically demanding chloro substituents. Introducing a gem-dimethyl unit into the ligand backbone (Group B) did not afford a dramatic change in polymerization behavior compared to those in Group A, with similar trends due to H (5), Cl (6) and Bu (7) ligand substituents. The isotacticity for the t-butyl derivative was found to be somewhat lower (77%) than for the non-substituted ethylene backbone derivative 4.

Lengthening the backbone to a C₃ alkylene linker gave rise to a dramatic increase in polymerization rate with the highest being recorded for the dichloro derivative 9. Comparing 1 with 8 reveals a 13-fold rate increase upon exchanging the C₂ for the C₃ linker while, for the t-butyl derivative, the increase is in excess of two orders of magnitude. There is also a noticeable increase in isotacticity for samples generated by the unsubstituted (8) and di-t-butyl-substituted (10) ligands. Interestingly, further substantial increases in polymerization rate are seen for the gem-dimethyl substituted C₃ backbone (Group D), though the iso-selectivity is diminished slightly.

ii) Phenylene-containing backbones

For the E series of initiators, where a more rigid phenylene linker is incorporated into the C₃ backbone, a substantial enhancement of polymerization rate for the dichloro derivative 16 relative to 9
was observed, the rates for the H and t-butyl derivatives being relatively comparable (cf. 8 vs 15 and 10 vs 17). Similarly high isotactic content PLA (86%) is obtained for the t-butyl derivative along with a narrow molecular weight distribution (1.05). The t-butyl derivative of a naphthyl linking unit (18) afforded a much higher activity than for all other derivatives containing the 2,6-di-t-butyl combination, but the iso-selectivity was lowered.

***Figure 9***

For initiators containing a biphenyl linker (Group G), the activities are dramatically lowered, and this is accompanied by a marked improvement in control over the polymerization. However, all three initiators afforded PLA with a very narrow molecular weight distribution implying a favorable rate of initiation versus rate of propagation and with little trans-esterification side reactions. It is also noticeable that the unsubstituted derivative 19 gave a narrow molecular weight distribution and a remarkably high isotactic content of 84%, comparable to di-t-butyl derivatives attached to other backbones. Interestingly, the dichloro initiator 20 gave a significant heterotactic bias ($P_r 0.63$), the only derivative within this Al(salen) family of initiators to have afforded heterotactic-biased PLA, though with a significant loss over molecular weight control. Since the lowering of activity and the surprising stereocontrol may be related to the rigidity of the biphenyl linker, we decided to examine complexes 22-24 in which a flexible ethylene linker connects the phenylene units. However, activities did not greatly improve and the tacticity control was largely lost.

**Discussion**

From the results obtained using these initiating systems it is apparent that the activity of each aluminum center is strongly influenced by the nature of the phenoxy substituents. For example, the 2,4-di-t-butylphenoxy derivatives 4 and 7 afford substantially slower propagation rates than any other member of Groups A and B. This observation is attributed to the size of the ortho substituents, which
are believed to obstruct either the approach of lactide monomer to the aluminum center, or a key transition state associated with ring-opening. This effect is seen throughout the ligand families employed in the study with rates for the complexes featuring ortho t-butyl-substituted ligands consistently lower than for all other members of the same family.

An electronic effect is also apparent, with electron withdrawing substituents attached to the phenoxy donors affording more active aluminum centers, presumably a consequence of enhanced metal electrophilicities. Hence, the halide-substituted bis(iminophenoxide) complexes typically exhibit greater polymerization activities than do their counterparts bearing unsubstituted phenoxide rings. An exception arises for complexes containing the 2,2'-diaminobiphenyl backbone where the unsubstituted derivative gave a 5-fold higher polymerization rate than for its 2,4-dichloro relative. A similar, though less pronounced, effect is found in Group H.

The C₃ linker clearly exerts a beneficial effect on polymerization rate, which is likely attributable to the greater flexibility imparted to the metal coordination sphere, and thus better accommodation of the geometric requirements of the transition state(s) for the ring-opening process. It might be expected that some aspects of these geometric effects will be apparent in the ground state structures of the aluminum pro-initiators. A comparison of the molecular structures of the ethylene backbone complexes with their propylene backbone relatives reveals two important differences. First, the ethylene backbone complexes contain NN bite angles of ca. 76-78° whereas the longer propylene linker affords bite angles in the range 83-88°. Accordingly, the τ parameter for the C₂ linker complexes are in the range 0.50-0.56, compared to 0.70-0.79 for complexes containing the C₃ linker i.e. there is a substantial constraint towards square-based pyramidal coordination for the ethylene-bridged compounds while the propylene backbone complexes favor trigonal bipyramidal coordination. However, a distortion towards a trigonal bipyramidal geometry does not solely account for the rate enhancements since the similarly TBP-biased complexes 17 and 20 gave less active catalysts. Further, complex 19, which shows the greatest distortion towards a TBP coordination geometry (τ = 0.91) afforded quite low activity. The ¹H NMR data for 17-20, however, indicate that they are ‘locked’ and therefore without the flexibility of their C₃-linker
counterparts. It seems likely, therefore, that the enhanced performance of the C₃ backbone catalysts is more a function of the flexibility of the linking unit, which may allow the complex to better access the key transition states involved in the ring-opening polymerization process. It would also appear to have a favorable effect on initiation since the initiators with C₂ linking units all display a significant induction period prior to the onset of polymerization.

The molecular weights of the PLA samples generally show good agreement with theoretical values in accord with a well-controlled coordinative insertion process (see Supporting Information). Molecular weight distributions, however, broaden at higher monomer conversions, i.e. low monomer concentrations, due to transesterification side-reactions; exceptions are the lower activity complexes in Group G which maintain low PDI’s throughout. High levels of transesterification are particularly pronounced for the smaller salen ligands, such as 1 and 2. However, changing the backbone structure from an ethylene linker to a propylene linker typically leads to a marked reduction in the degree of transesterification, an effect also noted by Nomura and co-workers.⁶

The origin of the isoselectivity observed using (salen)Al initiators is less readily pinpointed from these studies. Nonetheless, some trends are apparent. For example, comparison of the $P_m$ values for initiators from Groups A - E indicate that the nature of the phenoxy substituents is important. Systems containing ortho-t-butyl substituents afford the highest isoselectivities, 83(±6) % for 4, 7, 10, 13 and 17, whereas unsubstituted derivatives gave isoselectivities of 69(±6) % (for 1, 5, 8, 11 and 15). Interestingly, the 2,4-dichloro substituted complexes, 3, 6, 9, 12 and 16, gave somewhat lower isotactic contents of 56, 60, 60, 59 and 63 %, respectively, despite the presence of the sterically significant ortho-chloro substituent. The latter observation clearly indicates an electronic contribution to the stereochemistry of insertion.

The nature of the linkage between the imino donors is also important, with the good isoselectivities of Groups A – E contrasting with lower values for the more rigid diarylene backbone complexes of Groups F – H. Indeed, trends within Groups F – H are far less apparent than for their aliphatic counterparts, and the factors influencing stereocontrol may not be the same. For example, the unsubstituted complex 19
gave a higher isotacticity than its t-butyl relative, 21, while somewhat surprisingly 20 gave moderate heteroselectivity, to our knowledge the only (salen)Al system to date to afford a heteroselective bias.

In light of the conclusions of a recent theoretical study,35 we surmise that the isotactic assembly mode is favored because steric clashes between the propagating chain, the incoming monomer, and the salen substituents are minimized (relative to heterotactic insertion) during the rate determining transition state, and a mobile backbone would be expected to better accommodate such interactions. Preliminary results from a DFT quantum chemical study36 are in accord with this rationale and will be disclosed in due course.

Conclusions

A study of the factors influencing the ring-opening polymerization of rac-lactide by (salen)Al initiators has revealed several important effects: i) high activities are favored by electron-withdrawing substituents attached to the phenoxy-donor, ii) activities are enhanced by flexible 3-carbon linkers between the imino nitrogen donors, iii) activities are suppressed by large ortho-phenoxy substituents, and iv) isoselectivity is specially favored by a combination of a flexible aliphatic C3 linker and sterically demanding ortho-phenoxy groups.

Acknowledgements

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References


Figure Captions

**Figure 1.** Aluminum initiators and pro-initiators employed in the ring-opening polymerization of rac-lactide.

**Figure 2.** Synthetic pathway for the preparation of complexes 1–24.

**Figure 3.** Complexes 1–24 synthesized as part of this study.

**Figure 4.** The molecular structure of 6. Selected bond lengths (Å) and angles (°): Al–C 1.949(7); Al–O(1) 1.825(4); Al–N(7) 1.997(5); Al–N(10) 2.042(5); Al–O(16) 1.808(4); C(7)–N(7) 1.290(9); N(10)–C(10) 1.293(9); C–Al–O(1) 103.2(3); C–Al–N(7) 110.7(3); C–Al–N(10) 94.9(3); C–Al–O(16) 120.8(3); O(1)–Al–N(7) 90.3(2); O(1)–Al–N(10) 161.0(2); O(1)–Al–O(16) 89.4(2); N(7)–Al–N(10) 77.8(2); N(7)–Al–O(16) 127.2(2); N(10)–Al–O(16) 86.2(2).

**Figure 5.** The molecular structure of 17. Selected bond lengths (Å) and angles (°): Al–O(1) 1.835(2); Al–N(7) 1.995(2); Al–N(15) 2.096(2); Al–O(21) 1.786(2); Al–C(38) 1.958(3); C(7)–N(7) 1.288(4); C(15)–N(15) 1.289(4); O(21)–Al–O(1) 89.09(8); O(21)–Al–C(38) 122.74(14); O(1)–Al–C(38) 99.77(11); O(21)–Al–N(7) 121.60(10); O(1)–Al–N(7) 87.6(3); O(1)–Al–N(15) 87.32(9); O(1)–Al–N(15) 168.79(10); C(38)–Al–N(15) 91.09(11); N(7)–Al–N(15) 84.14(9).

**Figure 6.** The molecular structure of one (11) of the two independent complexes present in the crystals of 20. Selected bond lengths (Å) and angles (°): Al–C 1.976(10); Al–O(1) 1.852(6); Al–N(7) 2.053(7); Al–N(20) 2.032(8); Al–O(26) 1.792(6); C(7)–N(7) 1.312(11); N(20)–C(20) 1.327(11); C–Al–O(1) 98.7(4); C–Al–N(7) 112.4(4); C–Al–N(20) 94.7(4); C–Al–O(26) 121.5(4); O(1)–Al–N(7) 87.6(3); O(1)–Al–N(20) 166.4(3); O(1)–Al–O(26) 86.9(3); N(7)–Al–N(20) 85.5(3); N(7)–Al–O(26) 126.0(3); N(20)–Al–O(26) 87.6(3). Analogous date for I may be found in the Supporting Information.

**Figure 7.** The molecular structure of 24. Selected bond lengths (Å) and angles (°): Al–C 1.966(5); Al–O(1) 1.820(3); Al–N(7) 2.025(3); Al–N(22) 2.186(3); Al–O(28) 1.758(3); C(7)–N(7) 1.302(5); C(22)–N(22) 1.299(5); O(28)–Al–O(1) 94.9(2); O(28)–Al–C 119.3(2); O(1)–Al–C 93.6(2); O(28)–Al–N(7) 105.72(14); O(1)–Al–N(7) 88.14(14); C–Al–N(7) 134.6(2); O(28)–Al–N(22) 87.20(13); O(1)–Al–N(22) 174.32(14); C–Al–N(22) 89.9(2); N(7)–Al–N(22) 86.20(13).

**Figure 8.** Polymerization data for complexes 1–14: ([LA]₀/[Al]₀ =50; toluene, 70 °C; Mₙ (theory) = 7,200); errors on k_app values: ± 5 %.

**Figure 9.** Polymerization data for complexes 15–24: ([LA]₀/[Al]₀ =50; toluene, 70 °C; Mₙ (theory) = 7,200); errors on k_app values: ± 5 %.

Table captions

**Table 1.** The square-based pyramidal/trigonal bipyramidal parameter τ for the solid state structures of complexes 6, 7, 11, 13, 17, 19, 20 and 24.
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Figure 5. The molecular structure of 17. Selected bond lengths (Å) and angles (°): Al–O(1) 1.835(2); Al–N(7) 1.995(2); Al–N(15) 2.096(2); Al–O(21) 1.786(2); Al–C(38) 1.958(3); C(7)–N(7) 1.288(4); C(15)–N(15) 1.289(4); O(21)–Al–O(1) 89.09(8); O(21)–Al–C(38) 122.74(14); O(1)–Al–C(38) 99.77(11); O(21)–Al–N(7) 121.60(10); O(1)–Al–N(7) 88.72(9); C(38)–Al–N(7) 115.10(13); O(21)–Al–N(15) 87.32(9); O(1)–Al–N(15) 168.79(10); C(38)–Al–N(15) 91.09(11); N(7)–Al–N(15) 84.14(9).
Figure 6. The molecular structure of one (II) of the two independent complexes present in the crystals of 20. Selected bond lengths (Å) and angles (°): Al-C 1.976(10); Al-O(1) 1.852(6); Al-N(7) 2.053(7); Al-N(20) 2.032(8); Al-O(26) 1.792(6); C(7)-N(7) 1.312(11); N(20)-C(20) 1.327(11); C-Al-O(1) 98.7(4); C-Al-N(7) 112.4(4); C-Al-N(20) 94.7(4); C-Al-O(26) 121.5(4); O(1)-Al-N(7) 87.6(3); O(1)-Al- N(20) 166.4(3); O(1)-O(26) 86.9(3); N(7)-Al-N(20) 85.5(3); N(7)-Al-O(26) 126.0(3); N(20)-Al- O(26) 87.6(3). Analogous data for I may be found in the Supporting Information.
Figure 7. The molecular structure of 24. Selected bond lengths (Å) and angles (°): Al–C 1.966(5); Al–O(1) 1.820(3); Al–N(7) 2.025(3); Al–N(22) 2.186(3); Al–O(28) 1.758(3); C(7)–N(7) 1.302(5); C(22)–N(22) 1.299(5); O(28)–Al–O(1) 94.9(2); O(28)–Al–C 119.3(2); O(1)–Al–C 93.6(2); O(28)–Al–N(7) 105.72(14); O(1)–Al–N(7) 88.14(14); C–Al–N(7) 134.6(2); O(28)–Al–N(22) 87.20(13); O(1)–Al–N(22) 174.32(14); C–Al–N(22) 89.9(2); N(7)–Al–N(22) 86.20(13).
Figure 8. Polymerization data for complexes 1-14; ([LA]_0/[Al]_0 = 50; toluene, 70 °C; M_n (theory) = 7,200); errors on k_{app} values: ± 5 %.

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Figure 9. Polymerization data for complexes 15-24; ([LA]₀/[Al]₀ = 50; toluene, 70 °C; Mₙ (theory) = 7,200); errors on kₐₚₚ values: ± 5 %.
Table 1. The square-based pyramidal/trigonal bipyramidal parameter $\tau$ for the solid state structures of complexes 6, 7, 11, 13, 17, 19, 20 and 24.

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<th>$A^{[a]}$</th>
<th>$\alpha^{[b]}/^{\circ}$</th>
<th>$\beta^{[c]}/^{\circ}$</th>
<th>$\tau^{[d]}$</th>
<th>N-N bite/°</th>
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[a] Ligand $A$ is defined as being the donor atom not involved in the two largest angles at the metal center; [b] angle $\alpha$ is the second largest angle at the metal center; [c] angle $\beta$ is the largest angle at the metal center; [d] $\tau = (\beta - \alpha)/60^{\circ}$. 